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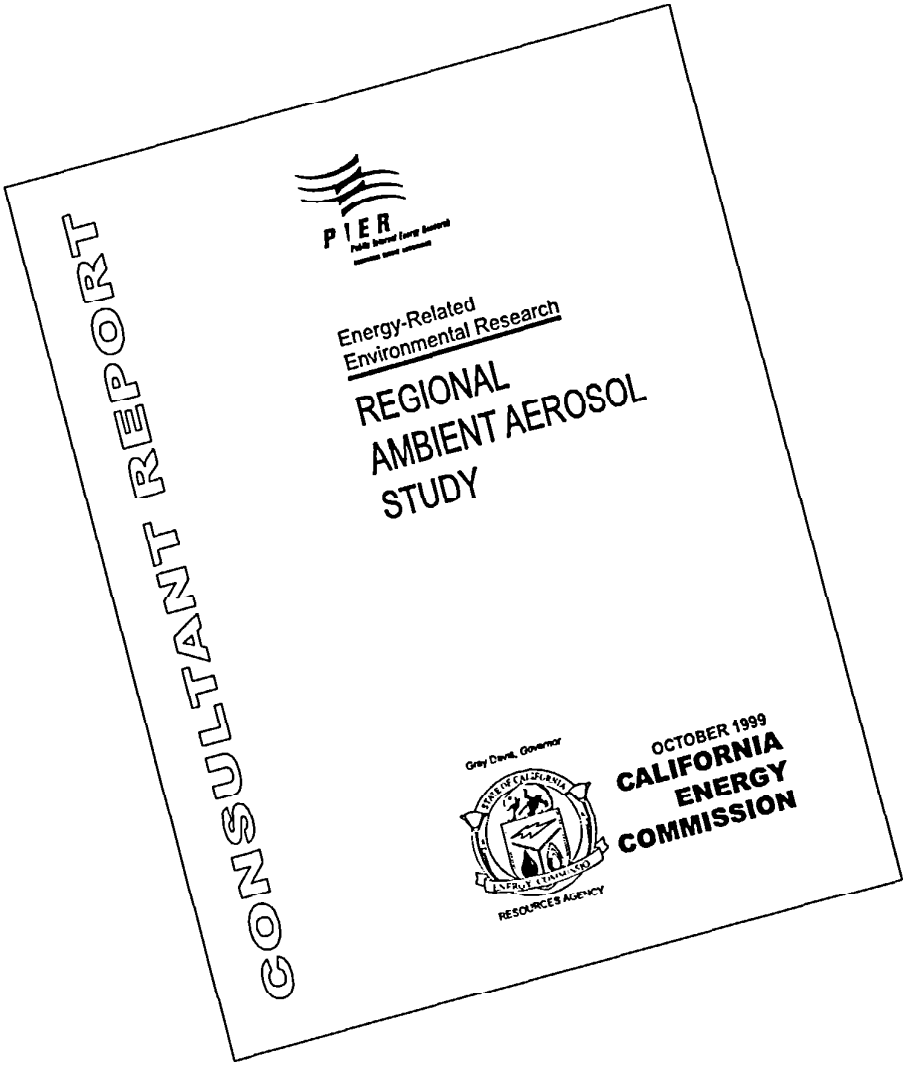

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million through the Year 2001 to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research.

In 1998, the Commission awarded approximately $17 million to 39 separate transition RD&D projects covering the five PIER subject areas. These projects were selected to preserve the benefits of the most promising ongoing public interest RD&D efforts conducted by investor-owned utilities prior to the onset of electricity restructuring.

What follows is the final report for the Regional Ambient Air Study project, one of nine projects conducted by Pacific Gas and Electric Company. This project contributes to the Energy-Related Environmental Research program.

For more information on the PIER Program, please visit the Commission's Web site at: http://www.energy.ca.gov/research/index.html or contact the Commission's Publications Unit at 916-654-5200.

Executive Summary

National and State standards for air quality have been established for both particulate matter (PM) and ozone (O_3). Standards for PM and O_3 are routinely exceeded within California's San Joaquin Valley and ozone standards are exceeded within the San Francisco Bay area.

To understand air quality problems in the San Joaquin Valley and provide tools for equitable and cost-effective air quality planning and decision-making, air quality studies have been in place since the mid-1980s. Continuation of this early work is being performed in the ongoing California Regional PM_{10} / $PM_{2.5}$ Air Quality Study (CRPAQS).

The main objective of the CRPAQS is to improve the scientific understanding of the PM_{10} / $PM_{2.5}$ problem in Central and Northern California. This includes a better quantification of emissions; a better understanding of the chemistry and physics involved in the transport, formation and removal of atmospheric PM_{10} / $PM_{2.5}$; and an improvement in the characterization of the meteorological conditions conducive to high PM_{10} / $PM_{2.5}$ concentrations. The final product of the CRPAQS project will be the development of a state-of-the-art, regional PM_{10} / $PM_{2.5}$ modeling system that will allow air agencies in central and northern California to develop technically sound air quality management plans to comply with PM_{10} / $PM_{2.5}$ state and national ambient air quality standards.

Pacific Gas & Electric (PG&E) has been providing technical and financial support to this air quality control effort since 1988. California Energy Commission funding has allowed PG&E to continue to provide technical contributions to the CRPAQS. Regional Ambient Aerosol Studies, the project addressed by this report, is the name for PG&E's research and development (R&D) project initiated to complement and assist CRPAQS. This report addresses the effort performed from January 1998 through September 1999.

The original objectives outlined in PG&E's proposal to the California Energy Commission include:

- Provide high-level scientific expertise to CRPAQS in areas such as field studies design, planning of CRPAQS, and critical review of technical documents.
- Continuing to serve as the project manager for the 1995 Integrated Monitoring Study (IMS 95).
- Continue PG&E's participation in CRPAQS's technical and policy committees.
- Disseminate scientific information through the participation in scientific workshops and conferences and the publication of technical papers in the peer-reviewed literature.

High-Level Scientific Expertise (Sections 2.0, 3.2 and 3.4)

Objective:

- Provide high-level scientific expertise to CRPAQS and the Central California Ozone Study (CCOS) in areas such as field studies design, planning of CRPAQS, and critical review of technical documents. PG&E and contractor Atmospheric and Environmental Research (AER) provided high-level scientific expertise to CRPAQS throughout this project. High-level scientific expertise was provided in six main areas. The objectives,

outcomes and recommendations for specific efforts are provided briefly in the following; summaries of the resultant technical reports are provided in Section 2.0 of this report; complete copies of these reports are found in Appendix I.

Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley (Section 2.1)

Objective:

- To formulate a conceptual model for fall and winter PM concentrations in the San Joaquin Valley using primarily the information obtained during the 1995 Integrated Monitoring Study.

Outcome:

- A conceptual model for fall and winter PM concentrations in the San Joaquin Valley, using the data gathered during the 1995 Integrated Monitoring Study, was developed. This model provides a better balance between meteorological and chemistry considerations in the analyses of PM episodes than previously developed models, allowing for increased accuracy in modeling PM concentrations.

Recommendations were made to the CRPAQS:

- Develop a better understanding of oxidant chemistry for the fall and winter seasons in the San Joaquin Valley to confirm important nitrate formation reactions (an important issue in the evaluation of the environmental impacts from the operation of NO_x-emitting fossil fueled electric power plants).
- Further investigate nitrogen oxides / volative organic compound / oxidant chemistry to confirm for the San Joaquin Valley methods to control acid formation effectively.
- Conduct further study of secondary organic aerosols from urban area anthropogenic (man-made) emissions and the atmospheric reactions of biogenic (natural) compounds.
- Research the source of fog buffering capacity and sensitivity to precursors of ambient ozone measurements at the parts per billion level.

Conceptual Model of Ambient Ozone Pollution in the California San Joaquin Valley (Section 2.2)

Objective:

- To develop a conceptual model for O_3 formation, transport, and accumulation in the California San Joaquin Valley primarily using the information obtained during the San Joaquin Valley Air Quality Study and the Atmospheric Utility Signatures, Predictions and Experiments programs of 1990.

Outcomes:

- A conceptual model, incorporating the physical dynamics and chemistry of O_3 formation in the San Joaquin Valley, was developed.
- Two major causes of high levels of O_3 concentrations in the San Joaquin Valley were identified: transport of O_3 and its precursors from upwind areas such as the San Francisco Bay area led to high O_3 levels in the northern valley; and emissions of precursors, mixing, and atmospheric reactions within the valley led to high O_3 levels downwind of urban areas such as Fresno and Bakersfield. These findings help

conceptualize the physical dynamics and chemistry of O_3 formation in the San Joaquin Valley.

Recommendations made to CCOS:

- Investigate further the volatile organic compounds / nitrogen oxide sensitivity issue, under differing meteorological conditions, to confirm model conclusions.
- Build an understanding of the source-receptor relationships to address O_3 at rural receptor sites.
- Use temporal variations at polluted rural sites as the subject of a modeling investigation.
- Perform model investigations to determine the O_3 sensitivity of the region to volatile organic compounds and nitrogen oxide with respect to an eight-hour standards measurement, to confirm the efficacy of control measures designed to reduce the maximum one-hour average concentration.
- Continue efforts to provide better emissions estimates for mobile, biogenic, oil production, and un-inventoried sources. This will allow models to be better applied to understand the relative importance of these precursor sources to O_3 production in the San Joaquin Valley.

1995 Integrated Monitoring Study: Assessment of Mathematical Models and Associated Data Needs (Section 2.3)

Objectives:

- Assess the ability of existing mathematical models to represent PM formation.
- Identify gaps in current knowledge and needs for model improvement.
- Recommend specific tasks for future field measurements, data analyses, and model performance evaluation to be performed under CRPAQS.

Outcomes:

- Assessed the ability of existing mathematical models and formulated a conceptual model for the formation of PM in the San Joaquin Valley based on the observations and analyses of data from the 1995 Integrated Monitoring Study project. Used this model to evaluate current PM air quality models, particularly the SARMAP air quality model. (SARMAP is the San Joaquin Valley Air Quality Study [SJVAQS] / Atmospheric Utility Signatures, Predictions and Experiments [AUSPEX] Regional Modeling Adaptation Program.)
- Identified gaps in current knowledge and specific tasks necessary for model improvement.
- Identified tasks necessary for the execution and evaluation of the source model, data required as inputs for the PM air quality model, and ambient concentrations and fluxes of PM and precursors needs to evaluate model performance. Provided recommendations to CRPAQS. See Table 5 for details.

Assessment of the SARMAP Meteorological Model/SARMAP Air Quality Model for Modeling Ozone Formation in the San Joaquin Valley (Section 2.4)

Objectives:

- Assess the ability of the SARMAP Mesoscale Model (MM5)/SARMAP Air Quality Model (SAQM) to represent O_3 formation processes
- Document the processes that are not well represented in the mathematical modeling system and recommend tasks for mathematical model improvement
- Identify gaps in current knowledge and recommend specific measurements and data analysis tasks.

Outcomes:

- MM5/SAQM modeling system was demonstrated to represent, in principle, the key features of the conceptual model for O_3 formation in the San Joaquin Valley.
- Specific areas for model development improvement were identified for MM5 and SAQM.

Recommendations made to CCOS:

- Perform modeling studies to elucidate the sensitivities of O_3 to its precursors at different locations where the eight-hour standards are expected to be exceeded.
- Perform modeling studies to investigate the zones of influence of emission sources due to long-range aloft transport.
- Improve MM5 by methods identified in the report including the reduction of numerical diffusion by the use of better algorithms, and the use of a full radiation scheme.
- Improve SAQM by methods fully identified in the report including the implementation of advanced sub-grid-scale treatment of plumes, evaluation of the performance of the dry deposition modules, and the resolution of vertical transport inconsistencies.

Comments on Field Program Plan for the California $PM_{2.5}$/PM_{10} Air Quality Study (Section 2.5)

Objective:

- Review and determine the adequacy of the conceptual model for PM formation in the San Joaquin Valley.

Outcomes:

- The conceptual model for PM formation was reviewed and found adequate for CRPAQS's purposes.

Recommendations made to CRPAQS:

- Perform direct measurements of dry deposition fluxes by the eddy correlation technique over a variety of land-use types for both PM and precursor gases to complete the understanding of major fluxes in the San Joaquin Valley system
- Include additional upwind boundary air chemistry measurements.
- Perform air chemistry measurements of radicals during the field monitoring program.
- Perform air chemistry measurements aloft during the field monitoring program.

Sensitivity of PM Nitrate Formation to Precursor Emissions in the California San Joaquin Valley (Section 2.6)

Objectives:

- Develop a box model that includes atmospheric chemistry and gas/particle thermodynamics to simulate wintertime PM formation
- Use the box model to study the sensitivities of oxidants and PM to precursors
- Investigate the use of photochemical indicators to predict the sensitivity of wintertime PM formation.

Outcomes:

- Developed and used a box model to investigate the response of PM nitrate to reductions in precursor emissions within the San Joaquin Valley.
- The formation of nitric acid and particulate nitrate was found to be sensitive to oxidants and to volatile organic compound emissions during the fall and winter.

Recommendations:

- In evaluating the environmental impacts of NO_x emissions, attention must be given to the potential impact of reduced NO_x emissions on possible increases in ambient ozone and particulate nitrates in various Central and Northern California locations.
- Benefits of NOx controls to reduce ambient ozone in some locations must be weighed against potential disadvantages of increased particulate PM nitrates.

Critical Review of Technical Documents

Objective:

- Provide high-level scientific expertise to CRPAQS in areas such as critical review of technical documents.

Outcomes:

- The Integrated Modeling Study 95: Assessment of Mathematical Models and Associated Data Needs (Appendix III) presents detailed critical review of numerous technical documents.
- Development of the Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley was partially based on critical review of documentation of other conceptual models. Summaries of these reviews are provided in Appendix I and II.
- Assessment of MM5/SAQM for Modeling Ozone Formation in the San Joaquin Valley included the critical review of relevant technical documents.

1995 Monitoring Study Project

Objectives:

- Documentation of 1995 Integrated Monitoring Study.

Outcomes:

- Completion of the 1995 Integrated Monitoring Study Overview Report documenting the key study elements and findings. (The final report is provided in Appendix III.)

CRPAQS Technical and Policy Committee Participation (3.3)

Objective:

- Continue PG&E's participation in CRPAQS's technical and policy committees.

Outcomes:

- Participated in the design and planning of the Central California Ozone Study (CCOS) as it evolved. This study was undefined when the proposal for this contract was submitted. It became a significant part of PG&E's effort as the contract progressed.
- Identified gaps in current knowledge including the volatile organic compounds or nitrogen oxide sensitivity of the oxidant system in the San Joaquin Valley; the rates of photolysis reactions in fog; the details of secondary organic aerosols formation; the source of fog buffering in some urban areas; and, the transport processes responsible for the regional distribution of pollutants under calm conditions.
- Identified needs of model improvement in areas of development and testing including the incorporation of a detailed aqueous-phase chemical mechanism, improved treatment of secondary organic aerosols, and the resolution of dry deposition prediction variances by air quality models.
- Supported the California Energy Commission in their decision to provide $3 million in funding to support the Central California Ozone Study.

Recommendations:

- Owners of existing and proposed new electric power plants within Central and Northern California need to understand the unique atmospheric chemical reactions occurring within power plant plumes aloft and the need for special treatment of these plumes through enhanced plume-in-grid modules in atmospheric modeling when evaluating the impact of nitrogen oxide (NO_x) emissions from their facilities.

Disseminate Scientific Information (Sections 3.1 and 3.5)

Objective:

- Disseminate scientific information through participation in scientific workshops and conferences and the publication of technical papers in peer-reviewed literature.

Outcomes:

- A team member (Paul Solomon) co-authored and published a paper, "Modeling the Effects of Emission Changes on $PM_{2.5}$ Using the UAM-AERO Model in the South Coast Air Basin," in the Proceedings of the $PM_{2.5}$ Conference in January 1998.
- Nine articles written as part of the 1995 Integrated Monitoring Study are scheduled for upcoming publication in a special issue of *Atmospheric Environment*, a premier air pollution peer-reviewed publication. One of these articles, "Understanding Particulate Matter Formation the Central San Joaquin Valley: Conceptual Model and Data Needs", was authored by AER.
- The article, "Ozone Formation in the California San Joaquin Valley: A Critical Assessment of Modeling and Data Needs", authored by Pun et al, has been submitted for publication in the *Journal of Air and Waste Management*.

Summary

PG&E and contractor AER used conceptual models to study the formation of both ozone and PM observed in prior air quality studies to build understanding about the formation of ozone and PM. From this, various air quality models were evaluated, predictions were made about PM nitrate formation, and recommendations were made about data needs and specifications for upcoming field studies.

A number of issues and concerns related to atmospheric ozone chemistry were linked to PM chemistry and vice versa. Specifically, emissions of nitrogen oxide played an important role in both the formations of ozone and PM nitrates. It was observed that changes in nitrogen oxide and volatile oxygen compounds emissions to effect a reduction in summertime ozone may be counterproductive to wintertime PM nitrates.

In addition, the importance of emissions aloft and their long-range transport were delineated compared to ground level emission. These two issues are critical to existing and planned fossil-fueled electric power plants in Central and Northern California. Ambient concentrations of ozone and PM both exceeding various ambient air quality standards in the Valley cause air regulatory agencies to focus on optimum control strategies to achieve attainment for both pollutants.

The importance of understanding unique atmospheric chemical reactions occurring within power plant plumes aloft was identified and special treatment of these plumes through enhanced plume-in-grid modules in atmospheric modeling was recommended. In addition, the discussion about aloft transport of emissions and the need for adequate boundary environmental data in upcoming field studies was well received by study planners and managers. Tracer releases during 1990 from Pittsburg, California provide evidence that emissions from tall upwind point sources may affect air quality as far downwind as the southern San Joaquin Valley. Fourteen percent of the tracer mass was detected at the surface in the southern part of the San Joaquin Valley the morning after the tracer release. Due to the possibility of long-range aloft transport, it was recommended for the source model that the mesoscale domain include upwind metropolitan areas such as the San Francisco Bay Area, Monterey, and San Luis Obispo.

After the California Regional PM_{10}/$PM_{2.5}$ Air Quality Study and the Central California Ozone Study field monitoring are executed, the resulting air quality models for ozone and PM should be able to more accurately address emissions from power plants as a result of many of the recommendations provided. Opportunities for inter-pollutant trade-offs related to new facilities, i.e., power plants, need to be carefully evaluated as project proponents negotiate to trade nitrogen oxide emissions for PM emissions, nitrogen oxide missions for volatile oxygen compounds emissions, vice versa, or with other combinations.

In summary, PG&E has been a supporter of knowledge-based research to further the understanding of important air quality issues in Central and Northern California since 1988. California Energy Commission funding to continue PG&E's involvement in the Regional Ambient Air Study (RAAS) has allowed PG&E to continue to support these studies, representing not only PG&E's goal to support improved quality of life issues (improved air quality) within its service territory to support its customers, shareholders, and employees

residing in the area, but also representing the fossil fueled power generation industry in Central and Northern California. PG&E supports the California Energy Commission in their recent decision to provide funding in support of the Central California Ozone Study. PG&E recommends that the new owners and operators of planned and existing power plants within the area understand the relevance and importance of the CCOS and CRPAQS to their continued operation of their power production facilities. Support of this study will help ensure that optimum ozone and PM control strategies are adopted in the future that will not disproportionately affect the interests of power producers. In addition, air quality models created in the Central California Ozone Study will be invaluable in the review of existing and proposed fossil fuel power plants.

Abstract

Under the Regional Ambient Aerosol Studies (RAAS) project, Pacific Gas & Electric (PG&E) continued to provide technical expertise to the ongoing California Regional PM_{10} / $PM_{2.5}$ (particulate matter in the 2.5 to 10 micrometer size range) Air Quality Study (CRPAQS). Early on in the project, the complementary Central California Ozone Study (CCOS) emerged. This ozone study dovetails into the particulate matter study by optimizing similar measurements and resources used in conducting CRPAQS.

This RAAS project supports the Public Interest Energy Research (PIER) program objective of improving the environmental and public health costs and risks of California's electricity. It focused on improving scientific understanding of the PM_{10} / $PM_{2.5}$ problem in northern and central California, particularly on quantification of emissions, the chemistry and physics involved in transport of PM, the formation and removal of PM_{10} / $PM_{2.5}$, and characterization of the meteorological conditions conducive to high PM_{10} / $PM_{2.5}$ concentrations. Findings include evidence that particulate matter (PM) in the 2.5 micrometer (μm) range tends to result from combustion processes including electric generating technologies, while PM in the 10 μm range results from sources such as windblown dust or seasalt.

In addition, the evolution of CCOS allows for the study and understanding of ambient ozone in the same study area.

PG&E and its subcontractor participated in technical and policy discussions related to CCOS and CRPAQS, revised and commented on technical documents prepared for the study, and participated in research activities culminating in technical papers presented at conferences; publication of technical papers.

Other activities included documentation of a 1995 field research program, and preparation of nine individual technical reports addressing conceptual models for ozone and particulate matter formation in the central California region.

Of particular importance are the needs to:

- perform specific power plant plume-in-grid modules in atmospheric modeling for ozone,
- build a better understanding of oxidant chemistry for the fall and winter seasons to understand particulate nitrate formation reaction,
- further investigate through modeling the relative roles of oxides of nitrogen and volatile organic compounds in forming ambient ozone and nitric acid in the study area, and
- build an understanding of source-receptor relationships to address 8-hour ozone concentrations in rural receptors sites.

1.0 Introduction

The U.S. Environmental Protection Agency (EPA) and the California Air Resources Board have each promulgated Ambient Air Quality Standards (AAQS) for particulate matter (PM) and ozone (O_3). Both the state and national AAQS for PM and O_3 are routinely exceeded within the San Joaquin Valley. Ozone standards are exceeded within the San Francisco Bay Area.

To understand air quality problems in the San Joaquin Valley and provide tools for equitable and cost-effective air quality planning and decision-making, air quality studies have been in place since the mid-1980s. The San Joaquin Valley Air Quality Study (SJVAQS) was begun in the mid-80s. In 1988, Pacific Gas & Electric (PG&E) joined in collaboration with the SJVAQS team through its own Atmospheric Utility Signatures, Predictions and Experiments (AUSPEX) project. These projects took part in a massive field study in 1990 and supported the SJVAQS, AUSPEX Regional Modeling Adaptation Program (SARMAP), which performed data analysis of the field data and development of a regional model. In 1994, work in the SARMAP program resulted in a model to predict ambient ozone.

Central California is a complex region from an air quality and meteorological perspective, owing to its proximity to the Pacific Ocean, its diversity of climates, and its complex terrain. Within central California, the San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) and the Great Basin Air Pollution Control District (GBAPCD) have been designated to be in serious non-attainment of the 1987 National Ambient Air Quality Standards (NAAQS) for PM and are required to implement emissions reduction measures. Although the area administered by the Bay Area Air Quality Management District (BAAQMD) has not been designated as non-attainment, measured 24-hour PM_{10} (suspended particles with aerodynamic diameters less than 10 µm) concentrations in San Jose have exceeded 150 micrograms per meter cubed ($\mu g/m^3$). Reduced visibility in the Mojave Desert, and even in the Grand Canyon, has been attributed, at least in part, to $PM_{2.5}$ (suspended particles with aerodynamic diameters less than 2.5 µm) exiting the San Joaquin Valley through the Tehachapi Pass.

Summer ozone air pollution is a serious problem in the California San Joaquin Valley. With the exception of the Los Angeles area, the San Joaquin Valley records some of the highest O_3 concentrations in the United States. For example, between 1984 and 1986, the San Joaquin Valley exceeded the National Ambient Air Quality Standard (120 parts per billion, averaged over one hour) an average of 75 times per year. In 1997, the EPA established a new eight-hour running average NAAQS for O_3 of 80 parts per billion (ppb), which was remanded on May 14, 1999. Based on the data from the O_3 episodes during SJVAQS/AUSPEX, several sites in the San Joaquin Valley are out of compliance with the proposed eight-hour O_3 NAAQS (Chow et al., 1998). Within the San Francisco Bay Area, attainment of the federal ozone standard was achieved through formal EPA designation in 1995 for the years 1990 to 1994. However, the area was redesignated to non-attainment in 1997 after numerous exceedances of the one-hour ozone NAAQS occurred in 1995 and 1996.

California Energy Commission funding for the Regional Ambient Aerosol Studies (RAAS) project has allowed PG&E to continue with important technical contributions in the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). The original specific activities outlined in PG&E's proposal to the Commission include:

- Continue PG&E's participation in CRPAQS's technical and policy committees
- Continue to serve as the project manager for the 1995 Integrated Monitoring Study
- Provide high-level scientific expertise to CRPAQS in areas such as field studies design, planning of CRPAQS, and critical review of technical documents
- Disseminate scientific information through the participation in scientific workshops and conferences and the publication of technical papers in the peer-reviewed literature.

Early on, as PG&E continued with its involvement with CRPAQS, the Central California Ozone Study (CCOS) project was developed to address areas of concern. PG&E expanded its role by actively becoming engaged in the planning and review of CCOS as it continued in development. PG&E has participated in these studies since 1988 using funding sanctioned by the California Public Utilities Commission (CPUC) for research and development (R&D) projects related to power production facilities. When the CPUC transferred the management and control of public utilities' R&D funds to the California Energy Commission, starting in 1998, PG&E successfully bid to the Commission for funding to continue and maintain involvement in the central and northern California air quality studies. This report describes the work conducted under this funding during 1998 and 1999.

1.1 Ambient Air Quality Standards

National Ambient Air Quality Standards for Particulate Matter

The U.S. Environmental Protection Agency promulgated NAAQS for PM on July 18, 1997. These standards were remanded back to the courts on May 14, 1999; and are currently undergoing another round of procedural review. The proposed standards pertain to particles with aerodynamic diameter of less than 10 µm (PM_{10}) and those with aerodynamic diameter of less than 2.5 µm ($PM_{2.5}$). Before the most recent remanding action, the standards were set at:

- Annual average PM_{10}: Three-year arithmetic average of the annual arithmetic average PM_{10} concentrations not to exceed 50 $\mu g/m^3$ at any monitoring site.
- 24-hour average PM_{10}: Twenty-four hour average PM_{10} concentrations not to exceed 150 $\mu g/m^3$ for a three-year arithmetic average of annual 99th percentiles at any monitoring site.
- Annual average $PM_{2.5}$: Three-year arithmetic average of the annual arithmetic average $PM_{2.5}$ concentrations not to exceed 15 $\mu g/m^3$ for a single community-oriented monitoring site or the spatial average of eligible community-oriented sites.
- 24-hour average $PM_{2.5}$: Twenty-four hour average $PM_{2.5}$ concentrations not to exceed 65 $\mu g/m^3$ for a three-year arithmetic average of annual 98th percentiles at any population-oriented monitoring site.

California Ambient Air Quality Standards for Particulate Matter

The California Air Resources Board has established the following standards:

- 24-hour average PM_{10} concentrations not to exceed 50 $\mu g/m^3$

- Annual geometric mean of PM_{10} concentrations not to exceed 30 $\mu g/m^3$.

National Ambient Air Quality Standards for Ozone

The U.S. Environmental Protection Agency promulgated a new eight-hour NAAQS for ozone on July 18, 1997, while maintaining the original one-hour ozone standard. The eight-hour standard was remanded back to the courts on May 14, 1999; and is currently undergoing procedural review. The National Ambient Air Quality Standards for ozone are:

- One-hour average of 0.12 parts per million (ppm) for the fourth highest hourly average over a three-year period
- Eight-hour average of 0.08 ppm for the fourth highest eight-hour average over a three-year period.

California Ambient Air Quality Standards for Ozone

The California Air Resources Board established the following standard for ozone:

- One-hour average of ozone concentrations not to exceed 0.09 ppm.

1.2 Fossil Fuel Electric Power Plants within Central and Northern California

To complement the discussion of air quality issues within northern and central California and to relate this report to electric power production, an inventory of existing and planned fossil fueled powered plants was assembled. By and large, these power plants burn only natural gas. Depending on their age, the power plants have varying emissions rates of nitrogen oxide (NO_x) and stack heights. The planned facilities have generally the lowest emission rates. The power plants, especially the existing facilities, generally release their emissions through relatively tall stacks within exhaust plumes that have considerable thermal buoyancy to rise in the atmosphere. As noted later in this report, these emissions are differentiated from ground level releases of NO_x and behave differently in the atmosphere.

Existing Power Plants

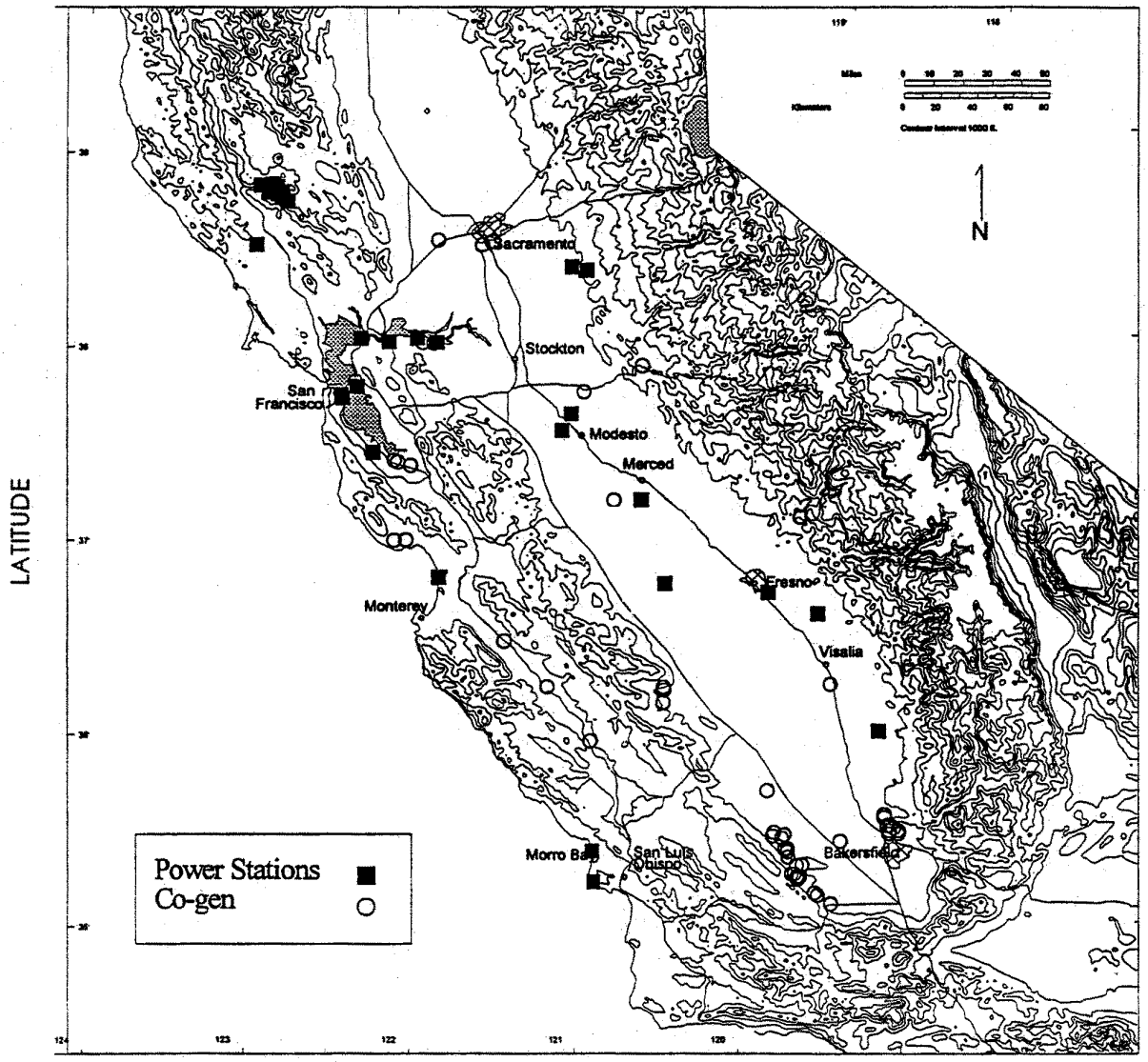
Table 1 provides a list of large (greater than 100 megawatt) power plants sites located within Central and Northern California, power plant production capacity and owner. Combined power plant production capacity totals exceeds 6,000 megawatts (MW).

Table 1. Existing Central and Northern California Fossil Fuel Electric Power Plants

Power Plant	Production Capacity	Owner
Moss Landing Power Plant	1712 MW (operable)	Duke Energy
Morro Bay Power Plant	1002 MW	Duke Energy
Potrero Power Plant	207 MW	Southern Energy
Delta Power Plants (Pittsburg and Antioch)	2682 MW	Southern Energy
Hunters Point Power Plant	379 MW	PG&E

Humbolt Bay Power Plant	105 MW	PG&E

Facilities less than 100 megawatts are not included in this list nor are gas turbines with low stack heights. These power generating units, especially the newer, larger units, all have relatively tall stacks compared to gas turbines, and thereby release emissions of NO_x at elevated levels (in contrast to ground level sources of NO_x, such as automobiles). Four of the older 170 MW units still in occasional operation at Pittsburg, California, have relatively short stacks and are predicted to experience plume downwash on occasion. There are other gas turbine and combined cycle power plant facilities owned and operated by traditionally non-utility companies including the Crockett co-generation facility, five GWF electric power generating units in the Martinez to Antioch area, and facilities owned and operated by various oil companies. Figure 1, originally presented by the Electric Power Research Institute (EPRI) in a proposal to the California Energy Commission in 1998 (EPRI, March 30, 1998), displays existing electric power production facilities.



(Source: EPRI, 1998)

Figure 1. Locations of Northern and Central California Electric Utility and Co-generation Facilities

Future Power Plant Sites

The California Energy Commission assembled a list (California Energy Commission, 1999) of proposed electric generation project sites in California. Table 2 provides a listing of those sites, power plant production capacity, and owner located within Central and Northern California.

Table 2. Proposed Central and Northern California Large Fossil Fuel Electric Power Plants

Power Plant	Production Capacity	Owner
Yuba City area, Sutter County	500 MW	Calpine
Pittsburg, Conta Costa	500 MW	ENRON
McKittick, Kern County	1043 MW	PG&E Generation
Pittsburg, Contra Costa	880 MW	Calpine & Bechtel
Fellows, Kern county	320 MW	Texaco Global Gas & Power
Elk Hills, Kern County	500 MW	Sempra & Oxy
Burney, Shasta County	500 MW	Ogden Power Pacific
Santa Clara County	600 MW	Calpine & Bechtel
Moss Landing Monterey County	1206 MW (repower)	Duke Energy
Morro Bay, San Luis Obispo County	530 MW (repower)	Duke Energy
Pasoria, Kern County	960 MW	Tejon Ranch
Newark, Alameda County	600 MW	Calpine & Bechtel
Midway-Sunset, Kern County	500 MW	ARCO Western Energy
California City, Kern county	1000 MW	AES
South San Francisco, San Mateo County	550 MW	AES
Kern County	400 MW	Unknown owner
Kern County	400 MW	Unknown owner
Yuba County	500 MW	Unknown owner
San Francisco Bay Area	500 MW	Unknown owner
San Francisco Bay Area	500 MW	Unknown owner

The power plants listed in Table 2 have filing dates from 1997 through 2001.If all of the power plants are built, an additional 12,489 MW of power production capacity will be added within the region: 4130 MW added within the San Francisco Bay Area, 5123 MW in the Kern area of the San Joaquin Valley, 1500 MW in the Sacramento Valley, and 1736 MW along the coast. The height of the emission release is unknown for each of these facilities.

1.3 Historical Perspective

The San Joaquin Valley Air Quality Study was established in the mid-1980s to understand air quality problems in California's San Joaquin Valley and to provide tools for equitable and cost-effective air quality planning and decision-making. In 1988, PG&E joined in collaboration with the SJVAQS through its own Atmospheric Utility Signatures, Predictions and Experiments project, a PG&E-funded research and development project with similar goals. Electric Power Research Institute, working in collaboration with PG&E, contributed approximately $6 million to the air quality study effort over a number of years.

As part of the joint research program of SJVAQS and AUSPEX, a major field measurement project was conducted in the summer of 1990. Field measurements were taken of meteorological and air quality variables at more than 300 sites throughout Central California from Sacramento to the Tehachapi mountains and from the Pacific Coast to the crest of the Sierra Nevada. Measurements involved ground-based instrumentation, aircraft, remote sensing, and balloon-borne instrumentation. Air quality measurements were obtained of ozone concentrations, the concentrations of ozone precursor chemicals, and the concentration and chemical composition of particulate matter. Meteorological quantities measured included temperature, humidity, solar radiation, wind speed, and wind direction.

In addition to this larger study, a smaller field study of air quality in San Luis Obispo County occurred. This study was performed under an Memorandum of Understanding between PG&E and the San Luis Obispo County Air Pollution Control District. Results of this study were used to augment the larger study and to evaluate the inter-basin transport of pollution with focus on NO_x emissions from the PG&E Morro Bay Power Plant (now owned and operated by Duke Energy).

The SJVAQS / AUSPEX collaboration and the 1990 field measurement program have been described comprehensively by Ranzieri and Thuillier (1994) and Solomon and Thuillier (1994).

Following the massive 1990 field study, SJVAQS joined with AUSPEX during the data analysis and subsequent modeling. This phase of the program was the SJVAQS / AUSPEX Regional Modeling Adaptation Program. In 1994, work within SARMAP resulted in a model to predict ambient ozone. This model was used in the State Implementation Plan (SIP) process for predicting ozone in later years within the San Joaquin Valley.

Near the conclusion of the SARMAP effort, interest developed within the San Joaquin Valley to investigate ambient particulate matter following the path of the successful ozone study. This study is called CRPAQS. An intensive field monitoring portion of this program is planned for the fall and winter of 2000 starting in late 1999.

To assist in the planning of the massive 2000 PM study, the 1995 Integrated Monitoring Study (IMS95), was conducted in the fall of 1995. IMS95 was a limited intensive field study to characterize PM within the San Joaquin Valley. Results and experience from this study have been used extensively in designing the upcoming CRPAQS.

It became apparent in late 1997 and early 1998, as CRPAQS evolved, that the modeling performed under SARMAP had under-predicted ambient ozone for the late 1990's. Results of SARMAP predicted that the San Joaquin Valley would be in attainment for the federal ozone

standard by 1999. Similar to other state implementation plans prepared throughout the nation, violations of the ozone NAAQS continued to occur after adoption in approximately 25 other regions of the nation. In the case of the San Francisco Bay Area, the region went from attainment (not needing an SIP) to non-attainment (starting in 1995). This non-attainment required a new SIP with concomitant additional emission controls to attain the ozone NAAQS. The BAAQMD's 1999 SIP is currently under review by the EPA. However, numerous exceedances of the one-hour ozone NAAQS in 1997, as well as the adoption in 1997 of a new federal eight-hour ambient ozone standard, prompted renewed interest in ozone within the San Joaquin Valley. With the extensive array of air monitoring and meteorological equipment planned for CRPAQS during the fall and winter of 2000, it was realized that addition of an ambient ozone field study during the summer 2000 could leverage considerable state-of-the-art field monitoring resources and environmental data. The Central California Ozone Study was conceived to take advantage of this opportunity.

Future data analysis and modeling to be conducted after the massive PM and ozone study of 2000, will occur within the framework of CRPAQS and CCOS respectively.

PG&E's effort in this project was named the Regional Ambient Aerosol Study. RAAS was initiated within PG&E's R&D program and existed until 1998. At this point, California Energy Commission Public Interest Electric Research (PIER) funding was used to continue PG&E involvement. This report is a summary of PG&E's work during 1998 to 1999.

1.3.1 SJVAQS/AUSPEX

The San Joaquin Valley Air Quality Study and Atmospheric Utility Signatures, Predictions, and Experiments were two components of a comprehensive study to address the issue of poor air quality in the California San Joaquin Valley. The study involved:

- Generating a large-scale air quality measurement program.
- Analyzing the causes of poor O_3 air quality
- Developing and applying a regional scale air quality modeling system that included a Mesoscale Model (MM5), an emission modeling system (EMS-95), and the SARMAP air quality model (SAQM).

The SJVAQS focused on determining the causes of the ozone levels exceeding NAAQS in the San Joaquin Valley. AUSPEX expanded the domain of research around SJVAQS. SARMAP, the adaptation program joining the two studies, was intended to develop a comprehensive model addressing O_3, aerosol, visibility, and acid deposition issues and to obtain a high-quality database for model evaluation and application (Blumenthal, 1993). To support these objectives, a field program was conducted during an eight-week period from July 9, 1990 to August 24, 1990. Fourteen intensive days, which corresponded to high O_3 episodes, were selected for detailed measurements. The technical objectives of the field program, detailed in Blumenthal et al, 1997, were to:

- Characterize the three-dimensional meteorological transport within the San Joaquin Valley, between the San Joaquin Valley and surrounding air basins, and among the surrounding air basins on the days leading up to and during O_3 episode

- Characterize the spatial and temporal patterns and frequency distributions of O_3, O_3 precursors, and PM concentrations in the study area
- Characterize pollutant fluxes
- Characterize emissions
- Characterize dynamic atmospheric processes in the study region
- Provide input and evaluation data for air quality and meteorological models, including initial and boundary conditions
- Develop an improved understanding of key chemical processes and intermediate species.

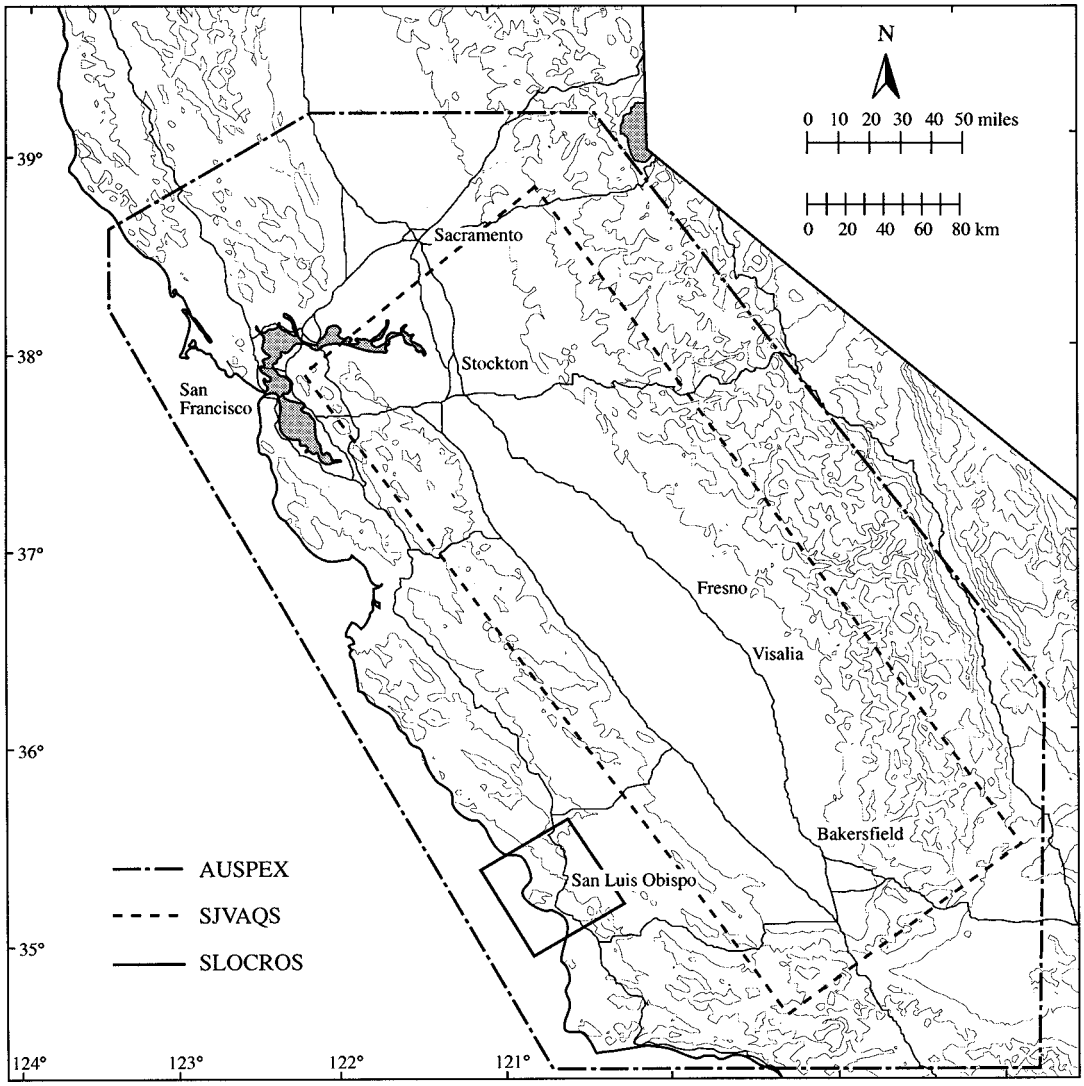
Figure 2 shows the SJVAQS / AUSPEX study domain (Ranzieri and Thuillier, 1994). The SJVAQS provided for a dense monitoring network within the domain of the San Joaquin Valley, ending just south of Sacramento. The AUSPEX study extended the spatial coverage to the coastal cities of San Francisco, Monterey, and San Luis Obispo, and to the Pacific Ocean. The northern and southern boundaries were extended to Sutter Buttes (north of Sacramento) and the Tehachapi Mountains, respectively. The Mojave Desert was also included in the southeastern part of the AUSPEX domain.

Surface air quality data were collected at 59 sites to supplement routine data from more than 70 stations. Forty-one of these sites measured O_3, nitric oxide (NO), nitrogen oxide, winds (speed and direction), and temperature. The remaining sites measured O_3 and winds as a minimum. Peroxyl acetyl nitrate (PAN) was measured continuously at 10 sites. Two to four samples of volatile organic compounds (VOC) (including carbonyl compounds) were taken at 36 sites and analyzed in laboratories. Ten of the O_3 sites also measured PM mass and $PM_{2.5}$ and PM_{10} chemistry. Light scattering and light absorption were measured at two sites. In total, air quality and / or meteorological data were collected at over 300 surface sites. Measurements that require collection of samples and subsequent laboratory analyses, such as VOC and PM chemistry, were obtained only on intensive episode days.

Point measurements of upper air meteorology were obtained from 49 sites. Continuous (hourly-averaged) upper wind measurements were taken using 7 radar profilers and 14 Doppler acoustic sounders throughout the study period. The range of the radar profilers was 2 kilometers (km) above ground level (AGL)., while that for the sounders was 500 meters (m). Twenty-nine balloon sounding sites were also set up to take four to eight (typically six) soundings per day of winds and temperature during O_3 episodes. On intensive days, up to nine instrumented aircraft measured both meteorology and air quality aloft.

Each aircraft made two to three flights per episode day. Different aircraft carried different instruments. Measurements of O_3, NO, NO_x, nitrogen dioxide (NO_2), VOC, light scattering, temperature, and dew point were obtained within the San Joaquin Valley to document the distribution of pollutants and offshore to characterize the boundary conditions.

Tracer studies were performed on intensive days to characterize the transport patterns from major source areas within and upwind of the San Joaquin Valley. Perfluorocarbon gas tracers were released from Bakersfield, Fresno, Hayward, Modesto, Pittsburg, and San Jose and measured with a surface monitoring network. The data obtained in tracer studies were also valuable for evaluating the performance of meteorological models.



(Source: Ranzieri and Thuillier, 1994)

Figure 2. The Study Domain of SJVAQS/AUSPEX

1.3.2 SARMAP

The SARMAP air quality model has been applied in Central California, including the San Joaquin Valley and surrounding air basins, to prepare the 1994 State Implementation Plan. The model was extensively tested and evaluated using the rich database of the San Joaquin Valley Air Quality Study. The model passed the model evaluation criteria of the U.S. EPA and the California Air Resources Board. Model attributes include: map projection capability to account for the curvature of the Earth; telescoping grid capability; a coordinate system that matches the coordinate system of MM5 to avoid interpolation between the two models; grid nesting capability (both one-way and two-way nesting); a high resolution vertical grid system (the

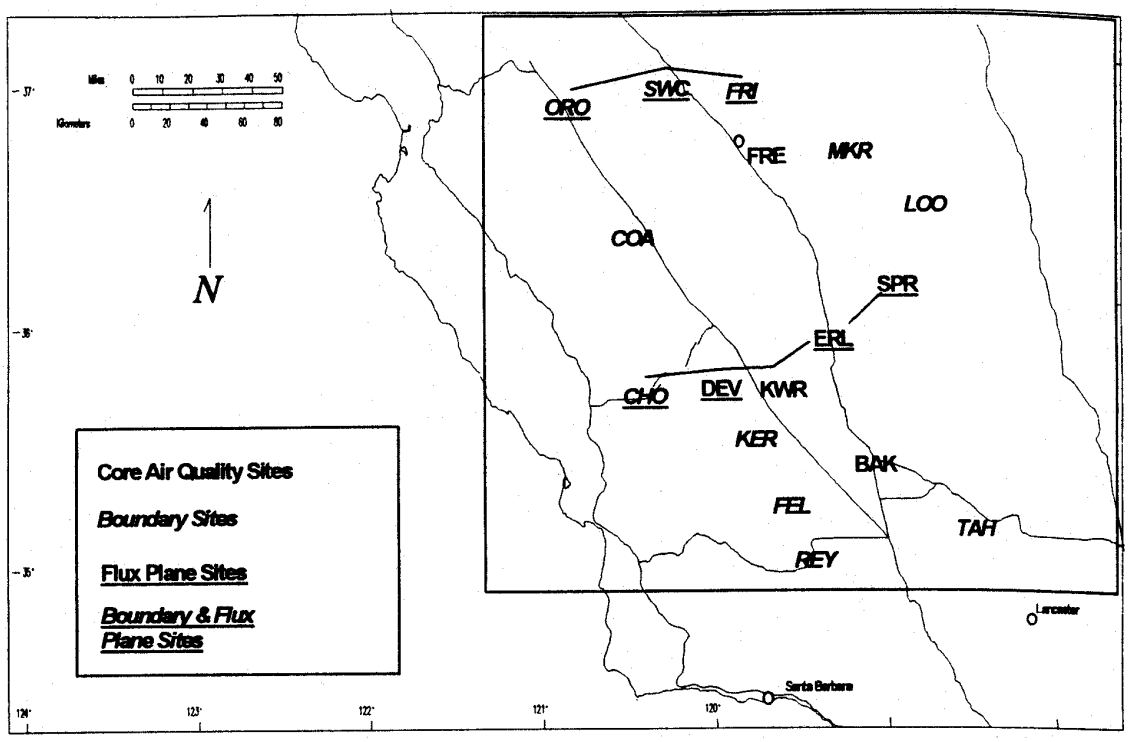
thickness of the layer near the ground cam be as low as 10 m with the surface layer submodule); two chemical mechanisms (Carbon-bond-IV and Statewide Air Pollution Research Center (SAPRC)); a Plume-in-Grid module; and three advection schemes. An aerosol module has been incorporated into the model. SARMAP was used in the SIP process to predict attainment of the ozone NAAQS within the San Joaquin Valley by 1999.

1.3.3 1995 Integrated Monitoring Study

IMS95 was the planning study of the CRPAQS, a comprehensive data collection and modeling effort. Under IMS95, two studies were undertaken during the fall and winter of 1995 to understand the formation of PM in the San Joaquin Valley. The study domain of IMS95 is shown in Figure 3.

Fall Study

The fall study was performed in the vicinity of Corcoran, California, with one core site (community-representative/community-oriented site) and 22 satellite sites. The satellite sites were set up to collect ambient samples in agricultural, industrial, and commercial/residential neighborhood areas. Twenty-four hour average PM_{10} samples were acquired daily from November 1, 1995 to November 14, 1995 at all locations. Daily 24-hour average measurements of ammonia (NH_3), light absorption, and PM_{10} mass were also reported. Detailed component analyses (including PM elements, chlorine$^-$, NO_3^-, SO_4^{2-}, volatilized NO_3^-, K^+, NH_4^+, organic carbon, elemental carbon, and artifact organic carbon) were performed on nine daily samples from selected sites.



(Source: Solomon and Altshuler, 1999)

Figure 3. IMS95 Winter Core, Boundary, and Flux Plane Air Quality Measurement Site Locations

Winter Study

The winter study featured high-resolution three-hour average measurements for PM_{10}, $PM_{2.5}$, nitric acid (HNO_3), and NH_3 at four locations: Bakersfield, Chowchilla (northern boundary site), Fresno, and Kern Wildlife Refuge (non-urban site). Daily 24-hour average NH_3, $PM_{2.5}$, and PM_{10} measurements were taken at selected sites. In addition to $PM_{2.5}$ and PM_{10}, size resolved-samples were collected at Bakersfield using a Multi-Orifice Uniform Deposit Impactor. Limited continuous (hourly) $PM_{2.5}$ and PM_{10} mass measurements were obtained using tapered element oscillating microbalances and beta-attenuation monitors, respectively. Hourly measurements of light scattering were also conducted using nephelometers. Component analyses were performed for samples on episode days. Supporting gas-phase measurements included hourly NO/NO_x (NO_2 by difference) and sulfur dioxide (SO_2), all days, and 3-hour or 24-hour average samples of hydrocarbon and carbonyl compounds at the urban sites (episode days).

A second component of the winter study was conducted at Walnut Grove, California, in the northern San Joaquin Valley, to characterize the vertical variations in fog/cloud chemistry and physics. Three-hour average measurements of fog composition were obtained at three different heights (ground level, 140 m, and 230 m above ground level). Limited droplet size-resolved data, pH for example, were also taken.

1.4 Upcoming Programs

1.4.1 CRPAQS Study Description

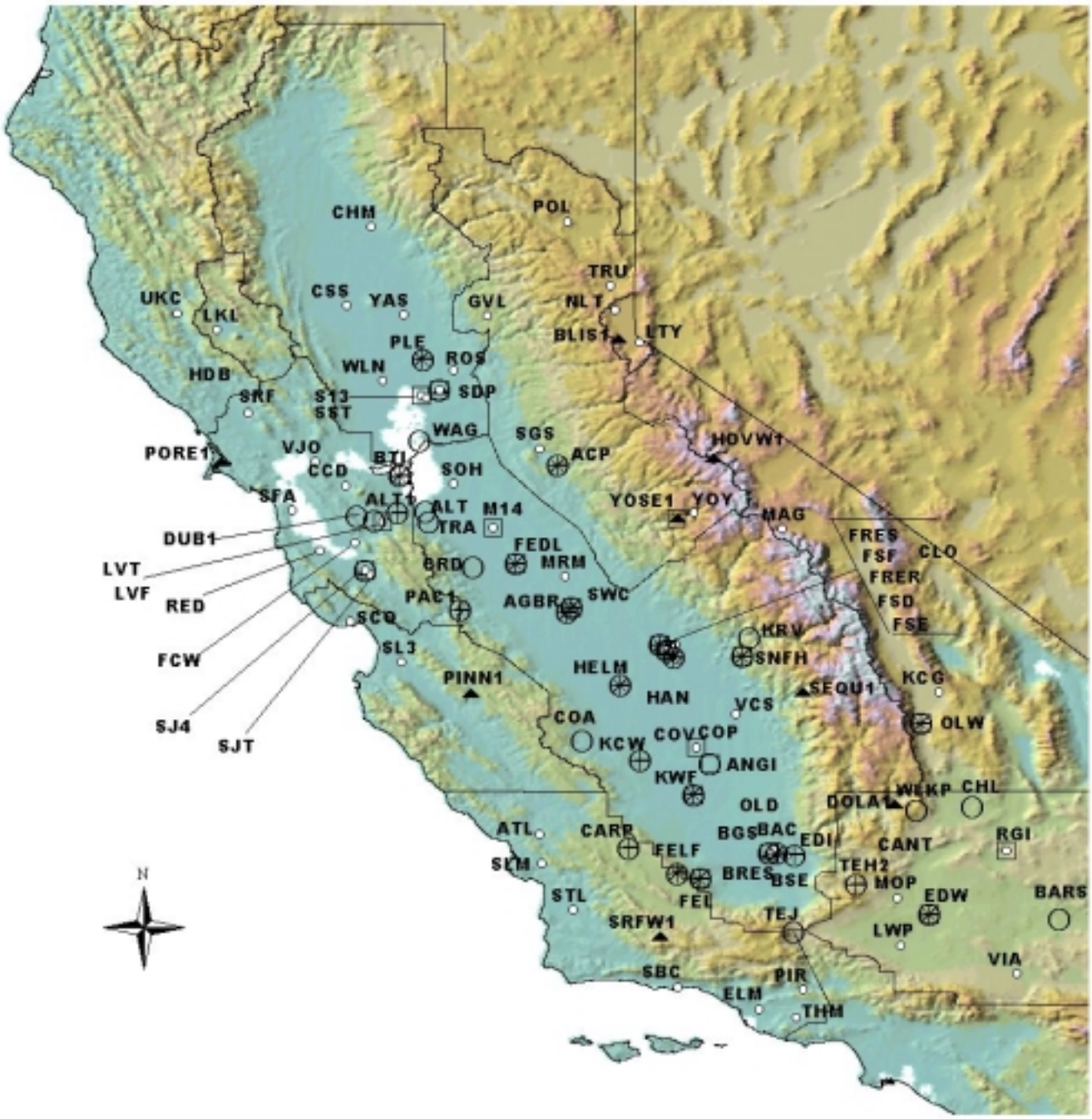
The main objective of the CRPAQS is to improve the scientific understanding of the $PM_{10}/PM_{2.5}$ problem in Central and Northern California. This includes a better quantification of emissions; a better understanding of the chemistry and physics involved in the transport, formation and removal of atmospheric $PM_{10}/PM_{2.5}$; and an improvement in the characterization of the meteorological conditions conducive to high $PM_{10}/PM_{2.5}$ concentrations.

The final product of the CRPAQS project will be the development of a state-of-the-art, regional $PM_{10}/PM_{2.5}$ modeling system that will allow air agencies in Central and Northern California to develop technically sound air quality management plans to comply with $PM_{10}/PM_{2.5}$ state and national ambient air quality standards. The following description of CRPAQS is taken largely from material displayed on a California Air Resources Board Web site (CARB 1999). The California Regional $PM_{2.5}/PM_{10}$ Air Quality Study of 1999 – 2000 contains three components: the annual study, the winter study, and the fall study. The monitoring domains are shown in Figure 4. The objectives of the CRPAQS, all related to the study of PM, are to:

- Obtain a quality data base
- Evaluate the backbone network (used to determine compliance)
- Examine temporal and spatial distributions of PM concentrations
- Examine boundary layer and regional circulation
- Estimate source zones of influence and contributions
- Determine sources of secondary aerosols

- Refine conceptual models
- Improve simulation methods.

The long-term average CRPAQS study will take place from December 1, 1999 to January 31, 2001, with daily continuous aerosol sampling and meteorological measurements at several sites to supplement the Air Resouces Board (ARB) backbone PM network. Upper air measurements of wind speed and direction will be acquired continuously (15-minute averaging time) at 11 sites using radar profilers, and at one site using a sodar. Upper air measurements of the virtual air temperatures will be obtained at the radar profiler sites using radioacoustic sounding systems (RASS). In addition, radiosondes will be launched twice a day at four sites to obtain aloft measurements of wind speed and direction, temperature, and relative humidity (RH). A 100-m micrometeorological tower will be set up at Angiola to obtain high time resolution measurements of meteorology and particle size at several levels. Information from the tower will aid in the interpretation of boundary layer evolution. Special studies will also be carried out for measurement technique evaluation, winter PM forecast, assessment of background site elevation, and summer organic aerosols.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N
PM2.5 minivol with quartz-NaCl & IC, AC, AA & TOR
PM2.5 minivol with Teflon/citric acid & grav, XRF, AC
Light Scattering/PM2.5 mass (nephelometer)
PM2.5 minivol-Teflon coated glass fiber & GC/MS
PM2.5 FRM single with Teflon & grav, XRF on 10 days
PM2.5 EPA or IMPROVE speciation sampler
Air Basins
100 0 100 200 Kilometers

Figure 4. Study Domain of CRPAQS

The winter study will be held toward the end of the annual study, from December 1, 2000 to January 31, 2001. In addition to continuous measurements of PM mass, size distribution, light scattering, sulfate, nitrate, and elemental carbon / organic carbon (EC / OC), gaseous measurements of oxidized nitrogen, ammonia, sulfur dioxide, nitric acid, and ozone will be obtained. Approximately 20 episode days will be selected for intensive monitoring. On those days, $PM_{2.5}$ elements, ions, some speciated organic compounds (both particulate and gas phases) will be obtained at intervals of five to six hours to supplement the continuous measurements. Additional upper air meteorological sites will also be set up to measure daily profiles of wind and temperature using radar profilers, RASS, and sodars. On episode days, two to six soundings of radiosondes will be made to capture the diurnal changes in upper air meteorology, including RH.

Details regarding the fall study are not clear, as the description of measurements in the monitoring plan recapitulates that for the annual study. Two special studies will be conducted to investigate agricultural dust suspension and deposition, and ammonia or nitric acid limitation in the vicinity of ammonia sources.

1.4.2 Central California Ozone Study

An ozone episode that was simulated using data acquired in 1990 by the San Joaquin Valley Air Quality Study will be usable for the 2003 SIP work addressing ozone for the San Joaquin Valley. The ability to address the proposed new eight-hour ozone standard will be substantially enhanced, however, if additional, more contemporary simulations designed more specifically around the new standard are developed. There is a unique opportunity to acquire field data for additional modeling in this area assuming approximately $10 million can be leveraged, to complement the planned fine particulate matter field study to be conducted in the same area during 2000. If the data to be collected during the summer of 2000 by the particulate matter study can be augmented, confidence in the ozone control strategies will be improved as they are incorporated in the SIP with substantially less money than if the proposed work were to be conducted independently.

Data collected within the Central California Ozone Study will be used to simulate one or more ozone episodes. This data will be used by the ARB and the districts to evaluate candidate SIP control strategies and to perform demonstrations of attainment required in the SIP. These simulations also will be used by the ARB and the districts to:

- Assess inter-basin transport
- Estimate impacts large emission sources would have on regional ozone levels
- Evaluate the air quality consequences of changes in land use, transportation, and industry. Such changes might include construction of large power plants, and oil and gas production facilities, or major transportation system changes.

Contemplated field monitoring within CCOS includes a range of data collection activities. The minimum program, Phase I, would help with the 2003 SIP for only the San Francisco Bay Area Air Basin and the Sacramento area. This minimum program, including assessment of the transport into and from adjacent air basins, would cost approximately $2.25 million.

A larger study within CCOS, Phase II, is being considered at a cost of $5 to $6 million. This study would be conducted for the San Francisco Bay Area and the entire Central Valley, with the kinds and amounts of data collected the minimum needed for modeling.

A more comprehensive measurement program, Phase III, would include all of Central California, from Redding in the North to the Mojave Desert in the South, and from the Pacific Ocean in the west to the Sierra Nevada Mountains in the east. This program would provide a database for modeling with minimum uncertainty, and is estimated to cost $10 million.

Technical Objectives

The primary objective of CCOS is to obtain a suitable database for grid-based, photochemical modeling. The ARB and districts will use this database to apply photochemical models to examine the effects of emission reductions on ozone concentrations and to prepare the demonstrations of attainment for the eight-hour ozone standard for non-attainment areas in Central California.

CCOS will be designed to collect data continuously during the summer of 2000 in between major elements of CRPAQS. Surface and upper air meteorological data as well as surface air quality data for NO_x and ozone will be continuously collected during the entire summer of 2000. This database will be suitable for modeling. To better understand the physics and chemistry of the formation of high ozone concentrations, and to reduce uncertainty in the models used for SIP, additional data will be collected during ozone episodes. Surface air quality data for hydrocarbons and carbonyls, air quality data aloft measured from aircraft, and data measured using special instruments such as Lidar will be collected during 20 high ozone days.

2.0 Technical Report

To meet the California Energy Commission contractual commitments, and with prior approval from the Commission and the California Air Resources Board (CARB) prior approval, Pacific Gas & Electric (PG&E) teamed with Atmospheric and Environmental Research (AER), after competitive bid, to meet the obligations of this project. Use of AER was an opportunity to engage a renowned expert in air pollution, Dr. Christian Seigneur, and his staff**,** in the planning and review process for the upcoming field and modeling studies. In addition, AER, not having been involved directly with previous Central California studies, provided a fresh perspective. Within this section, the work performed by this time to meet the technical objectives of the Regional Ambient Aerosol Studies (RAAS) project is described.

2.1 Concept Model of Particulate Matter Pollution in the California San Joaquin Valley

The final report for this project effort is provided in Appendix I of this document.

2.1.1 Study Background

Limited particulate matter ($PM_{2.5}$) measurements from Central California indicate that the proposed annual 15 microgram per meter cubed ($\mu g/m^3$) standard will probably be exceeded in several populated areas, especially in the San Joaquin Valley (Watson et al., 1998). These annual average concentrations are dominated by elevated concentrations that occur primarily during fall and winter. In addition, the National Ambient Air Quality Standards (NAAQS) 24-hour standard (currently remanded) for $PM_{2.5}$ (65 $\mu g/m^3$) was exceeded several times during the 1995 Integrated Monitoring Study (IMS95) and the 24-hour standard value for PM_{10} (150 $\mu g/m^3$) was exceeded twice during IMS95.

2.1.2 Study Objectives

The objective of the analysis was to formulate a conceptual model for fall and winter PM concentrations in the San Joaquin Valley primarily using the information obtained during IMS95. This conceptual model is a qualitative description of the physical and chemical processes that govern the formation of PM in the atmosphere, which, to the extent possible, is supported by quantitative information. The conceptual model is visualized in Figure 5. The conceptual model is an important link between the planning study, IMS95 and the comprehensive field program, the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). The model identifies the major characteristics of the meteorology and atmospheric composition of the area that are relevant to PM formation. Thus the conceptual model is a valuable tool: to guide data collection priorities of CRPAQS and to aid future model development and evaluation activities.

2.1.3 Study Findings

Chemical Composition and Transformations

A primary component of the fall PM_{10} was identified as geological material (dust), which accounted for 57 percent of the mass according to chemical mass balance (CMB) analyses. Limited information is available regarding the source of the dust particles. Given that wind speeds were typically less than 2 meters per second (m/s^{-1}), it seems unlikely that wind-blown

dust was a significant contributor to PM_{10}. Sources of mechanically generated aerosols, such as paved and unpaved roads and farming activities, are likely mechanisms causing elevated PM_{10} and may be addressed by tracer experiments. The need was identified for accurate geological material profiles and tracer-based organic profiles for major San Joaquin Valley primary sources to increase the resolution of the CMB.

Ammonium nitrate was identified as the second most important component of PM_{10} in the fall, accounting for about 16 percent of the mass at the Corcoran core site. The formation of ammonium nitrate warrants further discussion. One key question is whether the formation of nitrate is limited by the availability of nitric acid or ammonia. Kumar, Lurmann, and Pandis (1998) showed that the atmosphere in the monitoring domain within the southern part of the San Joaquin Valley was ammonium rich in the winter. It is likely that the system is also more sensitive to nitric acid than to ammonia during the rest of the year, especially in the summer when the oxidant chemistry is nitrogen oxide-sensitive (Lu and Chang, 1998) and, therefore, not conducive to the formation of nitric acid. It is recommended that the nitric acid sensitivity should be confirmed for fall conditions, which have different reaction rates (due to different temperature and solar radiation), mixing conditions, and emissions. Fog was not prevalent during the fall and the atmosphere was relatively dry; therefore, it was postulated that the OH reaction may be more important than the N_2O_5 hydrolysis route in the production of nitric acid (HNO_3) in the fall. To confirm the important nitrate formation reactions, development of a better understanding of oxidant chemistry for the fall season in the San Joaquin Valley is needed. Emphasis should be placed on studying the gas-phase oxidation pathways of nitrogen oxide (NO_x) to HNO_3, and the sensitivity of oxidants (OH, ozone, and NO_3) to NO_x and volatile organic compounds (VOC), as shown in Figure 6. Another PM component needing further investigation is the excess organic carbon (OC) present in the atmosphere. These are the organic compounds not accounted for by the source profiles explicitly included in the CMB study. Excess OC includes both primary (e.g., from meat cooking, wood burning, and motor vehicle exhaust) and secondary organic components. Tracer-based receptor modeling may be used to analyze the source of excess OC, and determine whether these are primary or secondary organic compounds.

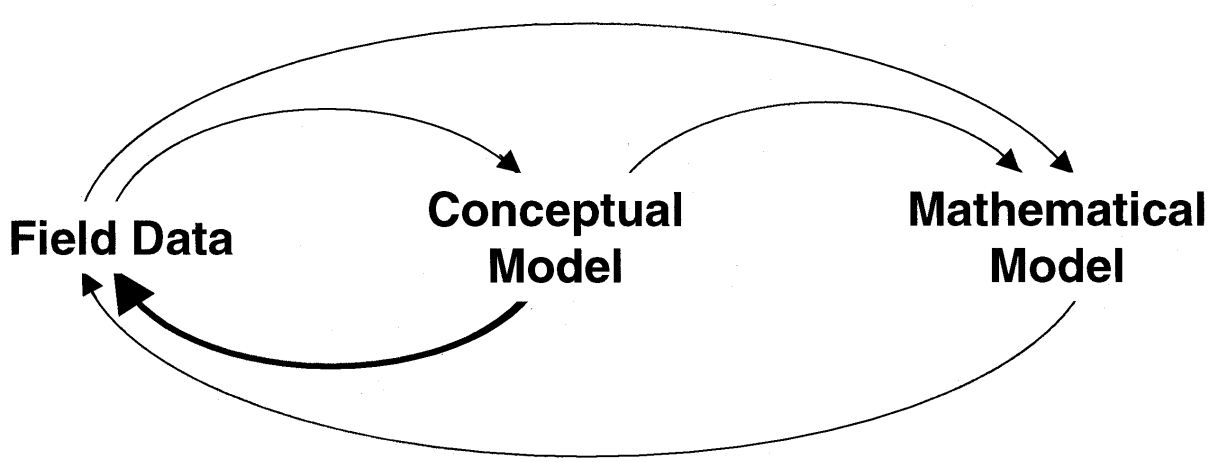


Figure 5. Framework of a Conceptual Model

Physical Transport

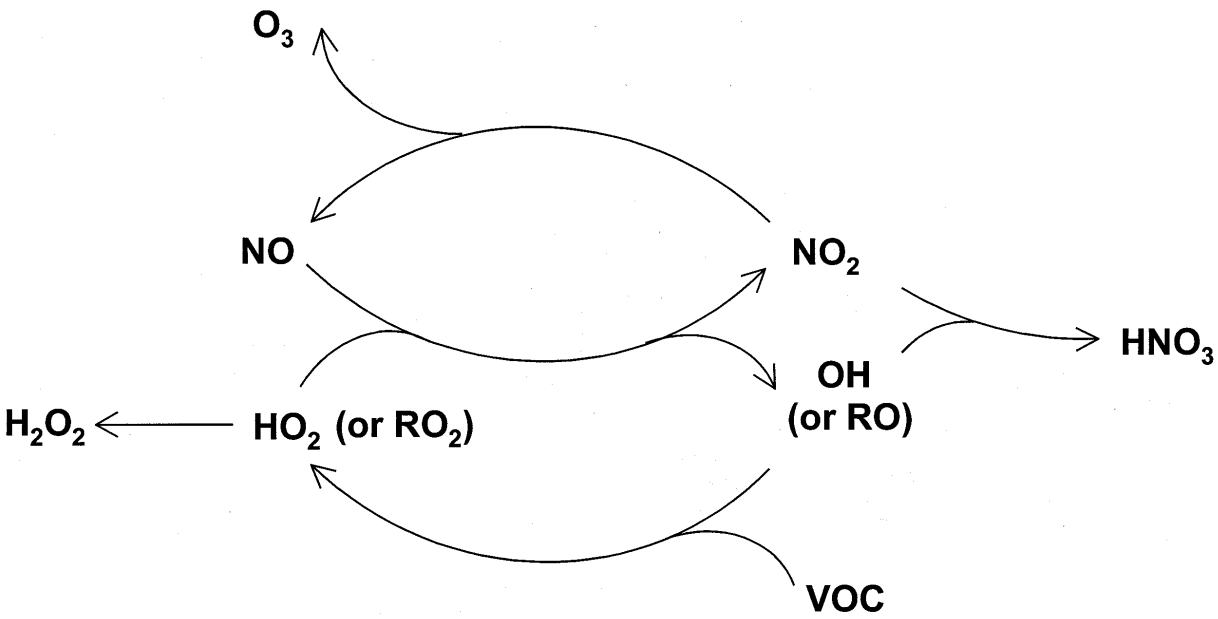
There is little direct evidence from which to infer the dominant physical transport processes affecting the concentrations of PM in the San Joaquin Valley in the fall. Collins (1998) showed that PM concentrations are generally highest during periods of light and variable winds which tend to come from the southeast. Lower PM concentrations were associated with stronger northeasterly winds. PM_{10} concentrations were observed to correlate well with the aloft temperatures measured at Oakland, California (850 millibars temperature at about 1500 meters or 5000 feet), indicating reduced mixing as a major cause of the observed PM episodes. Furthermore, both primary (e.g., dust) and secondary components (e.g., nitrates) increased during the fall episodes. These observations tended to support a sub-regional build-up of PM as the culprit of the pollution episodes under the particular fall conditions. The dominance (57 percent) of dust or geological material in the PM composition also supported the sub-regional build-up hypothesis, as coarse materials are generally not transported over great distances. The correlation of PM_{10} concentrations among the core and satellite sites (i.e., the fact that the concentrations at all sites increase and decrease together) indicated that meteorology was the driving force behind episodes in the Corcoran area, with a mean of 100 $\mu g/m^3$. Spatial variability recorded by the network was attributed to local influences. It was found that industrial sites tended to record higher concentrations than the residential sites. Average PM_{10} concentrations were 134 $\mu g/m^3$ at industrial sites, 113 $\mu g/m^3$ at agricultural sites, and 112 $\mu g/m^3$ at commercial/residential sites (Chow and Egami, 1997). Because of the intermittent nature of the many PM-generating activities, however, activity observations did not correlate well with the 24-hour data collected (Coe and Chinkin, 1998). No meteorological data were available at the monitoring sites to evaluate the contribution of local wind-blown dust.

Long-range surface transport from upwind pollutant sources to Corcoran was unlikely, as the surface wind speed was typically less than 2 meters per second (m/s) during the fall episodes in Corcoran. Mixing height, upper air winds, and concentration data are necessary to evaluate the impact of vertical mixing and long-range transport of precursors and PM aloft.

Deposition

Wet deposition was mostly a function of fog in the San Joaquin Valley PM episodes studied. The effects of fog are two-fold. First, particles that become fog droplets by absorbing water vapor are subsequently removed by gravitational settling. In addition, fog droplets provide the aqueous medium for the production of sulfates. The net effect of a fog event depends on the length of the event, the availability of precursors, oxidants, and catalysts, and the composition of the original PM. It is advisable to study the wet deposition phenomenon further, and to understand if any recycling of PM and gaseous pollutants occurs through volatilization at the conclusion of the fog event.

Wet deposition probably played a minor role in the dissipation of PM during the fall episode. No rain was reported during the PM monitoring period in November, and only patchy evening fog was reported in Fresno.



Note: Shows the two major interacting cycles (NO/NO_2 and OH/HO_2 or OH/RO_2) and the two major sinks for radical chain termination: H_2O_2 (NO_x sensitive) and HNO_3 (VOC sensitive)

(Source: Seigneur et al., 1998b)

Figure 6. Simplified Description of Photochemical Smog Formation

No information was available from IMS95 to determine whether dry deposition provides a dominant sink for PM and PM precursors in the San Joaquin Valley in the fall. Depending on the size of the coarse material (e.g., dust), dry deposition could play a role in the PM balance at the Corcoran location.

2.1.4 Study Conclusions and Recommendations

Summary of Conceptual Model

A data-driven approach was used in the formulation of a conceptual model for PM during IMS95. Available information was systematically compiled into a framework based on the chemical characteristics of and transport processes associated with the observed PM. A summary of the key features of the conceptual models for the fall and winter PM episodes in the San Joaquin Valley are presented in Table 3.

Comparison with the Conceptual Models of Watson et al. (1998)

Compared to previous conceptual models, this model places a stronger focus on understanding the chemical processes behind the formation of secondary compounds and, therefore, is postulated to provide a better balance between meteorology and chemistry in the analyses of the PM episodes. Watson et al. (1998) discussed the primary compounds in terms of their sources and secondary PM in terms of their precursors: ammonia (NH_3), sulfur dioxide (SO_2)

for sulfate, and NO_x (HNO_3) for nitrate. Another facet was added to the analysis of the secondary compounds and pointed out the need to address the availability of oxidants that govern the chemical transformation of precursors to PM. There was evidence to support that the oxidation of NO_x to HNO_3 was limited by the availability of oxidants, as was the oxidation of SO_2 to sulfate. In addition, different reactions, involving different oxidants, may contribute to the formation of secondary sulfate and nitrates depending on such variants as the time of day, the presence of fog and clouds, the amount of available light, and relative humidity.

To understand these chemical systems, and to design effective control strategies, it is recommended that further work be done to measure key oxidants accurately and to improve the understanding of the oxidant chemistry, particularly its sensitivity to NO_x or VOC. The effectiveness of any controls placed on the precursors will be dependent on the limiting reagents. In addition, it is important to coordinate the efforts to control oxidants in the summer and in the winter. Summer oxidants may be sensitive to NO_x. NO_x controls, however, must be accompanied by methods to address VOC concentrations if the oxidants involved in the wintertime formation of secondary PM are more sensitive to VOC than NO_x. This problem was investigated further by conducting simulations of particulate nitrate formation using a box model, further discusses in Section 2.6 of this report.

Another component that was not analyzed in detail in Watson's approach was secondary organic aerosol (SOA) formation. Limited analyses seem to indicate that it could be a non-negligible contributor at the rural sites. At the urban sites, Watson et al. (1998) narrated the events that led to PM formation during winter that involve:

- Accumulation of PM and precursors over night
- Mixing with aloft air in the morning and early afternoon (reduction in PM and precursors)
- Photochemical production and accumulation aloft (clear sky) of oxidants, nitric acid, and secondary aerosol
- Entrainment of secondary aerosol by stratus cloud droplets and aqueous oxidation of sulfur
- Radiation inversion separating pollutants aloft and those accumulating at the surface
- Mixing of ammonia and nitric acid by upper air transport.

This analysis seems to be consistent with available information. Some components of Watson's analysis, however, are hypotheses that cannot be confirmed with available evidence. Aspects of Watson's conceptual model that require verification include the aloft production of oxidants and secondary compounds, the role of cloud droplets, and the upper air transport as a mechanism of pollutant dispersion. The removal processes of wet and dry deposition were not addressed in Watson's conceptual model. Analysis of the physical transport and removal processes, based loosely on mass balance arguments, confirmed the lack of ground level advection and reduced vertical mixing as the principal meteorological conditions associated with PM build-up. Aloft transport is possible as a mechanism for pollutant dispersion under apparently stagnant conditions. Widespread sources of precursors and diffusion are possible explanations of the regional distribution of pollutants. To complete the understanding of the

mass fluxes within the valley, there is also a need to understand the wet and dry removal processes.

Watson et al. (1998) proposed a separate conceptual model for the fall. The basic features of Watson's fall conceptual model are feasible, with primary sources responsible for local influences and secondary compounds responsible for the "subregional influence." The key differences between the fall and the winter conceptual models are the contribution of dust and the lack of fog. Watson et al. (1998) also proposed that the stronger along-valley flows transport particles into the Mojave Desert, although IMS95 was too limited in its geographical scope to evaluate the full range of transport.

Several measurements are proposed to verify aspects of Watson's model: particle size distribution information will aid in the determination of particle lifetimes and the distance of dust dispersion; and measurements of photochemical oxidants will be useful in determining the sensitivity of the oxidant system for nitric acid production.

Oxidant production may be sensitive to NO_x or VOC; the terms "NOx limited" or "VOC limited" are commonly used to describe these phenomena. There is some evidence that ozone formation in the summer is sensitive to NO_x (Lu and Chang, 1998). Data from IMS95, however, seemed to indicate that the formation of oxidants and HNO_3 during the winter season was sensitive to VOC, although the indicator approach (Sillman, 1995; Lu and Chang, 1998) has not been verified for the cooler and foggier winter conditions. Oxidant chemistry should be investigated further to confirm the precursor (NO_x or VOC) sensitivity in the winter season. This basic understanding of the atmospheric system is important because any reduction of NO_x (e.g., for controlling summer ozone) may increase the abundance of HO_2 radicals and enhance the production of H_2O_2 (see Figure 6). Since ozone and H_2O_2 are both oxidizing agents of SO_2, the trade-off between the different reaction pathways needs to be understood.

Table 3. Summary of Conceptual Models

	Winter ($PM_{2.5}$)	Fall (PM_{10})
Chemical Composition and Transformations	Ammonium Nitrate (46%) Nitric Acid Sensitive Nitric Acid Formation Possibly Limited by Oxidants (OH, O_3, and NO_3) Availability Oxidants May be VOC-Sensitive Rather Than NO_x-Sensitive Organic Compounds (34%) Primary (e.g., Vegetative Burning and Mobile Sources) Secondary (Anthropogenic or Biogenic Precursors)	Geological Material (57%) Ammonium Nitrate (16%)
Transport Processes	Limited Ground-Level Transport Calm Winds Aloft Transport Possible Limited Vertical Mixing Wet Deposition (Fog) Dry Deposition Unknown Urban Influences (Primary Sources) on Regional Distribution (Secondary NH_4NO_3, SOA)	Limited Ground-Level Transport Aloft Transport Possible PM Build-Up Correlates with Reduced Mixing Height Limited Wet Deposition (Mild Fog) Dry Deposition Unknown Local Influences (Geological Material) on Sub-regional Distribution (Secondary NH_4NO_3)

After completion of the report, AER prepared a manuscript titled "Understanding Particulate Matter Formation in the California San Joaquin Valley: Conceptual Model and Data Needs" and submitted it for publication in the special issue *of Atmospheric Environment* for the IMS95.

2.1.4.1 Implications to CRPAQS

To confirm the important nitrate formation reactions, development of a better understanding of oxidant chemistry for the fall season in the San Joaquin Valley, California, is needed. Emphasis should be placed on studying the gas-phase oxidation pathways of NO_x to HNO_3, and the sensitivity of oxidants (OH, O_3, and NO_3) to NO_x and VOC during the fall. Secondary ammonium nitrate was an important component of PM. It was shown that nitric acid limited the yield of this secondary compound, as ammonia was abundant within the IMS95 study area.

To control nitric acid formation effectively, development of a better understanding of the NO_x/VOC/oxidant chemistry for the San Joaquin Valley is recommended.The formation of nitric acid should be studied in detail. Two chemical reactions are of interest: nitrogen dioxide (NO_2) + OH and N_2O_5 + water (H_2O). Since N_2O_5 is formed from the reaction of NO_2 with NO_3,

this reaction may be important in the evening or during a fog episode when NO_3 accumulates due to the lack of photolytic dissociation. N_2O_5 cannot be measured directly, but the formation rate of nitric acid via N_2O_5 hydrolysis may be inferred from measurements of NO_3. Other oxidized nitrogen species, including HNO_3, particulate nitrates, HNO_2, peroxyl acetyl nitrate (PAN), and other organic nitrates, may also be measured to improve the understanding of nitrogen chemistry. The accumulation of pollutants such as NO_2, HNO_3, was associated with stagnant conditions with limited surface transport. Under these conditions, the regional uniformity of secondary pollutants (such as ammonium nitrate and secondary organic aerosols) within the San Joaquin Valley is intriguing. Questions raised include:

- Was the time scale of reaction and deposition slower than the time scale of transport (advective or diffusive) under stagnant conditions?
- Or were widespread sources responsible for the regional scale concentrations of pollutants? In the fall episode, and in some winter episodes, the influence of regional sources was evident (Blanchard et al., 1998). It should be useful to better characterize the meteorological conditions that are associated with enhanced regional influence.

Further study of secondary organic also should be conducted. During IMS95, the relative contribution of secondary organic aerosols to PM was significant at the rural sites. In addition to the transport and transformation of anthropogenic emissions from urban areas, the atmospheric reactions assessed indicated that sulfate seemed to be a minor (6 percent) component of San Joaquin Valley PM in the fall and winter. With abundant SO_2 in the southern part of the valley, however, and the sensitivity of sulfate production to changes in oxidant concentrations, the mechanisms for sulfate formation should be examined more closely. This investigation will ensure that changes in precursor (NO_x or VOC) emissions designed to reduce ozone and other components of PM will not have adverse effects on the sulfate problem.

Two areas of research needs identified by IMS95 researchers are the source of fog buffering capacity and the sensitivity to precursors of ambient ozone measurements at the parts per billion (ppb) levels. Modern ozone instruments with sub-ppb detection limit and sensitivity (Seigneur et al., 1998a and references therein) may need to be considered in future field studies. Accurate relative humidity (RH) measurements are also needed to understand the importance of various aqueous-phase processes. Furthermore, McDade's finding (McDade, 1997) that light extinction was sensitive to particulate water, confirmed the need for such measurements for determining light scattering by PM.

One question IMS95 did not sufficiently address because of its limited scope was the magnitude of above-ground transport. There is some evidence that transport of pollutants aloft and subsequent mixing into the surface layer (in the middle of the afternoon) may be a mechanism of distributing pollutants within the valley in a multi-day episode. Aloft measurements of concentrations will be needed to determine the magnitude of this mixing process.

Dry deposition information is needed to complete the understanding of major mass fluxes in the San Joaquin Valley system. Direct measurements of dry deposition fluxes by the eddy correlation technique over a variety of land-use types are needed for both PM and precursor gases, including O_3, HNO_3, NH_3, and other nitrogen-containing compounds.

2.1.4.2 Implications to Electric Power Plants

Issues raised relating NO_x to nitrates are important to emission sources of NOx, such as electric, fossil fueled power plants. The understanding that ammonium nitrate, as a fine particulate, is controlled by the available nitrate in the atmosphere is important. Further that ambient nitrate is, in turn, controlled by ambient oxidant levels is critical. And lastly that ambient oxidants are, during winter-time, VOC limited and, during summer time, NO_x limited within the San Joaquin Valley, has important implications to any existing or potential new power plants emitting NO_x in the San Joaquin Valley. Ambient concentrations of ozone and PM both exceeding various ambient air quality standards in the Valley cause air regulatory agencies to focus on optimum control strategies to achieve attainment for both pollutants.

Further discussion about nitrates is provided in Section 2.6 of this report, which examines nitrate-NO_x-O_3-VOC relationships and interactions.

2.2 Conceptual Model of Ambient Ozone Pollution in the California San Joaquin Valley

The complete final report for this study is provided in Appendix II of this document.

2.2.1 Study Background

Ozone Problem in California's San Joaquin Valley

Summer ozone air pollution is a serious problem in the California San Joaquin Valley. With the exception of the Los Angeles area, the San Joaquin Valley records some of the highest O_3 concentrations in the United States. For example, between 1984 and 1986, the San Joaquin Valley exceeded the National Ambient Air Quality Standard (120 ppb, averaged over one hour) an average of 75 times per year. In 1997, the U.S. Environmental Protection Agency (EPA) established a new eight-hour running average NAAQS for O_3 of 80 ppb, which was remanded on May 14, 1999. Based on the past data from the O_3 episodes during San Joaquin Valley Air Quality Study (SJVAQS) / Atmospheric Utility Signatures, Predictions and Experiments (AUSPEX), several sites in the San Joaquin Valley are out of compliance with the proposed eight-hour O_3 NAAQS levels (Chow et al., 1998).

2.2.2 Study Objectives

The main objective in this study was to develop a conceptual model for O_3 formation, transport, and accumulation in the California San Joaquin Valley primarily using the information obtained during the SJVAQS / AUSPEX program of 1990. This conceptual model is a qualitative description of the physical and chemical processes that govern the formation of O_3, which, to the extent possible, is supported by quantitative information. Through the identification of the key processes and key knowledge gaps, the conceptual model for O_3 serves as a useful tool to guide future research and mathematical model development.

The methodology used to develop the conceptual model for O_3 formation in California's San Joaquin Valley is similar to the methodology developed for and applied to the development of the conceptual model for PM, discusses in Section 2.1 of this report, in the same geographic area

(Pun and Seigneur, 1998). This methodology is data-driven and works backward in time. The two components of the analysis are:

- An analysis of the chemical transformations
- An analysis of the physical transport processes.

2.2.3 Study Methodology

Chemical Processes

The atmospheric concentrations of O_3 and associated chemicals, such as VOC, NO_x, and PAN, provided the starting point for formulating a conceptual model based on chemical transformations. O_3 precursors, NO_x or VOC, may be transported over great distances to produce O_3 at a given location. Therefore, the physical transport processes of both O_3 and O_3 precursors are considered. The two analyses were then combined into the conceptual model.

Figure 7 illustrates the analysis framework for chemical transformations. O_3 is produced in the atmosphere from the reactions of VOC and NO_x. These compounds are emitted from anthropogenic and biogenic sources. This differentiation is particularly important for VOC since biogenic sources contribute significantly to the atmospheric burden of VOC at some San Joaquin Valley sites, particularly during summer. A major question is the sensitivity of O_3 concentrations to the availability of NO_x and VOC.

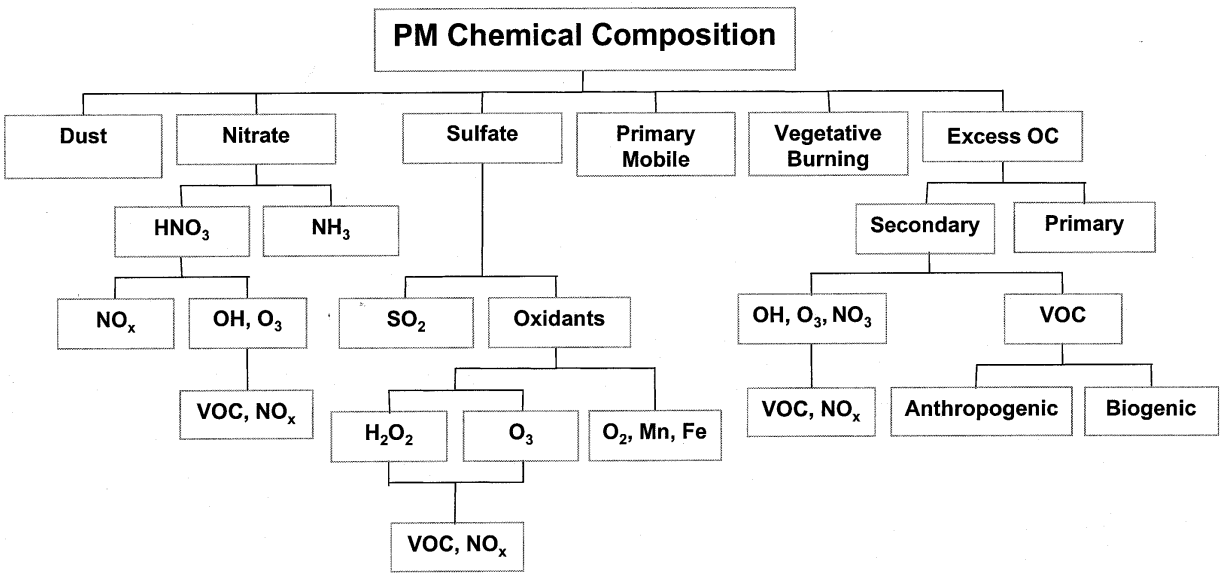
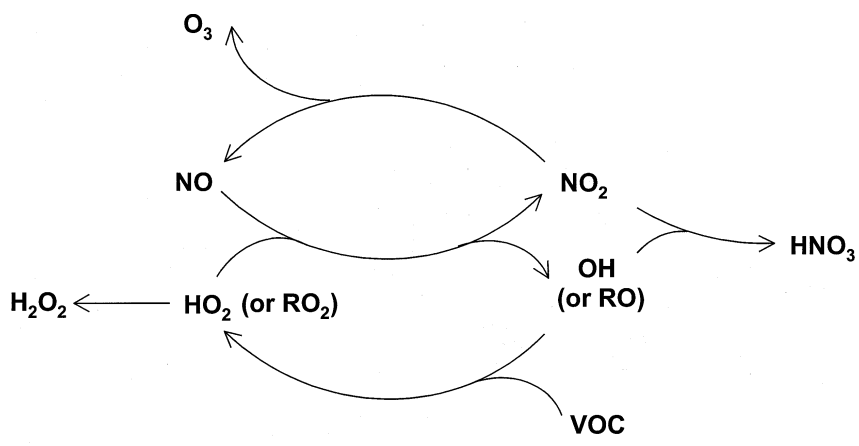


Figure 7. Analysis of Chemical Transformations Framework Leading to Os=zone Formation in the San Joaquin Valley

The major chemical pathways of the VOC / NO_x / O_3 system are shown in Figure 8. If VOC concentrations are low (VOC-sensitive regime), OH radicals are available to react with NO_2 to form HNO_3. If NO_x concentrations are low (NO_x-sensitive regime), HO_2 radicals tend to recombine to form H_2O_2 rather than to react with NO. Therefore, the ratio of HNO_3 and H_2O_2 may be used as an indicator of the VOC / NO_x sensitivity of the system. Other indicators that have been used include NO_y, formaldehyde (HCHO) / NO_y, O_3 / (NO_y- NO_x), and (NO_y-NO_x) /

NO_y (Lu and Chang, 1998). The sensitivity characterization provides information regarding which pollutant or combination of pollutants should be controlled to obtain the maximum benefits in O_3 reduction. This is important as sources of VOC and NO_x (power plants with tall stacks) are considered for emission controls.

To extrapolate this information to the specific sources to control for O_3 reduction in a particular area, additional information is needed to define the source- receptor relationship of the ozone precursors. At a location mostly affected by local emissions, control of local sources will achieve the desired reductions in precursors and ozone. At some receptor locations, however, upwind sources may need to be targeted for controls. Upwind areas may contribute to ozone at a given location via surface (automobiles, industry, domestic) and aloft (power plants and refineries with tall stacks) transport of emissions. Since the range of aloft transport is typically farther than surface transport, an upwind source may be hundreds of miles away from a receptor site affected by such transport. In this case, a regional strategy is necessary to address high O_3 concentrations. The sensitivity of O_3 concentrations to NO_x and VOC may differ for local and distant upwind sources. Regional strategies are likely to be more complex than local strategies.



Note: Shows the two major interacting cycles (NO/NO_2 and OH/RO_2 or OH/HO_2) and the two major sinks for radical chain terminations: H_2O_2 (NO_x sensitive) and HNO_3 (VOC sensitive)

Figure 8. Simplified Description of Photochemical Smog Formation

Physical Processes

The framework for the analysis of the physical processes is shown in Figure 9. The transport and removal processes that are important within the scales of the San Joaquin Valley include horizontal advection at the surface and aloft, vertical mixing, dry deposition, and wet deposition. Wet deposition is not important in the summer in the San Joaquin Valley and can be ignored. Dry deposition is an important removal process for some precursors as well as for O_3. Vertical mixing is a strong function of the diurnal cycle of the boundary layer height and other phenomena such as updraft and convective cells. Advection varies significantly between the surface and the free troposphere.

Above 1000 meters (m), the wind flow is governed by synoptic (or sub-synoptic) patterns. Although high mountain ranges lead to some channeling effects, terrain effects are generally limited at this height. Between about 200 m and 1000 m, the wind flow is strongly affected by the local terrain and the related local meteorology. Local pressure gradients, channeling, mountain-valley effects, and land / sea breezes near the coast interact with the synoptic patterns to create wind flows that vary significantly with time and location. This layer is typically decoupled from the surface at night, and significant advective transport can take place with little interaction with fresh emissions during the night.

The wind flow at the surface is coupled to the 200 to 1000 m layer during the day. The surface layer, however, is subject to a strong thermal inversion at night and calm winds and / or drainage flows are common. An analysis of physical transport processes must unravel how these various mechanisms transport O_3 and its precursors to and within the area of interest, such as the San Joaquin Valley.

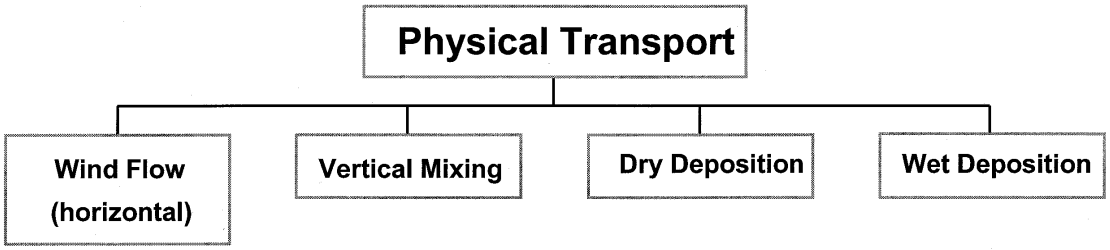


Figure 9. Transport Processes Important for the Formation and Accumulation of Ozone in the San Joaquin Valley

Sensitivity of O_3 to Precursors

Summer O_3 in most areas of the San Joaquin Valley appears to be more sensitive to NO_x controls than to VOC reductions alone. There may be areas, however, where NO_x reductions may be counterproductive to O_3 reduction. On August 6, 1990, ozone peaks were observed in the northern part of the San Joaquin Valley that could be attributed to downwind transport from the San Francisco Bay Area. The sensitivity of O_3 to its precursors under this meteorological scenario has not been verified. There is some evidence that summer O_3 in the San Francisco Bay Area is VOC-sensitive. Reductions in NO_x may result in an increase in O_3 according to modeling studies performed by the Bay Area Air Quality Management District (BAAQMD) (Martien and Umeda, 1993).

As a polluted air mass travels downwind, ozone accumulates from the reactions of VOC and NO_x. Since NO_x is depleted faster than VOC, O_3 production within the air parcel becomes increasingly NO_x-limited without fresh emissions of precursors. In this case, while VOC controls in the San Francisco Bay Area are beneficial for reducing O_3 production in the Bay Area, and transported O_3 at the receptor sites in the northern part of the San Joaquin Valley, NO_x controls are needed within the Valley to reduce the O_3 production potential in areas affected by both fresh emissions from within the Valley and aged air from the Bay Area.

2.2.4 Study Findings

Based on review of the results from the 1990 studies, two major phenomena appear to lead to concentrations in excess of the NAAQS in the San Joaquin Valley:

- Transport of O_3 and precursors from upwind areas (primarily, the San Francisco Bay Area) into the San Joaquin Valley leading to high O_3 levels in the northern part of the valley.
- Emissions of precursors, mixing, and atmospheric reactions within the San Joaquin Valley leading to high O_3 levels downwind of urban areas such as Fresno and Bakersfield.

The first phenomenon is favored by organized flow from the north/northwest into the valley. The second phenomenon is exacerbated by multi-day stagnation periods. Although these two phenomena are neither mutually exclusive nor collectively exhaustive, they help conceptualize the physical dynamics and chemistry of O_3 formation in the San Joaquin Valley. In addition, vertical mixing of transported emissions with local ground level emissions also occurs. Removal of O_3 by deposition is important and must be considered.

Pollutants and O_3 precursors from point and area sources accumulate in the mixed layer during the day in the San Francisco Bay Area and are transported or diffuse slowly into the northern part of the San Joaquin Valley through the Carquinez Straits following river pathways. Some inflow is also observed through the Pacheco Pass, bringing polluted air from the San Francisco Bay Area to the west side of the San Joaquin Valley.

On some episode days of the 1990 study, fluxes of O_3 and NO_x that accompanied sea breezes were significant. (VOC fluxes from the Bay Area were not measured.) An example was August 6, 1990 when onshore flows became more dominant after the high pressure system moved away from the San Joaquin Valley. Fluxes from the Sacramento Valley were also important. The combined NO_x fluxes into the northern part of the San Joaquin Valley may exceed the northern valley emissions. Precursor and O_3 transport is especially influential to ambient O_3 in the northern part of the San Joaquin Valley.

Under stagnant conditions, urban emissions of VOC and NO_x within the San Joaquin Valley can cause O_3 exceedances in areas downwind of major cities, such as Fresno, Bakersfield, and Sacramento. During an episode with significant sea breeze, the San Joaquin Valley also receives carry-over pollutants from upwind sources such as the San Francisco Bay Area or the Sacramento area. The northern part of the Valley is the most affected by upwind sources. Central and southern parts of the valley are also influenced. For example, the carry-over O_3, which is transported aloft at night, can reach concentrations as high as 80 to 100 ppb in Bakersfield.

2.2.5 Conclusions

The regional accumulation of O_3 within the San Joaquin Valley is the result of combined urban sources and transport, especially aloft transport in the evening. Urban sources mostly affect areas downwind on the same day of the emissions. During the night, pollutants (O_3 and VOC) trapped above the surface layer may be transported and mixed within the San Joaquin Valley by phenomena such as the nocturnal jet and the Fresno eddy. The nocturnal jet carries

pollutants towards the southern tip of the valley, including those released aloft above the inversion layer and those that had been mixed upwards from the surface point and area sources during the day.

In the morning, the O_3 and VOC precursors reached the southern end of the Valley. The carry-over burden of O_3 increased from the northern part of the San Joaquin Valley to the southern part and can be as high as 100 ppb in the downwind area. The carried over VOC represented a chemically aged mixture, with concentrations about a quarter of those measured at the ground level in the morning. The lower-level winds slow down but remain generally southward, with some upslope flow developing into the Sierras and the coastal range. Long-range transport appears to be especially important in influencing the O_3 concentrations at rural sites where few precursor emissions sources exist. Because no dry deposition can occur, high O_3 is preserved aloft at night. With efficient transport by the nocturnal jet, sources hundreds of miles upwind may contribute to high O_3 concentrations in the southern part of the Valley when the aloft air is mixed into the surface layer during the next day.

Urban emissions of VOC and NO_x contribute significantly to the O_3 production downwind, to locations such as Fresno and Bakersfield. This urban-scale O_3 production is supplemented by regional O_3 in the event of an episode. Regional scale O_3 may be a result of O_3 and precursors emitted in the northern San Joaquin Valley or in the San Francisco Bay Area, which are transported, typically aloft, throughout the Valley.

Several meteorological phenomena contribute to O_3 accumulation in the San Joaquin Valley. Synoptic high pressure and stagnation help trap pollutants within the Valley. The upper air nocturnal jet along the valley axis transports O_3 and precursors from the northern to the southern part of the part of the Valley. Daytime sea-breezes help inject fresh pollutants from the San Francisco Bay Area into the Central Valley under particular synoptic conditions. Upslope circulation into the Sierras and the Coastal Range generates divergence in the Valley, strengthening the subsidence and keeping the mixed layer rather shallow. The pollutants are therefore trapped in the Valley, without much possibility of escape except over the Chalome Pass and the Tehachapis to the south. Dry deposition, especially over agricultural land, appears to be an important physical removal process for surface level O_3 within the San Joaquin Valley. Aloft O_3 tends to remain high with no mechanism for removal until downward mixing occurs.

Meteorology serves in two major ways to enhance O_3 concentrations within the San Joaquin Valley during an episode. First, the synoptic high pressure and low mixing height trap pollutants within the San Joaquin Valley, allowing the accumulation of pollutants over a period of days. Second, upper air transport takes place at night to move pollutants from one location to another, where they are subsequently incorporated into the boundary layer during the day. This “carry-over” is especially important in the southern part of the San Joaquin Valley. The pollutants from the San Francisco Bay Area may also be transported through the delta and the mountain passes to contribute to high O_3 concentrations in the northern part of the Valley in the late afternoon.

VOC and NO_x emissions are very important in the production of O_3 in the central and southern part of the Valley, from Fresno to Bakersfield. Data analyses suggest that VOC emissions in the San Joaquin Valley and upwind source areas may be underestimated in the inventory.

Improvements of the emissions inventories are needed for mobile emissions, biogenic emissions, and uninventoried sources.

The chemistry of O_3 production involves the reactions of VOC to produce radicals that subsequently react with NO to produce O_3. Of the precursors, VOC and NO_x, available information indicates that O_3 is more sensitive to NO_x than VOC in most areas of the San Joaquin Valley. Reductions in NO_x, however, may be counterproductive to O_3 reduction in some areas.

The measured maximum dry deposition flux of 0.5 milograms per meter squared per hour ($mg/m^2/hour$) leads to an O_3 removal rate of about 3,000 tons per day in the San Joaquin Valley. Considering an average O_3 concentration of 80 ppb, this deposition rate leads to a residence time of about eight hours for O_3. Therefore, dry deposition is a significant flux for the mass balance of O_3 within the San Joaquin Valley. Dry deposition fluxes of precursors NO_x and VOC and products HNO_3, PAN, and PM need to be quantified. Wet deposition is not expected to be important in the summer in the San Joaquin Valley because of the low relative humidity and the lack of rain.

Peak O_3 concentrations were frequently observed in areas downwind of major urban areas. Strong diurnal profiles were also observed at these sites with maximum O_3 concentrations during the afternoon and minimum concentrations during the night. Rural locations tended to exhibit less diurnal variability, although the concentrations ranged from close to background values at Point Reyes to approximately 80 ppb at Sequoia. Some of the highest O_3 concentrations were observed in the southern part of the Valley, which is affected by upwind transport and local emissions of NO_x and VOC due to oil production.

Tracer releases from Pittsburg, California, provide evidence that emissions from tall upwind point sources may affect air quality as far downwind as the southern San Joaquin Valley. Fourteen percent of the tracer mass was detected at the surface in the southern part of the San Joaquin Valley the morning after the tracer release. Much of the long-range transport takes place at night by the nocturnal jet. Within the Central Valley, point source emissions released into the surface layer during the day may be trapped in the decoupled layer in the evening and transported towards the southeast. Furthermore, fresh emissions from elevated point sources in the path of the nocturnal jet may also be transported downwind and lead to O_3 production the next morning. Due to rapid aloft transport, the relative importance of point sources (that mix upwards) would simply depend on their rates and composition. Mathematical modeling of air quality in the San Joaquin Valley using a three-dimensional model with subgrid-scale treatment of plumes will be needed to properly address this question.

Limited analyses indicate that the formation of O_3 in the San Joaquin Valley in the summer is sensitive primarily to NO_x although reductions in both VOC and NO_x may be needed to reduce O_3 in some areas. According to Lu and Chang (1998), VOC sensitivity occurs mainly in the San Francisco Bay Area. There is some additional evidence (Martien and Umeda, 1993; Altshuler, 1995; Ziman, 1998) to support this hypothesis. Purely NO_x-sensitive locations are typically outside of urban areas. Since VOC sources are more abundant in the southern San Joaquin Valley, the chemistry in the southern part of the valley is expected to be relatively NO_x-sensitive compared to areas in the north. The analysis was performed based on maximum one-hour average ozone concentrations; conclusions regarding the sensitivity of the eight-hour

average cannot be inferred with certainty at this point. For example, if a receptor site is affected by air parcels from two different upwind locations at different times of the day, O_3 concentrations may be sensitive to NO_x at certain times and to VOC at other times. Moreover, if O_3 concentrations at a receptor within the San Joaquin Valley consist of transported O_3 (for example from the San Francisco Bay Area) and O_3 generated from emissions within the Valley, some fraction of the total O_3 burden may be sensitive to VOC whereas the other fraction may be sensitive to NO_x. It is conceivable that the area can be NO_x-sensitive with respect to the one-hour standard and VOC-sensitive with respect to the eight-hour standard. A similar sensitivity analysis is recommended for the San Joaquin Valley to analyze the most efficient control strategies for the eight-hour standard.

Due to the attention focused on the analysis of the August 3 to 6, 1990 episode, no analysis has been performed to address the weekday-weekend effects. Changes in VOC and NO_x emissions result in changes in ozone dynamics during the weekend. In addition, an indirect effect may be caused by reductions in vehicular emissions of PM and precursors, leading to increased ultraviolet (UV) radiation and photochemical activity (Dreher and Harley, 1998). Other analyses suggest, however, that weekday-weekend effects are not very pronounced in the San Joaquin Valley.

The morning ambient VOC to NO_x ratios ranged from 4.2 at San Francisco on August 6, 1990 to 27.5 at Bakersfield on August 5, 1990. The range of VOC to NO_x ratios in the emissions inventory is between 1.7 and 8.6. The emission inventory ratios at Livermore range from 4.8 to 8.2, with higher values on the weekends. The ambient ratios were between 6.1 and 19.3 during the SJVAQS / AUSPEX Regional Modeling Adaptation Program (SARMAP) (Magliano, 1996). In general, the ambient ratios exhibited much higher variability than the current emission inventories indicate. Uncertainties in mobile sources, biogenic, and oil production emissions need to be addressed.

It will be beneficial to address the issues of O_3 and PM sensitivities to precursors jointly since NO_x and VOC emission changes will affect both pollutants. In addition to addressing the exceedances of the O_3 NAAQS in the summer and PM NAAQS in the winter, it may also be beneficial to understand if any indirect effects exist between PM and O_3 in the summer. Dreher and Harley (1998) postulated that the weekend increases in O_3 in the San Francisco Bay Area may be related to reduced emissions by trucks. In addition to the reduced O_3 titration by NO, increased photochemical reactivity may result from reduced emission of black carbon by trucks. However, the weekend effect does not seem to be very prominent in the San Joaquin Valley (Altshuler, 1998). Carefully planned experimental field programs, data analyses, and mathematical modeling efforts should help address the PM-O_3 interaction issue effectively.

After completion of this study report, AER prepared a manuscript titled “Ozone Formation in the California San Joaquin Valley: A Critical Assessment of Modeling and Data Needs” and submitted it for publication in *Journal of the Air & Waste Management Association*.

2.2.6 Study Recommendations

Several aspects of the O_3 conceptual model are well understood:

- The combined effects of local and upwind production of O_3 from NO_x and VOC at sites such as Fresno and Bakersfield
- The transport (sea breeze) of O_3 from the San Francisco Bay Area affecting primarily areas in the northern San Joaquin Valley, the overnight aloft transport of O_3 and precursors by the nocturnal jet
- The low mixed layer height caused by subsidence and mountain effects.
- However, some details remain to be thoroughly understood:
- The sensitivity of the O_3 chemistry at different locations within the San Joaquin Valley
- The balance of transport, chemical, and deposition fluxes that gives rise to the observed concentrations
- The amount of O_3 that can be attributed to local point sources, mobile sources, and biogenic sources vs. that transported aloft from distant sources.

A key indicator for the sensitivity of the oxidant system to VOC or NO_x is the ratio of HNO_3 and H_2O_2. Although HNO_3 was measured at many of the AUSPEX sites during the SJVAQS/AUSPEX, H_2O_2 measurements were only taken aboard one of the aircraft used in the intensive studies. Measurements of H_2O_2 are highly recommended to characterize the sensitivity of O_3 to VOC or NO_x at urban, downwind, and rural locations.

Lu and Chang (1998) investigated the use of various photochemical indicators by simulating the August 5, 1990 conditions. They noted that most of the areas within the San Joaquin Valley were NO_x-sensitive. About 20 percent of the area, however, were classified as “transition” and the sensitivity of O_3 to its precursors needs to be confirmed for these areas. Furthermore, August 6, 1990 represented a different set of meteorological conditions, with less stagnation over the Valley and more transport from the Bay Area. As previously mentioned, there is evidence for VOC sensitivity in the Bay Area. Therefore, the northern part of the Valley, influenced by pollutants originating in the Bay Area, may exhibit VOC sensitivity rather than NO_x sensitivity under these conditions. The VOC/NO_x sensitivity issue should be investigated further, especially for different meteorological conditions, to ensure that the conclusions are not misguided.

The NO_x and NO_2 measurements suffered from interference from oxidized nitrogen species such as PAN and HNO_3. Accurate measurements of NO_x and NO_2 are important both for the understanding of the characteristics of air masses of different chemical “age” and for model evaluation purposes.

Mathematical modeling of air quality in the San Joaquin Valley using a three-dimensional model with subgrid-scale treatment of plumes will be needed to properly address this question.

Nitrate radical measurements were taken during the SJVAQS/AUSPEX. Concentrations of nitrate radicals in the San Joaquin Valley were sufficient to oxidize organic compounds at the same rate in the evening as they are oxidized by OH during the day (Smith et al., 1995). This was an unexpected conclusion: VOC oxidation at night by nitrate radical is typically expected to be two orders of magnitude slower than the day-time process initiated by OH (Atkinson,

1997). This conclusion shows that it is important to measure other radical species in addition to NO_3, especially OH, HO_2, and RO_2, which have never been measured in large-scale field programs in the San Joaquin Valley. The new eight-hour average NAAQS may be exceeded at both urban and rural sites. An understanding of the source-receptor relationships to address O_3 at the rural receptor sites needs to be developed, and regional control strategies may be needed to meet the eight-hour NAAQS. In that regard, the new standard can be more difficult to attain. The temporal variations at polluted rural sites should be the subject of a modeling investigation. In particular, the aloft transport of O_3 from upwind locations, vertical exchange with the valley surface layer or the free troposphere, local production from biogenic emissions, and O_3 scavenging by VOC may be key mass fluxes at these locations. The processes/fluxes that contribute to high eight-hour average concentrations need to be elucidated before effective attainment strategies can be identified. Model investigations to determine the O_3 sensitivity of the region to VOC and NO_x with respect to an eight-hour average also should be conducted to confirm the efficacy of control measures designed to reduce the maximum one-hour average concentration.

Even with significant improvements in the emissions inventory for the San Joaquin Valley, the reconciliation with ambient data still indicates significant uncertainties in VOC emissions. AER recommended continuing efforts to provide better emissions estimates for mobile, biogenic, oil production, and un-inventoried sources. With more accurate emissions information, models can be better applied to understand the relative importance of these precursor sources to O_3 production in the San Joaquin Valley.

In addition, O_3 fluxes and deposition fluxes of precursors and products are needed to provide a better understanding of the pollutant removal processes within the Valley. Measurements of deposition fluxes of nitric oxide (NO), NO_2, HNO_3, PAN, PM, and VOC are needed over a range of surfaces and for a variety of meteorological conditions. In addition, UV radiation measurements should be performed during the field study portion of the Central California Ozone Study.

2.2.6.1 Implications to Electric Power Plants

As a source of NO_x, fossil fueled electric power plants are concerned with atmospheric reaction of NO_x leading to O_3 and particulate nitrates. During wintertime, ambient ozone is VOC limited within the San Joaquin Valley. During summertime, ambient ozone is NO_x limited within the Valley. These atmospheric reactions have important implications to any existing or new power plants in the San Joaquin Valley or in upwind areas. Generally for summertime, power plant NO_x emissions need to be evaluated for the NO_x limited scenario when evaluating impacts on ambient ozone. During wintertime, when ambient O_3 is generally below standards, PM nitrate becomes a larger issue of concern. This material is further discussed in Section 2.6 of this document.

Further, the importance and relevance of upwind aloft emissions of NOx on the atmospheric chemistry occurring miles downwind has been described. The ability of aloft NOx emissions from power plants with tall stacks located within the Valley and in adjoining upwind areas to travel many miles before mixing downward in to surface air is of concern in evaluating ozone formation in downwind areas. Because power plant plume chemistry differs significantly from

ambient chemistry (e.g. Karamchandani et al., 1998), it is essential that the potential impact of power plant emissions be assessed with air quality models that include a comprehensive treatment of plumes (plume-in-grid modeling) such as the Electric Power Research Institute (EPRI) model (EPRI, 1999).

As ambient concentrations of ozone and PM both exceed various ambient air quality standards in the Valley, air regulatory agencies need to focus on optimum control strategies to achieve attainment.

2.3 1995 Integrated Modeling Study: Assessment of Mathematical Models and Associated Data Needs

The final report for this project effort is provided in Appendix III of this document.

2.3.1 Study Background

In Section 2.1 of this document, information was assimilated from the data analysis reports of the IMS95 into a coherent conceptual model for PM. The formulation of the conceptual model was based on an understanding of the chemical transformations and physical transport processes that contributed to elevated levels of PM in the San Joaquin Valley during the fall and winter seasons. Table 4 summarizes the key meteorological and air quality attributes of the PM conceptual model.

Table 4. Key Attributes of the Conceptual Model for PM Formation in the San Joaquin Valey in the Fall and Winter Seasons

Meteorology
Cool Temperatures
Stagnant Conditions (Calm Winds)
Fog (Primarily in Winter)
Complex Terrain
Valley Geography
Air Quality
Sulfate Poor Environment with Respect to Ammonia
Nitric Acid-Sensitive Conditions for PM Nitrate
Local Sources
Transport (Various Ranges)
Oxidant Production

2.3.2 Study Objectives

The conceptual model of PM formation in the San Joaquin Valley was used to guide the development of mathematical models. The objectives of this study were to:

- Assess the ability of existing mathematical models to represent PM formation

- Identify gaps in current knowledge and needs for model improvement
- Recommend specific tasks for field measurements, data analyses, and model performance evaluation.

In the complete report, provided as Appendix III, the following are discussed in detail:

- General modeling requirements based on the conceptual model and the selection of mathematical models for the San Joaquin Valley episodes
- The adequacy of current mathematical representations of the key processes responsible for PM formation in the San Joaquin Valley, focusing discussion on one model, the SARMAP Air Quality Model with Aerosol module (SAQM-AERO)
- Tasks for further model development
- Input data requirements, resolution (spatial, temporal, and size), chemical transformation routines, and physical transport and removal processes of the model.

2.3.3 Study Findings

A conceptual model was formulated and described in Section 2.1. This model was developed to address the formation of particulate matter in California's San Joaquin Valley based on the observations and analyses of data from the IMS95. Based on this conceptual model, current PM air quality models were evaluated, focusing on SAQM-AERO. Key objectives of this report included the identification of knowledge gaps, needs for model improvement, and recommendations regarding the field data needed for the execution and evaluation of mathematical models.

The study approach combined receptor modeling and source modeling for understanding the formation of primary and secondary PM in the San Joaquin Valley. Geological material accounted for more than 50 percent of the PM_{10} observed in the fall. The winter PM episodes were dominated by fine particles, which include secondary components (e.g., ammonium nitrate) and primary components (from vegetative burning and mobile sources). Receptor models, such as chemical mass balance, can be used to address the primary sources of PM, while source models, such as SAQM-AERO, are best used to simulate the formation of secondary PM nitrate and sulfate. Due to the possibility of long-range aloft transport, recommendation for the source model was a mesoscale domain that includes upwind metropolitan areas such as the San Francisco Bay Area, Monterey, and San Luis Obispo.

When used with the Mesoscale Model (MM5), a non-hydrostatic prognostic meteorology model, it was observed that SAQM-AERO provides adequate treatment for the complex meteorology within the San Joaquin Valley, except possibly for calm periods. Major uncertainties in the emissions input must be resolved by measurements. Concentration measurements at the boundaries, lateral and top, are also recommended. A 12 kilometer (km) by 12 km grid size can capture the major features of PM build-up within the San Joaquin Valley. During stagnation, however, a finer grid size may be necessary to decipher the diffusion processes. The vertical range of SAQM-AERO extends to 15 km, which is adequate for modeling aloft transport in the free troposphere. Near the surface, a surface layer submodel increases the resolution to improve model predictions when the mixing layer is shallow. Since

reduced mixing heights are typically associated with PM accumulation, such a feature should prove useful in the application of SAQM-AERO to the San Joaquin Valley.

The representation of chemistry within SAQM-AERO may not be adequate for wintertime PM formation. Most gas-phase chemical mechanisms for oxidant productions have not been thoroughly tested in cool, foggy conditions. CBM-IV, the only mechanism currently implemented in SAQM-AERO, does not explicitly treat organic peroxides, which may be important radical termination products if the oxidant chemistry is NO_x-sensitive.

Secondary organic aerosols are simulated in CBM-IV. The current partition scheme, however, amounts to a rudimentary fixed aerosol yield approach. The thermodynamic module, SEQUILIB, was found to perform well under the high nitrate, high ammonia conditions prevalent with the San Joaquin Valley (Zhang et al., 1998). Aqueous-phase reactions, however, are not represented. The aqueous oxidation of SO_2 to sulfate and the hydrolysis of N_2O_5 in the presence of droplets should be modeled if SAQM-AERO were to be applied to the San Joaquin Valley, where fog is typically associated with the winter PM episodes.

Gaps in current knowledge were identified including the:

- VOC or NO_x sensitivity of the oxidant system in the San Joaquin Valley
- Rates of photolysis reactions in fog
- Details of SOA formation
- Source of fog buffering in some urban areas
- Transport processes responsible for the regional distribution of pollutants under calm conditions.

The key areas for model development and testing needs were divided into two categories:

- Areas where development is absolutely needed for the San Joaquin Valley application
- Areas where testing is needed to ensure the accuracy of the model, and, if testing is not satisfactory, development is needed.

In areas where development is absolutely needed for the San Joaquin Valley application, the following must be performed:

- Incorporate a detailed aqueous-phase chemical mechanism
- Reduce numerical diffusion during stagnation
- Implement plume-in-grid treatment for point and area sources
- Improve treatment of secondary organic aerosols.

In areas where testing is needed to ensure the accuracy of the model and, if testing is not satisfactory, development is needed including the following:

- Implement Statewide Air Pollution Research Center (SAPRC) as an audit for the CBM-IV mechanism in SAQM-AERO
- Resolve mass adjustment issue by modifying mesoscale meteorological model (MM5) post-processing procedures

- Test photolysis rates by comparing calculated radiative fluxes with measurements of UV and broad radiation
- Resolve vertical transport inconsistencies (K-theory vs. ACM)
- Test surface layer submodel and modify as needed
- Resolve difference in dry deposition prediction of SAQM-AERO and other air quality models.

A host of information was identified for the execution and evaluation of the source model. Meteorological data, emissions data, and initial and boundary conditions (i.e., ambient concentrations) are required as inputs for the PM air quality model. Ambient concentrations and fluxes (e.g., deposition) of PM and precursors are needed to evaluate model performance. Table 5 summarizes these data needs for model input and evaluation.

Table 5. List of Recommended Measurements for Model Input and Evaluation

Data	Spatial Resolution	Temporal Resolution
Meteorology		
Wind Speed and Direction	Surface and Aloft	< 1 hour *
Temperature	Surface and Aloft	< 1 hour
Mixing Height	Surface or Aircraft	< 1 hour
Relative Humidity	Surface and Aloft	< 1 hour #
Solar Radiation	Surface and Aloft	< 1 hour
Fog / Clouds	Surface and Satellite	< 1 hour
Emissions (**$PM_{-2.5}$, PM_{-10}**, Precursor Gases)		
Profiles (Anthropogenic, Biogenic)	Representative Sources	N/A
Emission Factors	Major Sources	1 to 4 hours
$PM_{2.5}$ / PM_{10}		
Total Mass	Surface and Aloft	1 to 4 hours
Sulfate	Surface and Aloft	1 to 4 hours
Ammonium	Surface and Aloft	1 to 4 hours
Nitrate	Surface and Aloft	1 to 4 hours
Elemental carbon	Surface and Aloft	1 to 24 hours
Organic carbon (speciated)	Surface and Aloft	1 to 24 hours
Chloride	Surface and Aloft	1 to 4 hours
Gases		
O_3	Surface and Aloft	1 hour
NO	Surface and Aloft	1 hour
NO_2	Surface and Aloft	1 hour
VOC (Speciated)	Surface and Aloft	1 to 4 hours
HNO_3	Surface and Aloft	1 hour
NH_3	Surface and Aloft	1 hour

Data	Spatial Resolution	Temporal Resolution
H_2O_2	Surface and Aloft	1 hour
Organic Peroxides	Surface and Aloft	1 hour
PAN	Surface and Aloft	1 hour
OH	Surface	1 hour
HO_2	Surface	1 hour
NO_3	Surface	1 hour
CO	Surface and Aloft	1 hour
SO_2	Surface and Aloft	1 hour
Droplet Chemistry		During Fog Event Only:
Liquid Water Content	Surface and Aloft	1 hour
Sulfate	Surface and Aloft	1 hour
Nitrate	Surface and Aloft	1 hour
Ammonium	Surface and Aloft	1 hour
Chloride	Surface and Aloft	1 hour
H_2O_2	Surface and Aloft	1 hour
Sulfite	Surface and Aloft	1 hour
H^+(pH)	Surface and Aloft	1 hour
Dissolved Fe^{3+} and Mn^{2+}	Surface and Aloft	1 hour
Wet Deposition	Representative Locations	During Fog Event Only
Sulfate		1 hour
Nitrate		1 hour
Ammonium		1 hour
Dry Deposition	Different Surface Types (aircraft measurements or tower measurements)	Representative Meteorology
$PM_{2.5}$		
PM_{10}		
HNO_3		
NH_3		
SO_2		
O_3		

* 5-minute temporal resolution is desired during stagnation

5-minute temporal resolution is desired during fog

2.3.4 Study Conclusions and Recommendations

Due to the possibility of long-range aloft transport, a mesoscale domain that includes upwind metropolitan areas such as the San Francisco Bay Area, Monterey, and San Luis Obispo, is recommended for the source model.

During stagnation, however, a finer grid size may be necessary to decipher the diffusion processes. The vertical range of SAQM-AERO extends to 15 km, which is adequate for modeling aloft transport in the free troposphere. Near the surface, a surface layer submodel

increases the resolution to improve model predictions when the mixing layer is shallow. Since reduced mixing heights are typically associated with PM accumulation, such a feature should prove useful in the application of SAQM-AERO to the San Joaquin Valley.

The representation of chemistry within SAQM-AERO may not be adequate for wintertime PM formation. Most gas-phase chemical mechanisms for oxidant productions have not been thoroughly tested in cool, foggy conditions.

Gaps in current knowledge identified include the:

- VOC or NO_x sensitivity of the oxidant system in the San Joaquin Valley
- Rates of photolysis reactions in fog
- Details of SOA formation
- Source of fog buffering in some urban areas
- Transport processes responsible for the regional distribution of pollutants under calm conditions.

Necessary information for the execution and evaluation of the source model was defined. Meteorological data, emissions data, and initial and boundary conditions (i.e., ambient concentrations) are required as inputs for the PM air quality model. Ambient concentrations and fluxes (e.g., deposition) of PM and precursors are needed to evaluate model performance. Table 5 summarizes these data needs for model input and evaluation 2.3.4

2.3.4.1 Implications to the CRPAQS and CCOS Field Studies

The complete final study report (Appendix III) was shared with those responsible for the planning of the CRPAQS year 2000 study during the third quarter of 1998.

2.3.4.2 Implications to the Electric Power Production Industry

Recommendations regarding data needs for CRPAQS as defined in this report help to ensure that the optimum field study is conducted to run future air quality models. It is difficult to identify any specific benefit to the electric power production industry other than continuous improvement of the overall study design.

2.4 Assessment of MM5/SAQM Model of Ozone Formation in the San Joaquin Valley

The complete final report for this study is provided in Appendix IV of this document.

2.4.1 Study Background

The SARMAP was a collaborative effort by SJVAQS, AUSPEX, and EPRI for modeling and data analysis following the 1990 ozone field study. The SARMAP modeling system consisted of the MM5 (Seaman and Stauffer, 1996), the SAQM (Chang et al., 1997) and the data processing software for generating SAQM inputs. This modeling system simulates atmospheric dynamics and the chemistry, transport, and deposition of O_3 and precursors. In this work MM5/SAQM

was compared to the conceptual ozone model (further discussed in Section 2.2 of this document).

2.4.2 Study Objectives

Specific objectives were to:

- Assess the ability of MM5/SAQM to represent O_3 formation processes
- Document the processes that are not well represented in the mathematical modeling system and recommend tasks for mathematical model improvement
- Identify gaps in current knowledge and recommend specific measurements and data analysis tasks.

2.4.3 Study Methodology

In conducting this study, the following was performed:

- An assessment of the MM5
- Review of SAQM and the associated input processing software
- Recommendations were developed regarding field measurements and data analyses for improving the conceptual model, and tasks needed for mathematical model improvements and performance evaluation
- Conclusions were provided.

During the assessment of MM5, AER evaluated the extent to which the simulations of the SARMAP episode using the MM5 mesoscale model agree with the available data and examined whether there are weaknesses or deficiencies in MM5 that preclude it from agreeing with the conceptual ozone model developed earlier. This evaluation was based primarily on the work of Seaman et al. (1995) and Seaman and Stauffer (1996).

MM5 is a non-hydrostatic mesoscale model developed at the Pennsylvania State University and the National Center for Atmospheric Research (NCAR). Basic references for MM5 are Dudhia (1993) and Grell et al. (1993). The model can be run in nested mode, with one or more fine mesh inner grids communicating with a coarser mesh outer grid. This approach makes it possible to perform very fine resolution simulations on a small area without it being overly influenced by the lateral boundary conditions, which need to be imposed only on the outermost grid. Typically, an inner grid has a mesh size three times smaller than the outer grid in which it is embedded.

MM5 includes a complete set of physical parameterizations. In fact, since MM5 is widely used in the weather research community, several types of parameterizations have been developed for each physical process. Even the standard code supported by NCAR comes with several different choices.

A data assimilation system is also available for MM5. It is a Newtonian relaxation or “nudging” system, in which an extra term is added to the tendency equations. This extra term is proportional to the difference between the model solution and the observations or a large-scale analysis. Seaman et al. (1995) performed simulations with a triply nested grid with the inner grid covering the entire San Joaquin Valley basin with a horizontal mesh size of 4 km and a

vertical resolution of 30 layers from ground level to the tropopause. They used several configurations but, for this purpose, the most important results come from three experiments:

- A control run without data assimilation (called CNTRL)
- A run with nudging toward a larger scale analysis for the outer grid and nudging toward the special SARMAP observations in the inner grids (CFDA)
- A nudging run in which only a reduced set of special observations is used, with the rest being used for model evaluation.

Details about SAQM and the operation of the model are found in Appendix IV.

2.4.4 Study Conclusions and Recommendations

The MM5/SAQM modeling system was reviewed and it was concluded that:

- In principle, it represents the key features of the conceptual model for O_3 formation in the San Joaquin Valley
- Several aspects of the model related to vertical mixing and transport need to be tested and improved.

Modeling studies are recommended to:

- Elucidate the sensitivities of O_3 to its precursors at different locations where the eight-hour NAAQS is expected to be exceeded
- Investigate the zones of influence of emission sources due to long-range aloft transport.

Until now, O_3 and PM pollution issues have been considered independently. In the San Joaquin Valley, exceedances of the PM and O_3 NAAQS occur in different seasons. Recent studies (e.g., Meng et al., 1998) have shown that control strategies for O_3 may have adverse effects on PM in the same modeling scenario. Pun and Seigneur (1998) postulated that the formation of PM (nitrates) in the San Joaquin Valley is sensitive to the availability of oxidants. Since control strategies are seldom season-specific, measures for controlling summer O_3 will certainly affect the oxidant concentrations, hence PM (and nitrates) formation, in the winter.

Also, particulate matter has been shown to affect O_3 in modeling studies through their light extinction properties (Dickerson et al., 1997; Jacobson, 1998), typically leading to higher photochemical activity and higher O_3 concentrations aloft and lower photochemical activity and lower O_3 concentrations at the surface. Dreher and Harley (1998) postulated that this effect may partly explain the increased O_3 concentrations observed on weekends at some locations affected by heavy truck traffic during the week. Although PM is not a significant problem during the summer, its effect on O_3 formation has never been quantified in the San Joaquin Valley.

The effects of any control measures designed for the summer O_3 problem on PM need to be investigated. In this regard, a model that treats both PM and O_3 (Seigneur et al., 1999a) is required for air quality studies in the San Joaquin Valley.

2.4.4.1 Implications to the CCOS 2000 Field Study

Field Measurements and Data Analysis

Table 6 summarizes recommendations regarding the field data needed to improve the conceptual understanding of the system and to support model application and evaluation. Field measurements needed to apply air quality models include initial and boundary conditions. Initial conditions are not critical because the model can be run for a period of time to flush these initial conditions out of the domain (spinup period). Boundary conditions, on the other hand, are very important. They are needed at the edges and top of the modeling domain. Clean air concentrations should not be assumed at the edge of the domain because aircraft measurements have shown that the polluted air mass can extend for several kilometers offshore. Therefore, measurements are needed at the boundaries of the modeling domain for O_3 and its precursors.

The lack of information at the top boundary of the modeling domain has traditionally been a major source of uncertainty in model predictions. Since the SAQM model domain extends to the free troposphere, aloft measurements of O_3, VOC, and NO_x at a few locations will be needed for model performance evaluation purposes.

It is recommended that in future experimental campaigns, meteorological data be obtained in an area extending somewhat beyond the area of interest, especially in the regions where strong advection may be expected. Such data would be used with Four Dimensional Data Assimilation (FDDA) in MM5 to better characterize mesoscale wind flow patterns that extend to the edges of the modeling domain (e.g., flow up the Sacramento Valley from the flow divergence that occurs east of the Carquinez Straight). It would also be useful to obtain measurements of ground temperature and moisture or surface fluxes at various points throughout the domain. This information would be used in evaluating the causes of surface temperature over prediction by the model.

Even though significant improvements were made for the San Joaquin Valley emissions inventory in the 1990 field study, reconciliation with ambient data still indicates significant uncertainties in VOC emissions. Continuing efforts are needed to provide better emissions estimates for biogenic, mobile, oil production, and mobile source emissions. uninventoried sources. Based on reconciliation with ambient data, there are some concerns that the biogenic inventory may be overestimated. Biogenic compounds are highly reactive, and are, therefore, not prone to accumulation in the ambient atmosphere. Since exceedances of the new eight-hour O_3 standard are likely at rural locations with high biogenic VOC emissions, the formulation of effective strategies for these areas will require accurate biogenic emission inventories and proper representation of biogenic reactions in the chemical mechanisms. Major differences in the anthropogenic emissions inventories are observed between the weekday and the weekend. The effects of changes in NO_x and VOC emissions on O_3 concentrations should be studied using both data analysis and modeling approaches.

Table 6. Field Measurements to Improve the Conceptual Model and Support Air Quality Modeling

Data	Use
Emissions Inventories (mobile sources, biogenic sources, oil production, uninventoried sources)	Emissions input
Meteorological data (winds, temperature, RH) especially aloft, mixing layer height (including areas beyond the immediate area of interest); ground temperature and moisture or surface heat and moisture fluxes	Meteorology model input (FDDS), evaluation of meteorological model predictions (e.g., the boundary layer parameterization).
O_3 and precursors at boundaries of modeling domain and within domain (surface and aloft)	Boundary conditions/Initial conditions Operational (surface O_3) and diagnostic model evaluation (surface precursors, aloft O_3 and precursors)
Photochemical products (e.g., HNO_3, PAN, H_2O_2, organic peroxides)	Diagnostic model evaluation; assessment of the sensitivity of oxidants to precursors
NO_2, PAN, and other nitrogen species	Diagnostic model evaluation
NO_3 and other radicals (OH, HO_2/RO_2)	Diagnostic model evaluation
Dry deposition fluxes of NO, NO_2, HNO_3, PAN, VOC, and O_3 over a range of surfaces and atmospheric conditions	Assessment of key mass fluxes, diagnostic model evaluation

A key feature of the conceptual model is that high O_3 concentrations are preserved aloft at night because the thermal inversion insulates the aloft layer from the effects of surface NO_x emissions. The contributions of sources in different upwind areas to the aloft O_3 need to be analyzed. In addition, the effects of aloft point sources need to be studied to determine the zones of influence and dispersion characteristics of such sources. The nocturnal jet at 200 to 400 m may provide the vehicle for long range transport of these pollutants. To understand the impact of aloft transport, aloft winds and pollutant concentrations need to be accurately predicted by the meteorology/air quality modeling system. Aloft measurements of wind and concentrations must be taken at sufficient temporal and spatial resolution to provide for data assimilation (meteorological model) and model evaluation (meteorological and air quality models). While SJVAQS/AUSPEX seemed to have provided enough upper air meteorological data to support data assimilation (except in the northern part of Sacramento Valley), the concentration data were obtained much less frequently by aircraft. More aloft concentration data should be collected to allow for better characterization of the magnitude of aloft transport.

Measurements of H_2O_2/ROOH and HNO_3 are useful for estimating the relative sensitivity of O_3 to VOC and NO_x at urban, suburban, and rural locations. The sensitivities may be a function of location and meteorology. For example, some evidence indicates that the San Francisco Bay Area is in a VOC-sensitive regime during summertime, while most of the San Joaquin Valley appears to be more sensitive to NO_x. Sensitivities of O_3 to its precursors in the northern part of the San Joaquin Valley may alter as a result of increased transport from the San Francisco Bay Area.

In addition to measuring the relevant indicator species (e.g., HNO_3, H_2O_2, NO_y), a more comprehensive modeling study is recommended for evaluating the indicator approach (e.g., Sillman, 1995) under different meteorological scenarios.

The NO_x and NO_2 measurements suffered from interference from oxidized nitrogen species such as PAN and HNO_3. Accurate measurements of NO_x and NO_2 are important both for the understanding of the characteristics of air masses of different chemical "age" and for model evaluation purposes.

Nitrate radical measurements were taken during the SJVAQS/AUSPEX. The concentrations of nitrate radicals in the San Joaquin Valley were sufficient to oxidize organic compounds at the same rate in the evening as they are oxidized by OH during the day (Smith et al., 1995). This was an unexpected conclusion as VOC oxidation at night by nitrate radicals is typically expected to be two orders of magnitude slower than the day-time process initiated by OH (Atkinson, 1997) . This conclusion shows that it is important to measure other radical species in addition to NO_3, especially OH, HO_2, and RO_2, which have never been measured in large-scale field programs in the San Joaquin Valley.

In addition to O_3 fluxes, dry deposition fluxes of precursors and products are needed to provide a better understanding of the pollutant removal processes within the Valley. Measurements of deposition fluxes of NO, NO_2, HNO_3, PAN, and VOC are needed over a range of surfaces and atmospheric conditions.

Model Development

Specific areas recommended for model development of MM5 are:

- Use optimal interpolation to analyze the data to assimilate various types of data with different error characteristics.
- Reduce as much as possible the numerical diffusion by using better algorithms.
- Use a full radiation scheme and use a PBL scheme that is not overly sensitive to surface temperature in its definition of the PBL height.

Specific areas recommended for model development of SAQM are:

- Implement advanced subgrid-scale treatment of plumes.
- Evaluate the performance of the dry deposition module.
- Resolve mass adjustment by modifying the processing procedures of MM5 outputs.
- Resolve vertical transport inconsistencies.
- Test surface layer submodel and modify as needed.

2.4.4.2 Implications to Electric Power Producers

A key feature of the conceptual model is that high O_3 concentrations are preserved aloft at night because the thermal inversion insulates the aloft layer from the effects of surface NO_x emissions. The contributions of sources, such as existing or proposed electric power plants, in different areas upwind to the aloft O_3 need to be analyzed. In addition, the effects of aloft point sources (power plants) need to be studied to determine the zones of influence and dispersion

characteristics of such sources. Such studies should employ the best data and modeling tools available to ensure that the potential impacts of power plant emissions are not over-estimated. Power plants in Pittsburg, Antioch and Yuba City come to mind when reviewing potential aloft sources of upwind NO_x emissions.

2.5 Comments on Field Program Plan for the California $PM_{2.5}/PM_{10}$ Air Quality Study

The complete final report for this study is provided in Appendix V of this document.

2.5.1 Study Background

Several knowledge gaps were identified in the conceptual models for PM formation in the California San Joaquin Valley, in Section 2.1 of this document. To verify Watson et al.'s conceptual model, specific measurements for assessment were recommended:

- The effects of mixing in the morning and early afternoon, the influence of stratus clouds on secondary aerosols
- The extent of oxidant production (surface and aloft)
- The importance of aqueous sulfate production
- The magnitude of aloft transport in the winter.

In Section 2.1, the conceptual model of Watson et al. (1998) was augmented and the need to understand the formation of atmospheric oxidants during the winter season was emphasized. Oxidants play an important role in the production of secondary compounds, including HNO_3 (precursor to particulate nitrate), sulfate, and SOA. In the fall, the areas that need to be studied include:

- The sources of fugitive dust
- The dispersion processes responsible for the subregional distribution of PM
- The limiting reagent (i.e., HNO_3 or NH_3) for the formation of ammonium nitrate.

Table 7 summarizes the key areas of uncertainties and the measurements that may be taken to reduce those uncertainties. The field data needs are discussed further in the following.

It should be noted that, unlike summaries of reports summarized in earlier sections of this report, disproportionately large portions of the original work are summarized and included in the following. It is viewed that this particular report provided a unique opportunity to present a fresh perspective and input to the planning of the PM study. Accordingly, it is important to represent a more detailed look at work in this study area.

2.5.2 Study Objective

- Review and determine the adequacy of the augmented conceptual model for PM formation in the San Joaquin Valley.

Table 7. Knowledge Gaps

Question	Information Needed	Proposed Measurements in the Field Program Plan
Re: Ammonium Nitrate		
Is NH_3 abundant for NH_4NO_3? Everywhere in the Valley? During all seasons?	Ammonia inventory, spatial coverage, area sources, non-winter conditions. Measurements of NH_3, HNO_3, and NH_4NO_3.	Emission study (ES), special fall study in the vicinity of an ammonia source. 5 sites during winter episodes (HNO_3 and NO_2 separation if possible).
What chemical processes are responsible for the formation of HNO_3?	Diurnal profiles of NO, NO_2, NO_3, HNO_3, OH, O_3, including in fog. Spatial and Temporal distributions of fog and clouds. Measurements of solar radiation in fog.	NO, NO_y, NH_3, HNO_3, O_3 winter study continuous sites 5 minutes. Fog observed at airports and backbone sites. Solar radiation only measured at routine sites.
Is the formation of HNO_3 limited by oxidants or NO_x?	Same as above.	Same as above.
Is the formation of oxidants limited by VOC or NO_x?	Evaluation of the gas-phase chemical mechanisms and the indicator approach in the winter season (through modeling studies and field data, see below). H_2O_2, HNO_3/PM nitrate measurements.	No continuous H_2O_2 measurements.
Re: Secondary Organic Aerosols		
What is the abundance of SOA during non-winter seasons?	PM OC profiles for primary sources, especially tracer-based profiles in the San Joaquin Valley.. Ambient organic PM composition.	ES. Anchor sites.
What are the precursors of SOA?	Anthropogenic and biogenic VOC inventory. Understanding of gas-phase reactions forming condensable compounds (laboratory research and data analysis).	ES.

Question	Information Needed	Proposed Measurements in the Field Program Plan
Re: Sulfate		
Is the sulfuric acid formed neutralized by NH_3?	Inventories of NH_3 and SO_2.	ES.
What are the key chemical processes (gas-phase and aqueous-phase) for the formation of sulfate?	Measurements of OH, SO_2, O_3, H_2O_2, Mn^{2+}, Fe^{3+}, RH, pH, particulate water, including low concentrations in fog. Understanding of pH evolution and buffering capacity within fog droplets (laboratory analysis of fog composition, including organic buffering agents). Spatial and temporal distribution of fog and clouds.	No continuous measurements for H_2O_2, OH; SO_2 at only one (Bakersfield) site. Only total Fe, Mn, ions during episodes. Nine RH sites with 5-minute data. No continuous monitor for particulate water (maybe fog study?) Any collection of fog droplets? Limited fog observations likely taken at airports, nephelometers at backbone sites.
Re: Primary Sources		
How to improve receptor modeling?	Better profiles for primary sources (dust, mobile, burning): SJV specific, fingerprint compounds.	ES.
Re: Horizontal Transport		
Where does aloft transport take place?	Measurements of wind speeds as a function of time and height.	7 sites during episodes, 2 – 6 /day.
What is the extent of upper air transport of precursors? PM?	Measurements of diurnal upper air meteorology and concentrations of O_3, NO_x, VOC, SO_2, HNO_3, PM	Wind speed, direction, temperature, RH daily or 2-7 times / day. Aloft concentrations not measured except PM measurements aloft during one episode (to be compared to elevated Sierra sites).
What is the range of surface level transport during the fall?	Surface meteorology measurements taken at PM monitoring sites. PM size measurements (used to estimate deposition life time of particles).	Sensitive, fast wind and RH monitors at core sites. Wind measurements at transport sites. Daily 5-minute particle size distribution at 3 core sites for annual study.
What are the influences of widespread area sources (fall)?	PM emission inventories for geological material sources, uninventoried sources.	ES.

Question	Information Needed	Proposed Measurements in the Field Program Plan
Re: Vertical mixing		
Is upper air transport responsible for dispersion of pollutants?	Measurements of temporal and spatial variations of mixing height. Concentration profiles of PM and precursors in the vertical direction.	Aircraft study (winter special study, spatial variability), 2 to 6 soundings per day during winter episodes at 4 sites. Aloft concentration measurements not planned.
Re: Wet deposition		
What are the wet deposition fluxes?	Size fractionated fog samples. Collection of settled fog droplets. Measurements of sulfate, nitrate, OC, other elements/ions.	Fog study at Angiola tower may include some fog droplet sampling.
Is re-suspension of PM a concern after a fog episode?	Fog/PM/PM component fluxes during / after fog episodes.	Same as above.
Re: Dry deposition		
What is the extent of dry deposition?	Direct eddy flux measurements of PM and precursors over a range of surfaces and under a range of meteorological conditions (tower or aircraft).	Dust deposition/suspension experiments planned. Gases and fine particles mentioned for deposition experiments at the tower, but no details available.

2.5.3 Study Findings

Gas-Phase Measurements

Gas-phase data are needed for both the precursors of secondary PM and for oxidants. These data are important not only for the evaluation of chemical pathways for the formation of sulfate, nitrate, and secondary organic aerosols, but also for the evaluation of the gas-phase chemical mechanism used in the host air quality model. Gas-phase data from routine monitoring stations will be supplemented with five-minute NO_y / NO data and light hydrocarbons samples collected every sixth day in the annual study. For the winter study, continuous monitors are proposed for NO_y, NO, NH_3, SO_2, HNO_3, and O_3. Light and heavy hydrocarbons will be measured with five or six hour samples during PM episodes.

Missing in this list are NO_2, VOC other than hydrocarbons (such as oxygenates), and other radical and oxidants such as OH, H_2O_2, and NO_3. Although NO_2 may be separable from NO_y measurements, NO_2 should be measured independently because it is the immediate precursor to HNO_3, the probable limiting reagent for ammonium nitrate (NH_4NO_3) according to the conceptual models. With accompanying measurements of other nitrogen species, the important processes responsible for the formation of nitric acid and the limiting reagent in the system may be inferred.

Oxygenated organic compounds, such as aldehydes and ketones, are primary VOC as well as intermediate products of the atmospheric oxidation of VOC. Aldehydes contribute significantly to oxidant formation through their photolysis and atmospheric reactions. In addition, both aldehydes and ketones can provide useful information on the extent of reactions of organic compounds. AER recommended measurements of these compounds to initialize the model and are also very useful for the evaluation of chemical mechanisms. Note that chemical mechanisms for oxidant formation have not been evaluated for cool and wet conditions. OH is obviously a key gas-phase oxidant for both NO_2 and SO_2. H_2O_2 (possibly also organic peroxides, ROOH) is an important aqueous oxidant for SO_2. NO_3 is a precursor to HNO_3, both in the aqueous phase and gas phase when photolysis is reduced. Although ozone will be continuously monitored in the winter study of CRPAQS, an ozone monitor with sufficient sensitivity for measuring ozone in the fog has yet to be identified. Measurement of these radicals and oxidants will yield information directly relevant for understanding nitrate and sulfate chemistry.

Gas-phase measurements of ammonia and nitric acid during the annual study are recommended for use in determining the relative abundance of the precursors to NH_4NO_3 in the spring, summer, and fall. Higher temporal resolution (e.g., hourly data) may be beneficial for understanding emissions and chemical reactions of primary organic compounds. Five-minute measurements may be unnecessary for some of the other compounds, especially secondary compounds such as NO_y. Intermittent sources of NH_3, NO_x, and SO_2 may be detected using high resolution data; however, inference regarding the location of the source and the duration of the emission activity may be difficult under calm conditions.

Watson et al. (1998) postulated that the production of secondary aerosol, including sulfate and nitrate, takes place aloft and in cloud droplets. Therefore, it was recommended that measurements of aloft concentrations of precursor gases (SO_2, NO_x, NH_3) and oxidants (O_3, H_2O_2) should be taken to verify those aspects of their conceptual model. In addition, this information is useful in assessing the extent of vertical mixing at various times of the day, the importance of aloft production of oxidants, the importance of aloft transport of PM precursors and oxidants from upwind areas such as the San Francisco Bay Area, and the efficiency of upper air transport as a mechanism for pollutant dispersion within the San Joaquin Valley (e.g., for NH_3).

Particle Measurements

There is a strong emphasis on particle measurements in the Field Program Plan: continuous measurements of PM_{10}, $PM_{2.5}$, size distribution, light scattering, and $PM_{2.5}$ components at resolution of 5 minutes (sulfate, nitrate, elemental carbon / organic carbon) to 6 hours. PM size distributions in the fall are useful for estimating deposition rates of geological particles and the zones of influences of the emission sources. Indirect evidence may also be obtained from the size distribution regarding the dominant processes for the production of secondary compounds. For example, sulfate of gas-phase origin tends to deposit onto smaller particles than sulfate formed in the aqueous phase (Hering and Friedlander, 1982; Meng and Seinfeld, 1994; Hering et al., 1997).

The special study of fog intensity and composition should address some of the questions raised in IMS95. Since details of the fog study to be conducted at Angiola tower were not available

when the report was prepared; it could not be assessed whether additional measurements should be recommended. The following areas require additional research:

- The agent(s) responsible for the unexplained fog buffering capacity observed in urban fog droplets
- Accurate measurements of oxidants (O_3, H_2O_2), catalysts (Fe or Mn), and SO_2 at low levels to confirm the relative importance of the sulfate-forming reactions
- Wet deposition fluxes of fog water and fog components such as nitrate, sulfate, ammonium, and organic compounds.

Surface and Upper Air Meteorological Measurements

The temporal and spatial variations of the mixing layer height have a strong impact on the dispersion and transport of PM and PM precursors. A special study is scheduled during the winter of 2000 for an aircraft investigation of the spatial variations of the mixing layer depth. During the winter episode, 17 stations will be operational with radar profilers and radioacoustic sounding systems (RASS), and 10 stations will be equipped with sodars for continuous (15 minute) measurements (versus 11 radar profilers/RASS and 1 sodar during the annual study). In addition, two to six soundings will be made at six upper air radiosonde stations to measure wind, temperature, and relative humidity as a function of height. The backbone network contains only 11 stations that make one to two soundings per day. Higher spatial and temporal resolutions are desired for both the annual study and the intensive studies in the fall and winter to characterize the mixing conditions in the San Joaquin Valley and to provide information from which the impacts (time, location) of aloft transport may be inferred.

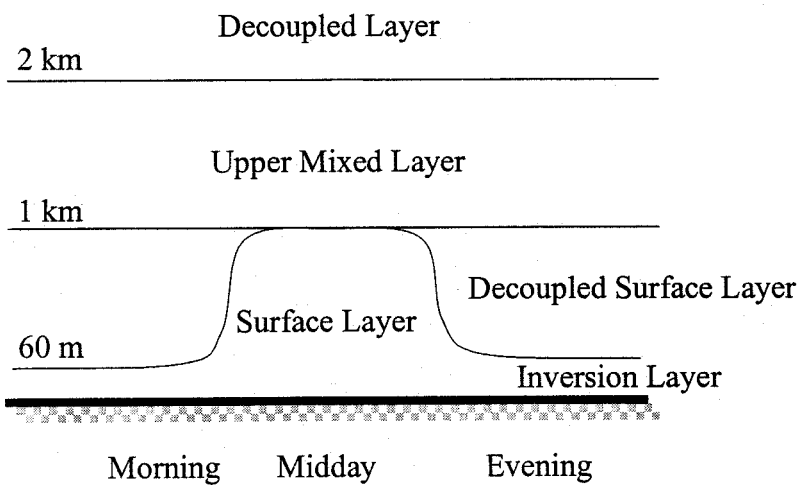
Measurements of solar radiation are essential to assess the importance of NO_3 as a precursor for the production of HNO_3. Fog reduces the amount of radiation available at the surface and reduces the photolysis rate of NO_3. Together with increased water content, the accumulation of NO_3 may increase the importance of N_2O_5 hydrolysis as a pathway for the formation of HNO_3. To properly analyze the production of nitrate, measurements of solar radiation are recommended, especially during a daytime fog episode.

The spatial and temporal distribution of fog and clouds may be an important factor affecting the efficiency of the production of nitrate and sulfate. Fog observations are made at the airports by automatic surface observation systems and at the backbone sites, indirectly, by nephelometers. Information about the vertical extent of fog is, however, limited to the observations of the special study. The spatial and temporal extent of clouds may be observed by satellites, but the use of satellite data is not currently included in the Field Program Plan.

Vertical Mixing and Aloft Transport

The impacts of aloft transport and reaction processes are key areas of uncertainty in the conceptual models and are related to vertical mixing within the San Joaquin Valley. The mixing layer height during the day is variable in time and in space. Different estimation techniques tend to result in inconsistent answers. Since PM correlates well with aloft temperature, which can be related to atmospheric stability, a consistent understanding of the daytime mixing layer is needed to evaluate the dispersion processes of PM.

Evening inversion plays an important role in trapping emissions within a shallow layer next to the surface, resulting in increased concentrations of PM (and probably precursors as well) at the urban sites. The conceptual model in Section 3 of the Field Program Plan states that as the inversion layer breaks, the trapped material is mixed into the "valley wide" layer aloft; this is where chemical reactions take place to produce secondary compounds such as HNO_3 during the day. Stronger winds aloft are postulated to be a mechanism for the dispersion of pollutants. This conceptual model seems simpler than the conceptual model, shown in Section 2.1 of this document, developed by Pun and Seigneur (1998a) based on the findings of Dye et al. (1997). Dye et al. found that the atmosphere within the San Joaquin Valley is typically divided into three layers (Figure 10). Wind speeds with the surface layer are typically low. The upper mixed layer is characterized by uniform wind flows at higher speeds (up to 10 m/s). According to Dye et al. (1997), this layer is between 1 and 2 km.



(Source: Dye et al., 1997)

Figure 10. Vertical Layers in the San Joaquin Valley

It is not clear in the Field Program Plan which layer is the so-called "valley wide" layer and where aloft transport, suggested by the conceptual model, takes place. Watson et al. (1998) described the mixing situation as follows.

During winter nights and mornings, a shallow (30 to 50 m above ground level) radiation inversion forms, which only begins to couple to the valley-wide mixed layer between 10:00 and 12:00 Pacific Standard Time (PST), and reasserts itself after sunset at 18:00 PST.

From this description, the valley-wide mixed layer seems to be the equivalent of the decoupled surface layer depicted in Figure 10. That the wind speed in the decoupled surface layer (typically less than 5 m/s) can be responsible for the aloft transport inferred in the model, should be confirmed. Another possibility is that transport takes place in the upper mixed layer. Upper air measurements to characterize the height of this layer, and concentration measurements aloft to understand the vertical extent of mixing in the afternoon could be useful. Currently, no upper air measurements of chemical/PM concentrations are planned. Ground level measurements at elevated sites are proposed; however, they will characterize the Valley slopes and may not represent aloft conditions in the center of the valley. A winter special study

is planned to compare PM measurements taken at 250 m above ground level in the valley and those taken at the Sierra Foothills sites. There is no back-up plan, however, to study the aloft concentrations of PM and their gaseous precursors if the foothill sites are found to be unrepresentative of concentrations aloft in the valley.

Data for Receptor Modeling

Receptor models are particularly useful tools for understanding the source contributions of primary sources. The requirements of running a receptor model such as chemical mass balance are accurate ambient measurements of PM composition and detailed source profiles specific to the area of interest. Key areas of uncertainty include fugitive dust profiles, motor vehicle emissions categories such as cold start, running losses, and exhaust, and various vegetative burning profiles. Accurate measurements of PM source profiles (specific for the San Joaquin Valley) and the measurement of compounds that provide source signatures will extend the resolution of CMB to a larger number of sources and allow more accurate determination of source contributions of all relevant sources.

Data Needs for PM Air Quality Model Evaluation

The data needed for executing and evaluating PM source models are discussed in Section 2.3 of this document and by Pun and Seigneur (1998b) and are summarized in Table 8. The meteorology and chemistry measurements proposed in the Field Program Plan should form a reasonable database for model execution and evaluation. Several areas, however, require supplemental data.

In general, additional aloft measurements of meteorology are desirable. The planned measurements combine continuous measurements (11 radar profilers/RASS and 1 sodar during the annual study; 17 radar profilers/RASS and 10 sodars during the winter study) with radiosondes (twice per day during the annual study and up to six times per day during winter episodes). The continuous measurements provide 15-minute temporal resolution for wind speed, wind direction, and temperature data. However, the range of radar profilers (wind measurements) and RASS (virtual temperature measurements) are limited to 500 to 800 m, respectively, while sodars can measure wind speed and direction up to 2000 m. The ranges of the continuous measurements fall short of the decoupled layer. Radiosondes, which obtain data from 0.1 to 10 km above ground level, are only launched two to six times a day during CRPAQS.

Other improvements are also desired in the meteorology network. The spatial and temporal variations of mixing height and observations of fog and clouds are important inputs for data analysis and for the meteorological model. In addition, measurements of solar radiation during a fog episode will aid the testing of the current assumptions made in air quality models and provide useful information to refine chemical kinetic calculations within the fog module.

Table 8. Data Needs for Episodic Modeling

Data	Spatial Resolution	Temporal Resolution	Proposed Measurements in the Field Program Plan
Meteorology			
Wind Speed and Direction	Surface and Aloft	< 1 hour *	Surface/tower: 1-5 min; aloft: 4-7 radiosondes twice per day to 2-6 times per day (w); 15-min average data from 11 to 17 radar profilers, 1 to 10 sodar
Temperature	Surface and Aloft	< 1 hour	Same as wind measurements for radiosondes; 15-min average data from 11 to 17 RASS
Mixing Height	Surface or Aircraft	< 1 hour	Winter aircraft measurements (f?), temperature profile soundings 2-6 times per day at 4 sites (w)
Relative Humidity	Surface and Aloft	< 1 hour	Surface: 5 min, aloft 2-6 times per day at 4 sites (w)
Solar Radiation	Surface and Aloft	< 1 hour #	Radiation at backbone sites only (f?)
Fog / Clouds	Surface and aloft (coverage and depth)	< 1 hour	Fog/cloud observations probably obtained at airports (f?)
Emissions			
(PM-2.5, PM-10, Precursor Gases)			Details of emission study unavailable
Profiles (Anthropogenic and Biogenic)	Representative Sources	Not applicable	
Emission Factors	Major Sources	1 to 4 hours	
PM-2.5 / PM-10			
Total Mass	Surface and Aloft	1 to 4 hours	10 min (annual, winter anchor sites)
Sulfate	Surface and Aloft	1 to 4 hours	5 min (PM-2.5 winter anchor sites)
Ammonium	Surface and Aloft	1 to 4 hours	24 hour
Nitrate	Surface and Aloft	1 to 4 hours	10 min (PM-2.5 winter anchor sites)
Elemental carbon	Surface and Aloft	1 to 24 hours	30 min (PM-2.5 winter anchor sites)
Organic carbon (speciated)	Surface and Aloft	1 to 24 hours	OC 30 min, speciation 5-6 hours (PM-2.5 winter anchor sites, episodes)
Chloride	Surface and Aloft	1 to 4 hours	3-6 hours (PM-2.5 winter anchor sites, episodes)
Gases			No aloft gases measurements planned (except for a special winter study)
O_3	Surface and Aloft	1 hour	5 min (winter anchor sites)
NO	Surface and Aloft	1 hour	5 min (winter anchor sites)
NO_2	Surface and Aloft	1 hour	5 min (winter anchor sites; separated from NO_y if possible)
VOC (Speciated)	Surface and Aloft	1 to 4 hours	5-6 hours (hydrocarbons only; no oxygenates such as aldehydes)
HNO_3	Surface and Aloft	1 hour	5 min (winter anchor sites)
NH_3	Surface and Aloft	1 hour	5 min (winter anchor sites)

Data	Spatial Resolution	Temporal Resolution	Proposed Measurements in the Field Program Plan
H_2O_2	Surface and Aloft	1 hour	None
Organic Peroxides	Surface and Aloft	1 hour	None
PAN	Surface and Aloft	1 hour	Lumped into NO_y
OH	Surface	1 hour	v
HO_2	Surface	1 hour	None
NO_3	Surface	1 hour	None
CO	Surface and Aloft	1 hour	Backbone sites (annual, f?)
SO_2	Surface and Aloft	1 hour	5 min (winter anchor sites)
Droplet Chemistry		Fog Only	Details of fog study unavailable
Water Content	Surface and Aloft	1 hour	
Sulfate	Surface and Aloft	1 hour	
Nitrate	Surface and Aloft	1 hour	
Ammonium	Surface and Aloft	1 hour	
Chloride H_2O_2	Surface and Aloft	1 hour	
Sulfite	Surface and Aloft	1 hour	
H^+(pH)	Surface and Aloft	1 hour	
Dissolved Fe^{3+} and Mn^{2+}	Surface and Aloft	1 hour	
Wet Deposition	Representative Locations	Fog Only	Details of fog study unavailable
Sulfate		1 hour	
Nitrate		1 hour	
Ammonium		1 hour	
Dry Deposition	Different Surface Types (aircraft measurements or tower measurements)	Representative Meteorology	Dust (coarse PM) deposition study at Angiola tower (Tower measurements of gases and fine particles mentioned, but details unavailable)
$PM_{2.5}$			
PM_{10}			
HNO_3			
NH_3			
SO_2			
O_3			

* 5-minute temporal resolution is desired during stagnation

5-minute temporal resolution is desired during fog

f? frequency unknown

w winter study supplements annual study with additional sites and increased frequency of observations

Emissions inventories are particularly important for the performance of PM air quality models and should be independently verified. Coupled with accurate source profiles, source strength (emission factors) information obtained in a separate emission study will allow the independent evaluation of the emissions programs within the air quality modeling system.

Emissions measurements are a critical component of a field program designed to generate a database for model performance evaluation. A model performance evaluation is meaningless when poor model performance can be attributed to large uncertainties in the input data. Although details regarding the emissions study are limited, we recommend the verification of the abundance of ammonia emissions relative to nitric acid production as a priority. The temporal and spatial profiles of NH_3 and SO_2 are also uncertain. Accurate source profiles of San Joaquin Valley sources will be beneficial to the application of receptor modeling from which the contributions of secondary organic aerosols can be determined. In addition, a review of the anthropogenic and biogenic VOC emissions inventories is necessary for the accurate modeling of oxidant chemistry and SOA formation.

The particulate-phase data needed for source models of PM include both mass concentration and composition. Since the evaluation of PM source models is a strong emphasis of the CRPAQS field study, a fairly complete set of measurements is proposed.

These data should form a good database for the operational evaluation of a PM air quality model, as well as the diagnostic evaluations addressing PM components and diurnal profiles. Some redundancy has been built into the mass measurements. Several PM measurements are also taken at high time resolutions compared to our recommendations. The redundancy and excess resolution provide opportunities for tradeoffs in other areas. Time resolutions in the measurements of NH_3, HNO_3, and other precursors (i.e., shorter averaging time) should be increased to make them comparable to those of the PM chemical components.

Measurements of gases are important for the evaluation of the chemistry modules, which typically have only been evaluated against data taken in warm temperatures. The biggest challenge for CRPAQS may be to incorporate aloft measurements of PM precursors and oxidants. Even surface measurements are inadequate for several important oxidants and precursors, including radical species such as NO_3, OH, HO_2, and molecular species such as H_2O_2, NO_2, and PAN. Some of these species are likely to be important for the understanding of sulfate and nitrate chemistry and should be taken during some fog episodes. Higher frequencies of speciated VOC measurements (including oxygenated VOC, particularly aldehydes) are also desired, because of their importance as precursors to SOA and to oxidants.

To understand the effects of fog, it is recommended that droplet chemistry be studied. This involves collecting size-resolved fog samples both at the surface and aloft and analyzing their composition in terms of water, sulfate, nitrate, ammonium, chloride, H_2O_2, sulfite, pH, and dissolved metals. A resolution of one hour is recommended, because fog episodes typically last less than 10 hours.

A set of measurements is needed to evaluate the prediction of fluxes in the PM air quality model, and to ensure that there are no major compensating errors in the model. For example, if a model over predicts wet deposition and under predicts dry deposition, it may perform well with a test case with fog. However, if the model is then applied to an area without fog, the predictions will be erroneous. The main fluxes of concern are emissions, advection, vertical mixing, wet deposition, and dry deposition. Data needed for the independent evaluation of emissions and vertical mixing were discussed previously.

The amount of pollutants entering the valley at the surface could be determined by the horizontal flux (concentration and wind measurements) at a well-defined point of transport, such as a mountain pass. During IMS95, the wind flow was too poorly defined at flux plane monitoring sites to calculate the fluxes entering the monitoring area. This conclusion was not unexpected given the dominance of stagnation. Aloft fluxes of pollutants should also be evaluated due to their potential importance for the transport of precursors and oxidants from upwind source areas (such as the San Francisco Bay Area) or within the San Joaquin Valley. These fluxes may be estimated from aircraft measurements of concentrations at a flux plane with good characterization of upper air winds.

Wet deposition of sulfate, nitrate, ammonium, and organic compounds can be measured directly by collecting fog samples at the ground surface and analyzing the chemical composition.

Some dry deposition measurements are planned at Angiola. In addition to dust, fine and coarse PM should also be studied. Dry deposition measurements of precursor gases, including HNO_3, NH_3, SO_2, and oxidants such as O_3 are also recommended. All deposition measurements need to be conducted under a variety of meteorological conditions, and for different surface types. Aircraft measurements are recommended for sampling a variety of surfaces during a sampling period of a particular type of meteorology. Well-planned tower measurements, however, are also a viable option.

2.5.3.1 Conclusions and Recommendations

The priorities for the CRPAQS field study were identified as follows in terms of measurement categories (not in order of importance).

Particulate matter

- PM mass: $PM_{2.5}$ and PM_{10}
- PM composition: sulfate, ammonium, nitrate, elemental carbon, speciated organic carbon, chloride.

Gas-phase species

- Precursors of PM (surface, aloft): NO, NO_2, speciated VOC (including aldehydes), HNO_3, NH_3, SO_2
- Oxidants: O_3, H_2O_2, organic peroxides
- Radicals: OH, HO_2, NO_3 (highest priority to OH).

Emissions

- Source profiles, inventories of NH_3, SO_2, VOC with good spatial and temporal resolution (hourly for weekday and weekend) and, for VOC, chemical speciation.

Meteorology

- Mixing layer height: spatial and temporal resolution
- Wind speed and direction, temperature, RH, radiation flux (surface and upper air).

Miscellaneous

- Dry deposition measurements of PM and precursor gases
- Droplet chemistry for PM components and precursors
- Wet deposition measurements of PM component

Measurements that are considered as low priority include the following:

- Particle size distribution of $PM_{2.5}$. Some size distribution of PM_{10} may be useful in the fall study to characterize settling velocities of coarse PM. Although particle size distribution of $PM_{2.5}$ can provide some useful information on the chemical pathways that led to secondary PM formation, chemical measurements of PM, precursors, and oxidants are considered to be more important.
- Measurements of NH_3 and HNO_3 near an NH_3 emission source to study NH_3/HNO_3 limitation. Such an area should be characterized by high NH_3 concentrations compared to HNO_3 concentrations and, therefore, it is not clear what information will be gained from this study. Measurements of NH_3. It should be conducted in priority in the areas which experience high NH_4NO_3 levels, i.e., receptor areas. If the NH_3 source area corresponds to such a receptor area, then, such measurements may be justified.

Duplicate measurements are very useful for evaluating the measurement techniques. The extent of such measurement duplication must, however, be weighed against other priorities such as sufficient spatial coverage and temporal resolution; measurements of other variables.

Tradeoffs

Based on the measurements that are proposed in the Field Program Plan and the data needs identified in Section 2.5 of this document, the following tradeoffs are recommended. The study design principles outlined in Section 4.1 of the Field Program Plan explained the reasons behind the proposed measurements. One of the main objectives is to generate a database for use in the performance evaluation of PM air quality models. Recommendations for alterations of the study design are based on that objective.

Major tradeoff categories include:

- More detailed measurements at a few sites versus less detailed measurements at many sites
- Time/space resolution versus time/space coverage
- Measurements of some variables versus other variables.

These tradeoffs are discussed in the following.

More Detailed Measurements at a Few Sites vs. Less Detailed Measurements at Many Sites

One of the study design principles (Section 4.1 of the Field Program Plan) is that “more detailed measurements at a smaller number of locations” are “of greater utility than less detailed measurements at many locations.” This may not be true for model evaluation purposes. At present, the understanding of the distribution, transformation, and especially transport of PM is still limited. Although detailed information may aid in the basic understanding of the formation of secondary PM and in refining the conceptual models, the data requirements may

not be completely compatible with the construction of a quality database for model execution and evaluation. It may be more important to test the model's ability to reproduce the general features of PM spatial and temporal distribution within the San Joaquin Valley rather than gain a detailed understanding of the patterns of PM formation at a few specific locations. Furthermore, whereas $PM_{2.5}$ mass measurements are relatively easy to make, some of the detailed measurements are pushing the sensitivities of current measurements (e.g., high frequency particle size distribution, NH_3 and HNO_3 measurements) and may be relatively uncertain. The quality of the data may affect their value. Good PM mass data at a large number of sites may be more useful for analysis and model evaluation than detailed data at a few locations, particularly if some of those detailed measurements have poor accuracy / precision.

The Field Program Plan posed the question "Is more frequent and more complete Aerosol chemistry" really "preferable to a larger number of locations with only mass concentrations"? The argument given in Section 4.1 of the Field Plan is that without chemical compositions, elevated mass concentrations cannot be explained and remain anomalies. Determining PM chemical composition is important. In Section 4.4 of the Field Program Plan, a number of short duration (5 to 10 minutes) measurements are proposed for the annual and winter studies at the anchor sites ($PM_{2.5}$ mass, PM_{10} mass, $PM_{2.5}$ carbon, $PM_{2.5}$ light scattering, and $PM_{2.5}$ light absorption, and various meteorological measurements). For example, the proposed 5 to 10 minute averaging time for the $PM_{2.5}$ measurements for the annual study will result in 105,120 data points per site per measurement. While these measurements may be used to identify wind gusts and intermittent sources, their benefits must be weighed against the cost of acquisition, storage, quality assurance, and analysis of such a large body of data for a long-term study. Before these measurements are commissioned, one should carefully assess the expected quality of the data, the information they will yield, how they will be analyzed, and how they will be used to further our understanding of PM pollution in the San Joaquin Valley.

Although high time resolution data are useful in analyzing anomalous PM phenomena, the use of the high time resolution data in modeling is likely to be limited. First, an anomalous episode may not be a likely candidate for episodic modeling. Second, even if the anomaly is captured by the chemical composition data, it may not be captured in the meteorology and emissions data used to support the modeling exercise. Third, the time-scale of the intermittent elevated concentrations may be too short to be captured by the model, whose typical time scale is one hour. If an unexpected high PM concentration is observed, it is obviously desirable to be able to confirm and explain it. The cost of this "frequent" and "complete" aerosol chemistry must be weighed against the alternative cost of spatial coverage of measurements. From the point of view of model evaluation, spatial coverage with reasonable temporal resolution (e.g., one hour) is preferable to high time resolution data limited in spatial coverage.

In addition, resolution in time may be traded for resolution in space such that high time resolution is obtained only at a few representative sites. Instead of 10 minute PM mass data at three anchor sites for the annual study, hourly measurements for PM mass is recommended at anchor and selected satellite sites, with 10 minute data at one representative site.

Time/Space Resolution vs. Coverage

In the design of a field program, tradeoffs were identified that exist between the coverage (range) and the resolution in each of the dimensions x, y, z, and t. The spatial domain of

CRPAQS extends from Chico to the South Coast Air Basin (NS) and from the Mojave Desert to 200 km west of San Francisco (EW) (as shown in Figure 11). The time frame for the annual study is December 1999 to January 2001, and December 2000 to January 2001 for the winter study (with 20 intensive days). Depending on the flexibility in the domain and the monitoring period, tradeoffs can be made between the time resolution of the measurements and the monitoring period, or the spacing of monitoring sites and the study domain.

The domain and lengths of the annual, winter, and fall studies seem reasonable. As discussed in Section 2.3 of this document and in a report by Pun and Seigneur (1998b), it is essential to include as much of the upwind emission sources as possible. Therefore, a domain that extends north to Chico and includes the San Francisco Bay Area is appropriate. The PM National Ambient Air Quality Standards include both 24-hour and annual average values. Actually, the annual average value must be averaged over three years (making the standard more a three-year running average standard than a one-year average). Therefore, the one-year period planned for CRPAQS is a minimum and the success of the program will depend on that year being fairly representative of longer-term averages. Twenty intensive days are planned for the winter study. This plan should allow for four to five episodes (assuming four to five days per episode). Seigneur et al. (1998b) stressed the importance of evaluating the performance of three-dimensional air quality models for several episodes characterized by different meteorologies and atmospheric chemistry. The winter study should provide a useful database to that end. We recommend, however, that other intensive measurements be conducted at other times of the year. Although high $PM_{2.5}$ concentrations occur during wintertime, we need to assess how emission control options that are beneficial for reducing wintertime $PM_{2.5}$ will affect $PM_{2.5}$ concentrations during other seasons (this is relevant to the annual standard) and O_3 concentrations during summertime (this is relevant to the eight-hour average O_3 NAAQS).

In summary, coverage of CRPAQS is not overstated and it would not be wise to increase time/space resolution of the measurements by reducing the coverage.

Measurements of Some Variables vs. Other Variables

As shown in Table 8, a number of measurements were identified that need to be incorporated into the Field Program Plan, based on our list of data needs for model evaluation. These measurements may be traded against redundancy (and also temporal or spatial resolution) of other measurements. They can also be traded against other measurements (which would then be eliminated from CRPAQS). The measurements recommended to add are listed in Table 8. A few suggestions of possible tradeoffs are presented in Table 9.

Table 9. Possible Tradeoffs for CRPAQS Measurements

Recommended Additional Measurements	Possible Tradeoffs
1. Measurements of NO_2 2. Ground-level measurements of key radicals (OH, NO_3, HO_2, RO_2; in order of priority) 3. Measurements of H_2O_2 4. Particulate phase ammonium (to match the resolution of sulfate and nitrate during an episode) 5. Measurements of oxygenated VOC (e.g., aldehydes) 6. Aloft measurements of gas-phase chemistry 7. Solar radiation in fog 8. Additional gas-phase measurements for the annual study (e.g., NH_3, HNO_3, SO_2, O_3, VOC) 9. Dry deposition 10. Increased spatial (x, y) resolution of aloft meteorology, especially mixing height.	1. PM size distribution 2. Special fall study of NH_3/HNO_3 limitation 3. Some duplicate measurements of $PM_{2.5}$ mass, ions, or elements during the winter study 4. Time resolution of component measurements 5. Surface meteorology sites.

2.6 Sensitivity of PM Nitrate Formation to the Precursor Emissions in the California San Joaquin Valley

2.6.1 Background

Ambient data from the 1995 Integrated Monitoring Study (IMS95) show that areas in the California San Joaquin Valley exceed the short-term $PM_{2.5}$ National Ambient Air Quality Standard (24-hour average concentration of 65 $\mu g / m^3$). Of the key components of $PM_{2.5}$, ammonium nitrate (NH_4NO_3) typically accounts for close to 60 percent of $PM_{2.5}$ in rural areas. Therefore, it is important to investigate the PM-precursor relationships of NH_4NO_3 for the formulation of effective $PM_{2.5}$ control strategies, especially in rural areas.

In the earlier described conceptual model of PM formation in the San Joaquin Valley, in Section 2.1 of this document, It is postulated that the formation of NH_4NO_3 is limited by the availability of HNO_3, because NH_3 emissions seem abundant in the San Joaquin Valley. HNO_3 is itself a secondary component, formed in the atmosphere as a product of photochemical reactions involving NO_2, hydroxyl radical (OH), and ozone (the O_3 reaction involves intermediates nitrate radical, HNO_3, and dinitrogen pentoxide, N_2O_5). While NOx are directly emitted, the radical species are produced from precursors NOx and VOC. Therefore, their formation may be NOx-sensitive or VOC-sensitive. Clearly, the chemistry regime has important implications toward the choice of effective emission controls.

2.6.2 Objectives

To investigate the sensitivity of PM nitrate formation under conditions prevalent in the San Joaquin Valley during the winter season, a modeling study was performed. This work was designed to complement any field measurements that may help unravel the details of nitrate chemistry in the ambient environment. The objectives were to:

- Develop a box model that includes atmospheric chemistry and gas/particle thermodynamics to simulate wintertime PM formation
- Use the box model to study the sensitivities of oxidants and PM to precursors
- Investigate the use of photochemical indicators (Sillman, 1995; Lu and Chang, 1998) to predict the sensitivity of wintertime PM formation.

Details of the modeling are contained within the report provided in Appendix VI.

2.6.3 Findings

A box model was developed and used to investigate the response of PM nitrate to reductions in precursor emissions within the San Joaquin Valley. The formation of nitric acid and particulate nitrate was found to be sensitive to oxidants and to VOC emissions, as shown in Figure 11. In fact, a decrease in NO_x emissions led to an increase in PM due primarily to an increase in O_3 concentrations.

The model simulations point to the fact that PM formation in the San Joaquin Valley during winter is HNO_3-sensitive, that HNO_3 formation is oxidant-sensitive, and that oxidant formation is VOC-sensitive. The conclusion that PM formation is HNO_3-sensitive is also obtained if one uses the generic analysis of Ansari and Pandis (1998). The indicator species of Lu and Chang (1998), although developed for summertime conditions, also indicate that oxidant formation is VOC-sensitive.

It should be noted that the box model represents some domain-averaged chemistry but cannot characterize the locally specific chemical regimes. Further work should extend this box model analysis to a three-dimensional modeling study so that the transport processes can be simulated and spatial variability within the valley can be addressed.

2.6.4 Conclusions Recommendations

The work described concerning nitrates in the San Joaquin Valley complements other work reported for the South Coast Air Basin. In 1998, Kumar, Lurmannn, and Chico, (1998) reported their use of the Urban Airshed Model-Aerosol Module (UAM-AERO) in predicting ambient PM concentrations during an October 17 to 20, 1995 episode in the South Coast Air Basin. Through this effort, they were able to estimate impacts of controlling various precursor gases on resulting PM, including nitrates. Evaluation of their results shows that a 50 percent reduction in NO_x emissions leads only to a 9 to 13 percent reduction in $PM_{2.5}$ nitrates, a significantly non-linear relationship. A 50 percent reduction in ammonia emissions was predicted to result in 20 to 34 percent reductions in ambient nitrates; a 50 percent reduction in both VOC and NOx were predicted to decrease ambient nitrates by 21 to 23 percent; a 50 percent reductions in ammonia, VOC, and NOx resulted in a predicted reduction in ambient nitrate of 32 to 42 percent. In

another report, Lurmannn, et. al. (1997, pp. 268) predicted for the South Coast Air Basin that a 50 percent reduction in NO_x in the fall resulted in a 42 percent increase in nitrates. This response was due to the chemical system operating in a higher VOC-to-NO_x regime where nitric acid production was much more efficient and where there was ample ammonia to make ammonium nitrate

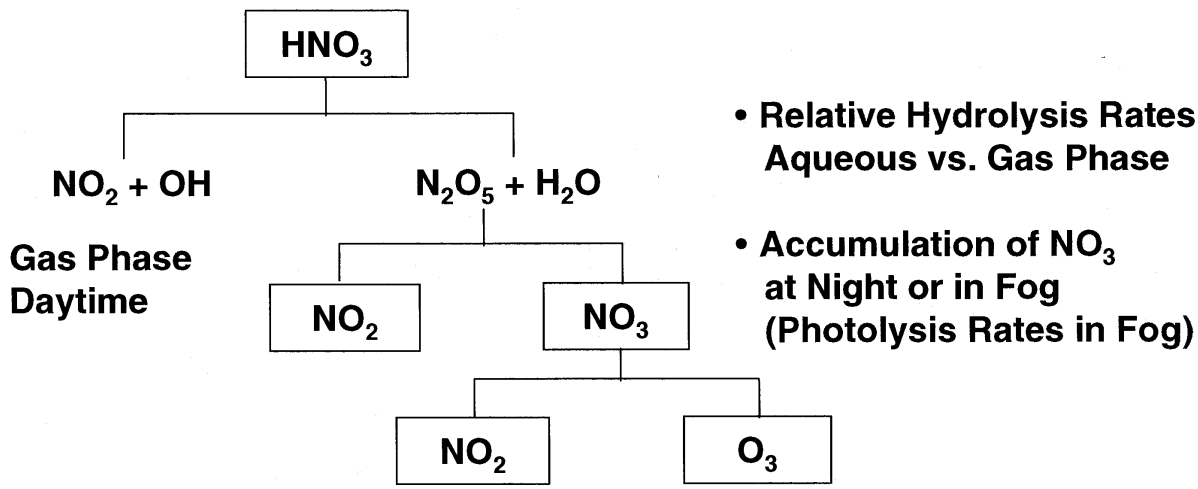


Figure 11. Formation of Nitric Acid in Ambient Air

Other work by Karamchandani, et al., demonstrated the conversion of power plant emitted NO_x to nitrate in the atmosphere. As NO_x plumes are emitted and travel and disperse downwind, different regimes occur with different atmospheric chemistry. Close in, near the point of emission, NO_x emissions scavenge ambient ozone. Further downwind, after many hours, the diluted power plant plume then participates in atmospheric photochemical reactions. Figure 12 demonstrates the change in plume NO_x chemistry as a hypothetical power plant (tall stack) plume is transported downwind. The early-on destruction followed by later-on formation of ozone within the plume has important implications in the ultimate creation of $PM_{2.5}$ nitrates.

2.6.4.1 Recommendations

Having hypothesized that ambient nitrate formation in the San Joaquin Valley is oxidant and therefore VOC limited during the winter, an important perspective was raised as the year 2000 PM study was designed. The study needs to include adequate measurements to characterize ozone, VOC, and hydroxyl radicals during the intensive studies. Further, it is important to understand the PM-precursor relationships of NH_4NO_3 as effective $PM_{2.5}$ control strategies are formulated, especially in rural areas. It is also recommended that a three-dimensional modeling study be conducted so that the transport processes can be simulated and spatial variability within the valley can be addressed.

2.6.4.2 Implication to Electric Power Producers

Production of electricity using air and fuel in a combustion device (boiler or engine) results in the production of varying emissions rates of NO_x. As such, these sources are subject to potential control of their NO_x emission in order to reduce ambient concentrations of ozone and $PM_{2.5}$ nitrates to attain various state and national air quality standards. Proposed new facilities often need to provide emission offsets to receive an operating permit. Knowledge of the inter-relationships of NO_x emissions and resulting ambient concentrations of $PM_{2.5}$ nitrates is important as new emission regulations are debated and as emission offsets for new projects are considered. Opportunities for inter-pollutant tradeoffs need to be carefully evaluated as project proponents negotiate to trade NO_x emissions for PM emissions, NO_x emissions for VOC emissions, vice versa, or with other combinations.

Another important implication is that ambient nitrate chemistry changes during the year. As indicated for the South Coast Air Basin, opposite trends occur in the formation of nitrate between summer and winter. Furthermore, highest ambient nitrate concentrations occur in the fall and winter seasons. These patterns also exist within the San Joaquin Valley and need to be considered as new projects are considered or as new emission control regulations are debated for existing sources.

Implications of changing plume atmospheric chemistry as power plant plumes are mixed and dispersed downwind of power plants are important as area impacts and population and environmental exposures to ozone and $PM_{2.5}$ nitrates are evaluated. These issues relate to long-range transport of power plant NO_x, and are of concern both locally and nationally as downwind air basins look for air pollution solutions from their upwind neighbors. Within Northern and Central California, no clear resolution has occurred in the debate about the San Francisco Bay Area emissions and their impact on the Central Valley, and vice versa.

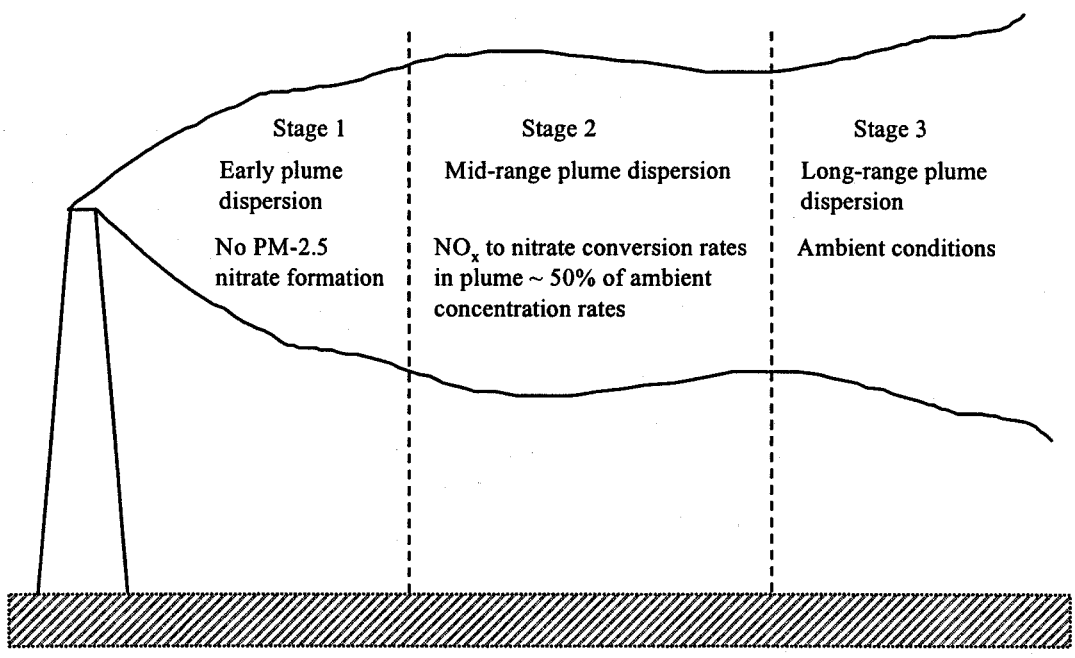


Figure 12. Change in Power Plant Plume NO_x Chemistry

3.0 Summary of Other PG&E Involvement

3.1 1995 Integrated Monitoring Study Overview Report

Within the scope of work agreed upon with the California Energy Commission and Pacific Gas & Electric (PG&E) was the completion of the 1995 Integrated Monitoring Study (IMS95) Overview Report. Dr. Paul Solomon of PG&E was the Project Manager for the IMS95 and had considerable involvement and responsibility with the total program. Before Dr. Solomon's departure from PG&E in March of 1998, he assembled a collections of papers related to the design, operation, measurements, and post-field activities related to IMS95. In July of 1999, PG&E completed Dr. Solomon's original report. The completion of the report is significant in that it documents many of the key elements and finding of the IMS95 monitoring efforts and, thus, lays the groundwork for future field investigations. The IMS95 Overview Report is provided as Appendix III of this document.

3.2 Involvement with Bay Area Air Quality Management District

Mr. Sam Altshuler, Project Manager for the Regional Ambient Aerosol Study (RAAS), was also a member of the Bay Area Air Quality Management District (BAAQMD) Advisory Council. Through his involvement with the Advisory Council and BAAQMD staff, Mr. Altshuler was able to bring attention to the value of the emerging Central California Ozone Study (CCOS) program to the San Francisco Bay Area. Sitting on the Advisory Council, Mr. Altshuler participated in many discussions related to the recent re-designation of the Bay Area as non-attainment for the one-hour ozone National Ambient Air Quality Standards (NAAQS).

In addition, the adoption of the eight-hour NAAQS for ozone, before its remanding on May 14, 1999, stimulated discussion within the Bay Area about the need for additional knowledge and understanding of ozone formation within the Bay Area. As a result of Mr. Altshuler's activities within the BAAQMD, additional focus and support was drawn out of the BAAQMD for CCOS as it was developed. Currently the BAAQMD is contemplating a contribution to CCOS in excess of $1 million to optimize the benefits of CCOS for the Bay Area. Specifically, the BAAQMD is planning extensive, complementary field monitoring and modeling in the Livermore, California, area to better understand why exceedances of the ozone NAAQS occur at the Livermore air monitoring station, the site with the worst ozone air quality in the Bay Area.

3.3 Technical and Policy Meetings

Mr. Altshuler, Project Manager for RAAS, and Mr. Eugene Shelar, Technical Manager for RAAS, attended routine policy and technical committee meetings throughout 1998 and 1999. At these meeting, perspectives of the electric utility industry were represented. Many of the recommendations provided were directly relevant to emissions from electric fossil fueled power plants emitting nitrogen oxide (NO_x). Information about these meetings has been submitted during the quarterly progress reports for RAAS. The contracted involvement of Atmospheric and Environmental Research (AER) by PG&E into the review and planning processes of California Regional PM_{10} / $PM_{2.5}$ Air Quality Study (CRPAQS) and CCOS has been

viewed as a worthwhile effort. In addition they delivered their reports on time to be useful to the committees. High level expertise provided included the support the CCOS program. Several briefings were given to the California Energy Commission about the importance of this study. Ultimately, the California Energy Commission committed $3 million to CCOS. This contribution will help maintain a focus of study to include discussion and review about the impacts of NO_x emitted by electric power plant. With the many new power plants proposed within California, results of CCOS should prove invaluable to the California Energy Commission as they evaluate future air quality impacts from proposed facilities.

3.4 Weekday and Weekend Ozone Analyzes

It has been an observed phenomenon that weekend ozone concentrations are generally higher than weekday concentrations at key locations within the San Francisco Bay Area (Altshuler, et al., 1995). During the summer months, May through September, average weekend peak hour concentrations were observed to be 10 to 20 percent higher than on weekdays. The term "Weekend Effect" has been used to connote the phenomena. It was further observed that a disproportionate number of violations of the state and federal one-hour Ambient Air Quality Standards (AAQS) also occurred on weekends.

It was postulated that the Weekend Effect occurred as a result of changing volatile organic compounds (VOC) and NO_x emissions occurring from weekday to weekend. Assessment of emissions suggests that weekend NO_x emissions are approximately 30 percent less than weekday emissions as a result of less bus and truck traffic, reduced industrial activity, and reduced electric power production by fossil fueled facilities within the Bay Area. Further, VOC emissions were estimated to decline only by about 10 percent on weekends relative to weekdays as a results of stable biogenic emissions, stable gasoline evaporative emissions, increased retail gasoline dispensing, and increased homeowner use of polluting lawnmowers and other yard equipment. This relative change in emissions, when combined with an Empirical Kinetic Modeling Approach (EKMA) model, is postulated to cause an increase in ozone formation within the Bay Area.

The presence of the Weekend Effect was postulated to be a natural indicator of whether or not an area was NO_x limited or VOC limited with respect to ozone formation. The Weekend Effect has important ramifications to emissions control strategies designed to reduce ambient ozone. Strategies designed to only reduce weekday emissions, such as reducing urban commute vehicle emissions, may not significantly impact or reduce the occurrence of ozone violations on weekends.

PG&E researchers also observed the presence of the Weekend Effect in Monterey and San Luis Obispo (Morro Bay) areas but not in the inland central valleys.

To augment assessment of ambient ozone experience within the San Joaquin Valley, PG&E conducted a screening of recent ozone experience at several key sites located in the southern end of the San Joaquin Valley. The results are shown in Figures 13 to 18. As can be seen, the presence of the Weekend Effect was not seen at Fresno or Bakersfield. The trends seen at Parlier are relatively insignificant compared to Bay Area experience. The absence of the Weekend Effect within the San Joaquin Valley suggest that the area is, on average, neither VOC nor NO_x

limited with respect to ozone formation in the Valley. It is postulated, based on review of considerable ozone data within California, that the Weekend Effect occurs in California in areas only along the coast where significant ambient temperature gradients exist between coastline and 20 to 50 miles inland. The cause and effect mechanism to support this hypothesis is unknown.

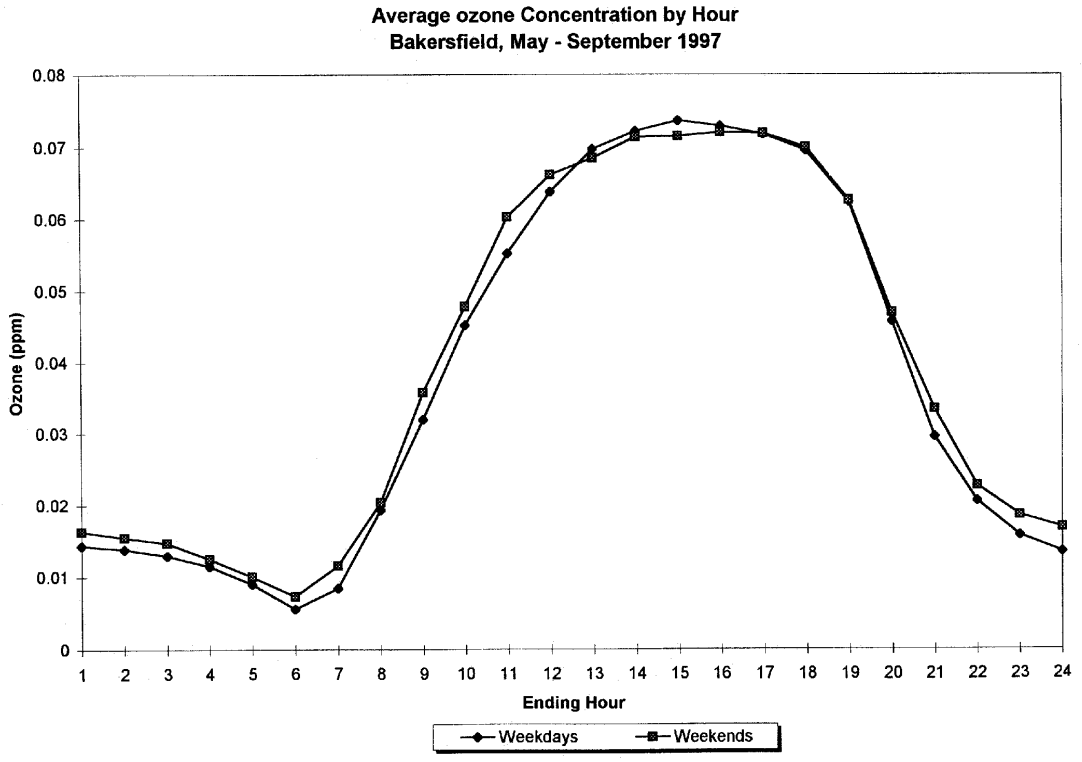


Figure 13. Weekend Effect Analysis for the San Joaquin Valley, Bakersfield 1997

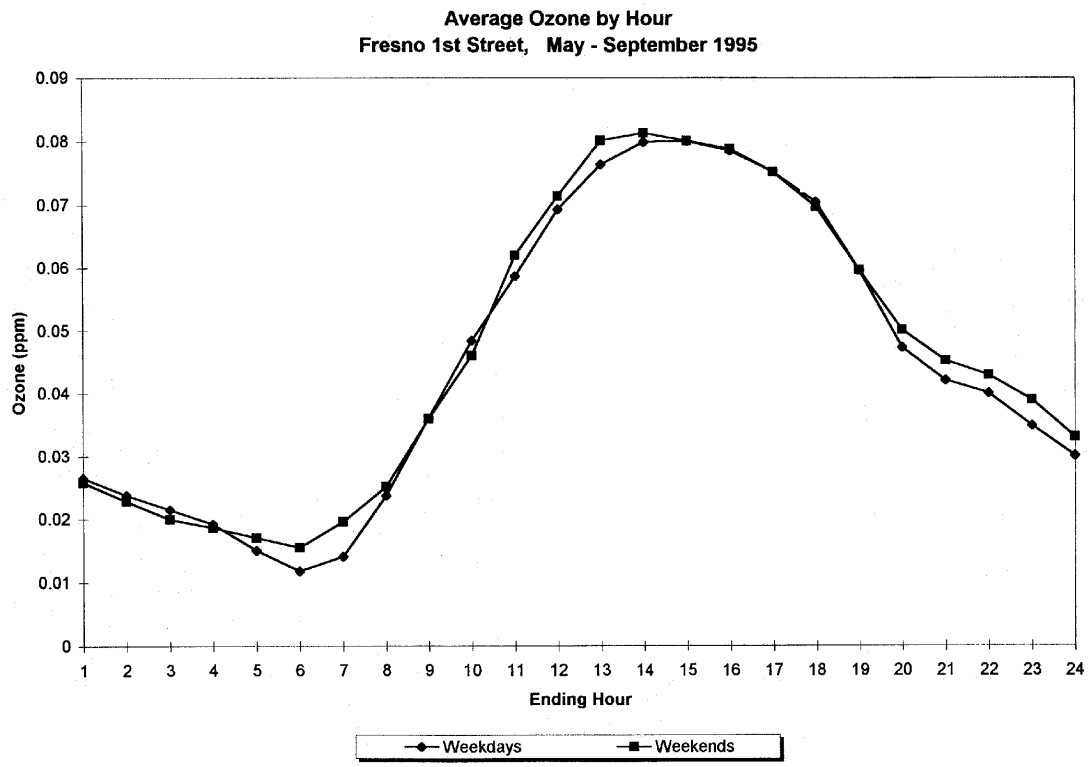


Figure 14. Weekend Effect Analysis for the San Joaquin Valley, Fresno, 1995

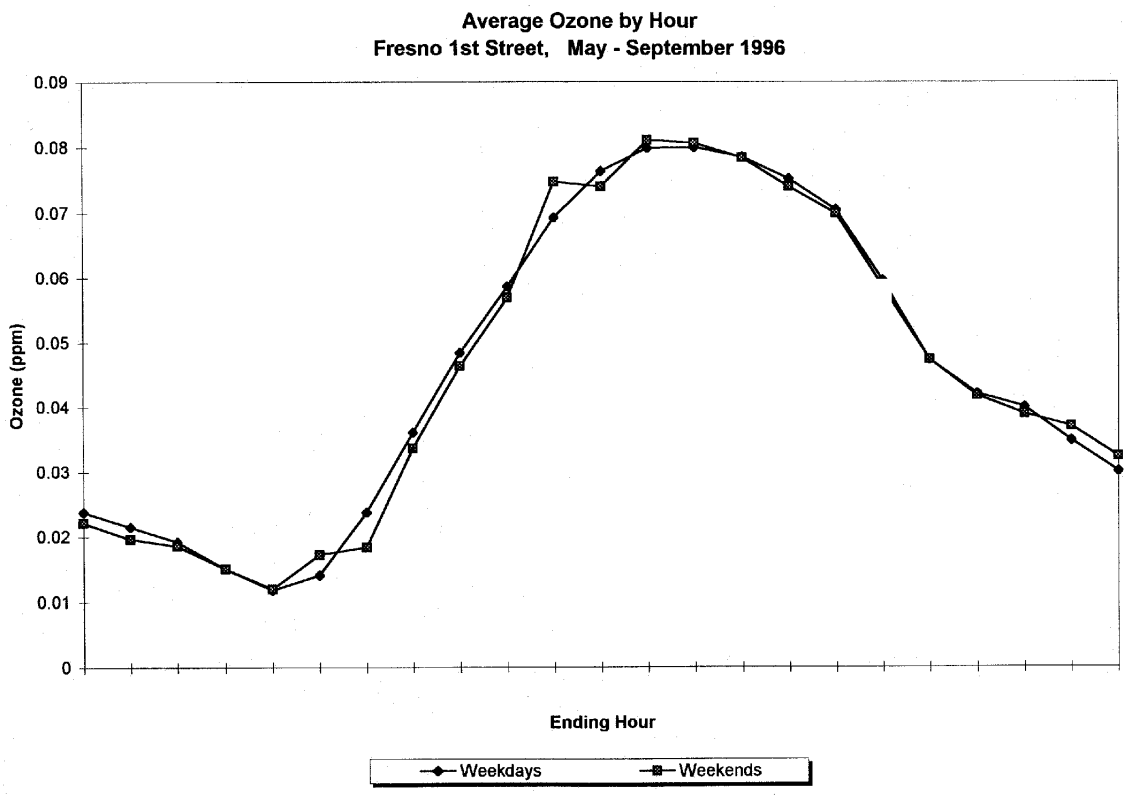


Figure 15. Weekend Effect Analysis for the San Joaquin Valley, Fresno, 1996

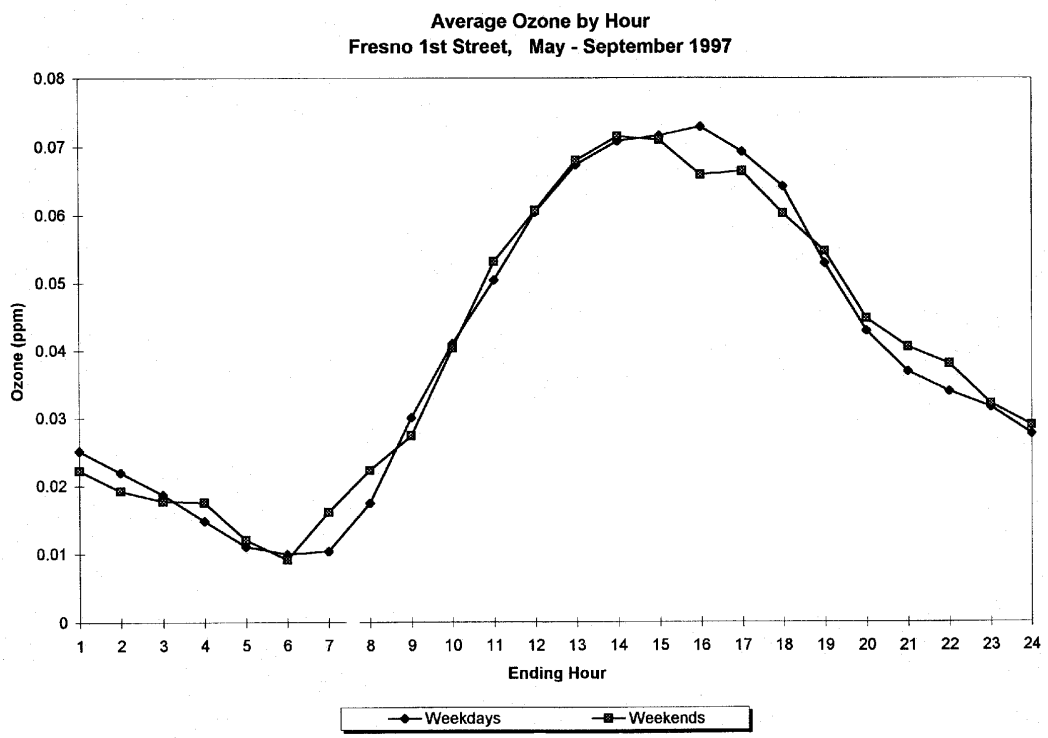


Figure 16. Weekend Effect Analysis for the San Joaquin Valley, Fresno, 1997

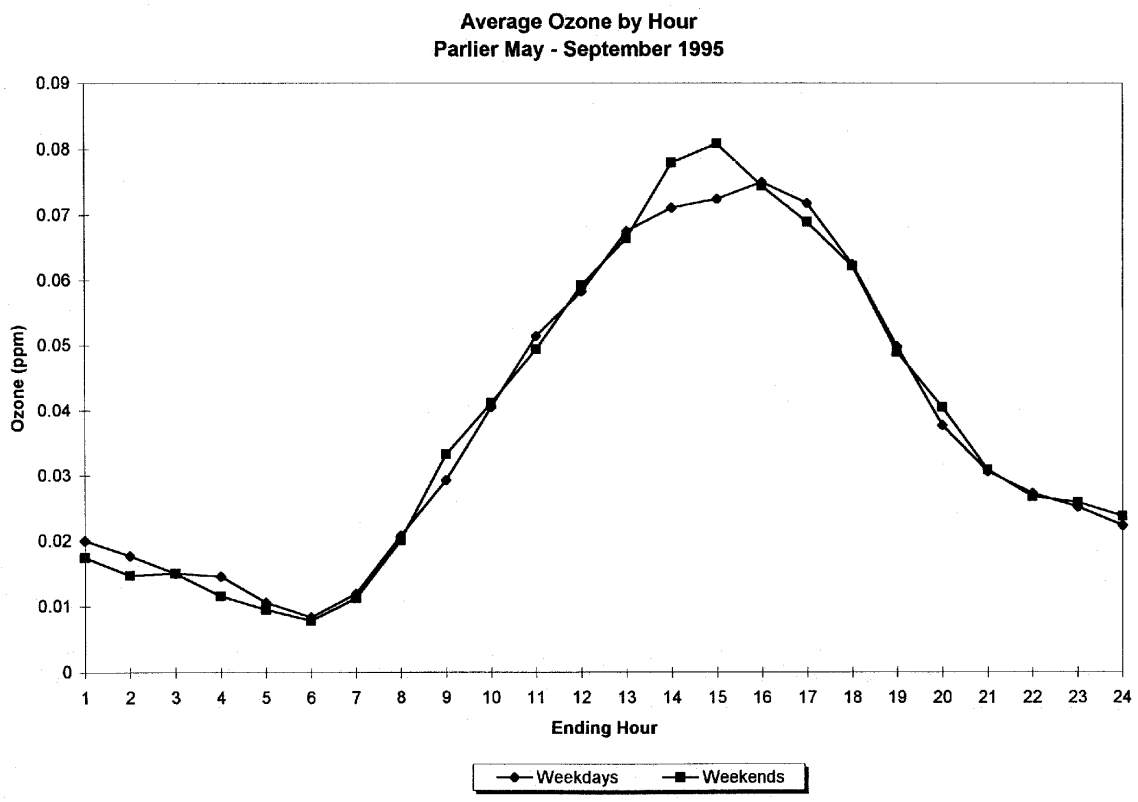


Figure 17. Weekend Effect Analysis for the San Joaquin Valley, Parlier, 1995

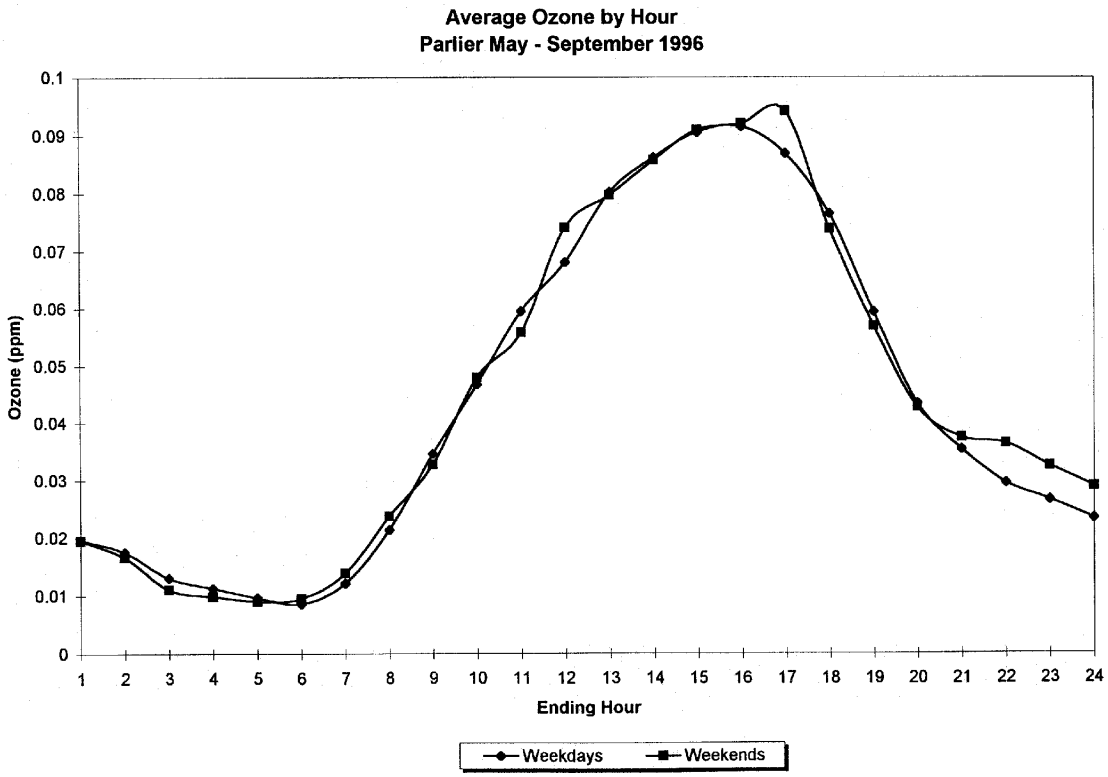


Figure 18. Weekend Effect Analysis for the San Joaquin Valley, Parlier, 1996

3.5 Peer Reviewed Publishing of IMS95 Reports

To enhance the status and credibility of Central California air quality studies, PG&E, as part of the RAAS effort agreed to coordinate the publishing of key papers in a special issue of *Atmospheric Environment*, a premier air pollution publication. Nine articles survived the peer review process and are slated for publication in an upcoming, special publication. Publishing credible, peer-reviewed papers has been one of the long-term goals of the central California air quality studies. Not only does professional journal publishing get the information out into the public domain, but it adds credibility to the work as it is later used in designing ozone and particulate matter (PM) control strategies. In addition, as air pollution experts review the results, new ideas are surfaced that result in advancement of the science and engineering of ozone control.

4.0 Summary

Pacific Gas & Electric (PG&E), working closely with subcontractor Atmospheric and Environmental Research (AER), was able to identify a number of important issues related to field data needs, modeling needs, and research needs associated with:

- The planning of the California Regional PM_{10} / $PM_{2.5}$ Air Quality Study (CRPAQS)
- The planning of the Central California Ozone Study (CCOS)
- The review of the 1995 Integrated Monitoring Study (IMS95).

Conceptual models were used to study the formation of both ozone and particulate matter (PM) observed in prior major air quality studies to build understanding about the formation of ozone and PM. From this, various air quality models were evaluated, predictions were made about PM nitrate formation, and recommendations were made about data needs and specifications for upcoming field studies. AER was able, through their efforts, to provide an excellent balance of chemistry and meteorology.

A number of issues and concerns related to atmospheric ozone chemistry were linked to PM chemistry. Specifically, emissions of nitrogen oxide (NO_x) appeared to play an important role in both the formation of ozone and PM nitrates. It was observed, however, that changes in NO_x and VOC emissions to effect a reduction in summertime ozone may be counterproductive to wintertime PM nitrates. Opportunities for inter-pollutant tradeoffs need to be carefully evaluated as project proponents negotiate to trade NO_x emissions for PM emissions, NO_x emissions for VOC emissions, vice versa, or with other combinations.

In addition, AER delineated the importance of emissions aloft and their long range transport compared to ground level emission. These two issues are critical to existing and planned fossil fueled electric power plants in Central and Northern California. Ambient concentrations of ozone and PM both exceeding various ambient air quality standards in the valley cause air regulatory agencies to focus on optimum control strategies to achieve attainment for both pollutants.

The importance of understanding unique atmospheric chemical reactions occurring within power plant plumes aloft was identified and special treatment of these plumes through enhanced plume-in-grid modules in atmospheric modeling was recommended. In addition, the discussion about aloft transport of emissions and the need for adequate boundary environmental data in upcoming field studies was well received in the field. Tracer releases from Pittsburg, California, provide evidence that emissions from tall upwind point sources may affect air quality as far downwind as the southern San Joaquin Valley. Fourteen percent of the tracer mass was detected at the surface in the southern part of the San Joaquin Valley the morning after the tracer release. Due to the possibility of long-range aloft transport, it is recommended that the source model uses a mesoscale domain that includes upwind metropolitan areas such as the San Francisco Bay Area, Monterey, and San Luis Obispo. After the field monitoring studies for CRPAQS and CCOS are executed, the resulting air quality models for ozone and PM should be able to more accurately address emissions from power plants as a result of many of the recommendations provided.

Beyond direct involvement in CRPAQS and CCOS, PG&E also coordinated the publishing of the results of IMS95, both internally and through the peer-reviewed literature; worked to raise the importance of CCOS within the Bay Area Air Quality Management District (BAAQMD); and evaluated the existence of the Weekend Effect within the San Joaquin Valley.

In summary, PG&E has been a supporter of knowledge-based research to further the understanding of important air quality issues in Central and Northern California since 1988. California Energy Commission funding to continue PG&E's involvement in RAAS has allowed PG&E to continue to support these studies, representing not only PG&E's goal to support improved quality of life issues (improved air quality) within its service territory to support its customers, shareholders, and employees residing in the area, but also representing the fossil fueled power generation industry in Central and Northern California. PG&E supports the California Energy Commission in their recent decision to provide funding in support of CCOS. Support of CCOS will help ensure that optimum ozone and PM control strategies are adopted in the future that will not disproportionately affect the interests of power producers. In addition, air quality models created in CCOS will be invaluable in the review of existing and proposed fossil fuel power plants.

5.0 References

Altshuler, S. L., T.D. Arcado and D. R. Lawson, Weekday vs. Weekend Ambient Ozone Concentrations: Discussion and Hypotheses with focus on Northern California, *Journal of the Air and Waste Management Association*, December 1995, pp. 967-972.

Altshuler, S., 1998. Presentation at the workshop on draft emission inventory and draft attainment assessment, Bay Area Air Quality Management District, San Francisco, California, October 8, 1998.

Ansari, A.S. and S.N. Pandis, 1998. Response of Inorganic PM to Precursor Concentrations, *Environ. Sci Technol.*, 32, 2706-2714.

Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and Alkenes, *J. Physical. Chem. Ref. Data*, 26, 215-290.

Blanchard, C.L., H. M. Michaels, S. J. Tanenbaum, and J. Fine, 1998. Spatial Representativeness of Monitoring Sites and Zone of Influence of Emission Sources. Draft Final Report for Tasks 4.2.1 and 4.5.3. Contract Number 97-1PM. California Air Resources Board, Sacramento, California.

Blumenthal, D. L.., 1993. Field program plan for the San Joaquin valley Air Quality Study (SJVAQS) and the Atmospheric utility Signatures. Predictions, and Experiments (AUSPEX) Program, Version #3, Post-Field Revisions, STI-98020-1241-FR, The Valley Air Pollution Study Agency, Sacramento, CA.

Blumenthal, D. L., F. W. Lurmann, P. T. Roberts, H. H. Main, C. P. MacDonald, W. R. Knuth and E. M. Niccum, 1997. Three-dimensional distribution and transport analyses for SJVAQS/AUSPPEX, Final Report STI-91060-1705-FR, San Joaquin Valley-wide Air Pollution Study Agency, c/o California Air Resources Board, Sacramento, CA.

CARB, 1999. Http://www.ARB.CA.gov/ccaqs/crpaqs/plans/981220/PART1.pdf.

California Energy Commission, letter from Gregory M. Newhouse, August 6, 1999 regarding current and future power plant siting in California.

Chang, J.S., S. Jin, Y. Li, M. Beauharnois, C.-H. Lu, H. C. Huang, S. Tanrikulu, and J. DaMassa, 1997. The SARMAP Air Quality Model. Final Report, California Air Resources Board, Sacramento, California.

Chow, J.C., J.G. Watson, D. H. Lowenthal, R.T. Egami, P.A. Solomon, R.H. Thuillier, K. Magliano and A. Ranzieri, 1998. Spatial and temporal variations of particulate precursor gases and photochemical reaction products during SJVAQS/AUSPEX Ozone Episodes, *Atmospheric Environment*, 32, 2835-2844.

Coe, D.L. and L. R. Chinkin, 1998. Emission Source Activity Detection: Analysis of CMB Model Results and Daily Activity Data for IMS 95. Draft Final Report STI-997212-1775-DFR. California Air Resources Board, Sacramento, California.

Collins, J.F., 1998. Characterization of Boundaries and Backgrounds in the San Joaquin Valley Integrated Monitoring Study 1995. Draft Final Report. California Air Resources Board, Sacramento, California.

Dickerson, R.R., S. Kondragunta, G. Stenchikov, K. L. Civerolo, B. G. Doddridge, B. N. Holben, 1997. The Impact of Aerosols on Solar Ultraviolet Radiation and Photochemical Smog, Science 278, 827-830.

Dreher, D.B. and R. A. Harley, 1998. A Fuel-Based Inventory for Heavy-Duty Diesel Truck Emissions. J. Air & Waste Manage. Assoc. 48, 352-358.

Dudhia, J., 1989. Numerical Study of Convection Observed during the Winter Monsoon Experiment Using a Mesoscale Two-dimensional Model. J. Atmospheric. Sci. 46, 3077-3107.

Dudhia, J., 1993. A Nonhydrostatic Version of the Penn State-NCAR Mesoscale Model: Validation Tests and Simulation of an Atlantic Cyclone and Cold Front. *Mon. Wea. Rev.* 121, 1493-1513.

Dye, T.S., J. J. Kwiatkowski, C. P. MacDonald, S. E. Ray, L. R. Chinkin, and C. G. Lindsey, 1997. Measurement Methods Validation: Adequacy and Validation of Meteorological Measurements Aloft During IMS95. Draft Final Report. STI-997218-1766-DFR. California Air Resources Board, Sacramento, California.

EPRI, 1999. SCICHEM: A new Generation Plume-in-grid Model, TR113097, EPRI, Palo Alto, California.

EPRI, The Central California Ozone Study, Volume 1, prepared in response to RFP from CEC 500-97-503 Energy-Related Environmental Research.

Grell, G.A., J. Dudhia and D.R. Stauffer, 1993. A Description of the Fifth-Generation Penn State / NCAR Mesoscale Model (MM5). NCAR Technical Note No. 398+1A. 107 pp., National Center for Atmospheric Research, Boulder, Colorado.

Jacobson, M.Z., 1998. Studying the Effects of Aerosols on Vertical Photolysis Rate Coefficient and Temperature Profiles over an Urban Airshed, J. Geophysics. Res. 103: 10593-10604.

Karamchandani, P., A. Koo, and C. Seigneur, "Reduced Gas-Phase Kinetic Mechanism for Atmospheric Plume Chemistry", Environmental. Science & Technology, 1998, 32, pp.1709-1720.

Kumar, K., F. W. Lurmann, and S. Pandis, 1998. Analysis of Atmospheric Chemistry During 1995 Integrated Monitoring Study. Draft Final Report STI-997214-1791-DFR. California Air Resources Board, Sacramento, California.

Kumar, N., F. W. Lurmann, and T. Chico, "Modeling the Effects of Emission changes on $PM_{2.5}$ Using the UAM-AERO Model in the South Coast Air Basin", Proceedings of the $PM_{2.5}$ Conference, January 28-30, 1998, Long Beach California, pp. 737-747.

Lu, C.H. and J. S. Chang, 1998. On the Indicator-Based Approach to Assess Ozone Sensitivities and Emissions Features. *J. Geophys. Res.* $_{10}$3: 3453-3462

Lurmann, F. W.; A. S. Wexler, P. N. Spyros, S. Musarra, H. Kumar, S. Hering, and J. H. Seinfeld, "Development of an Acid Deposition Model for the South Coast Air Basin", Final Report prepared for the California Air Resources Board, January 28, 1997.

Magliano, K.L., 1996. Descriptive analysis and reconciliation of emissions and ambient hydrocarbon data, SJVAQS / AUSPEX technical topic team #5 report, California Air Resources Board, Sacramento, California.

Martien, P. and T. Umeda, 1993. Photochemical model sensitivity tests on the effects of utility boiler NO_x controls on ambient ozone concentrations. Technical Memorandum, BAAQMD, TM 93001, San Francisco, California.

McDade, C.E., 1997. IMS95 Data Analysis Work Elements: 7.3 Contribution of Chemical Constituents to Visibility Reduction, 7.4 Contribution of Chemical Constituents to Light Extinction Budget, 7.5 Contribution of Emission Sources to Light Extinction Budget. Draft Final Report. Contract Number 97-7PM. California Air Resources Board, Sacramento, California.

Meng Z., D. Dabdub, J. H. Seinfeld, 1998. Chemical Coupling Between Atmospheric Ozone and Particulate Matter. Science 277, 116-119.

Meng, Z. and J. H. Seinfeld, 1994. On the Source of the Submicron Droplet Mode of Urban and Regional Aerosols, Aerosol *Sci. Tech.*, 20, 253-265.

Pun, B. and C. Seigneur, 1998a. Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley. Draft Report CP045-1-98. Pacific Gas and Electric Company, San Ramon, California.

Pun, B. and C. Seigneur, C., 1998b. Integrated Monitoring Study 95: Assessment of Mathematical Models and Associated Data Needs. Draft Report CP045-2-98. Pacific Gas and Electric Company, San Ramon, California.

Pun, B.K., J.F. Louis, and C. Seigneur, 1998. A Conceptual Model for Ozone Formation in the San Joaquin Valley. Draft Report CP049-1-98. Pacific Gas & Electric Company, San Ramon, California.

Pun, B. K. and C. Seigneur, "Sensitivity of PM Nitrate Formation to Precursor Emission in the California San Joaquin Valley", prepared for Pacific Gas and Electric Company, April 9, 1999.

Ranzieri, A. and R. Thuillier, 1994. SJVAQS and AUSPEX: A collaborative air quality field measurement and modeling program, Planning and Managing Regional Air Quality Modeling and Measurement Studies: A Perspective Through the San Joaquin Valley Air Quality Study and AUSPEX, ed. by P.A. Solomon. Published by Lewis Publishers, Chelsea, Michigan in conjunction with Pacific Gas & Electric Company, San Ramon, California, pp. 1-28.

Seaman, N.L. and D.R. Stauffer, 1996. SARMAP Meteorological Model Final Report. San Joaquin Valleywide Air Pollution Study Agency and California Air Resource Board, Sacramento, California. 173 pp.

Seaman, N.L., D.R. Stauffer and A.M. Lario-Gibbs, 1995. A Multiscale Four-Dimensional Data Assimilation System Applied in the San Joaquin Valley during SARMAP. Part 1: Modeling Design and Basic Performance Characteristics, J. Applied. Meteor. 34, 1739-1761.

Seigneur, C., P. Pai, P. Hopke, and D. Grosjean, 1999a. Modeling Atmospheric Particulate Matter. Environment. Sci. Technology., in press.

Seigneur, C., B. Pun, and Y. Zhang, 1998b. Review of Methods for Source Apportionment in Three-Dimensional Air Quality Models for Particulate Matter (Draft). Document Number CP030-98-1. EPRI, Palo Alto, California.

Seigneur, C., B. Pun, P. Pai, J. F. Louis, P. Solomon, C. Emery, R. Morris, M. Zahniser, D. Worsnop, P. Koutrakis, W. White, and I. Tombach, 1998a. Guidance for the Performance Evaluation of Three-Dimensional Air Quality Modeling Systems for Particulate Matter and Visibility (Draft). Document Number CP033-98-1. American Petroleum Institute, Washington, District of Columbia.

Sillman, S., 1995. The Use of NO_y, H_2O_2, and HNO_3 as Indicators for Ozone-NO_x-Hydrocarbon Sensitivity in Urban Locations. *J. Geophys. Res.* $_{10}$0: 14175-14188.

Smith, N., J.M.C. Plane, C.F. Nien and P.A. Solomon, 1995. Nighttime radical chemistry in the San Joaquin Valley, *Atmospheric Environment*, 29, 2887-2897.

Solomon, P.A. and R. H. Thuillier, *SJVAQS/AUSPEX/SARMAP Air Quality Field Measurement Project*, Report 009.2-94.1 prepared for Research and Development, San Ramon, California: Pacific Gas & Electric Company.

Solomon, P.A. and S. L. Altshuler, *Project Overview: 1995 Integrated Monitoring Study Design, Operation, Measurements, and Post-Field Activities*, Pacific Gas & Electric, Technical and Ecological Services Report No.: 026.22-98.2

Watson, J.G., D. Dubois, P. M. Roth, C. McDade, R. Hackney, E. Niccum, K. Magliano, and A. Ranzieri, 1998. Field Program Plan for the California Regional $PM_{2.5}$ / PM_{10} Air Quality Study. DRI Document #9801.1D3. California Regional PM_{10} / $PM_{2.5}$ Air Quality Technical Committee.

Ziman, S., 1998. Presentation at the workshop on draft emission inventory and draft attainment assessment, Bay Area Air Quality Management District, San Francisco, California, October 8, 1998.

Zhang, Y., C. Seigneur, J. H. Seinfeld, M. Z. Jacobson, F. Binkowski, 1998. A Comprehensive Evaluation of Aerosol Modules Used in 3-Dimensionsal Air Quality Models. 1998 Annual Meeting of the American Association of Aerosol Research, June 22-26, 1998 Cincinnati, Ohio.

APPENDIX I

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APPENDIX I

CONCEPTUAL MODEL OF PARTICULATE MATTER POLLUTION IN THE CALIFORNIA SAN JOAQUIN VALLEY

Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley

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Executive Summary

The main objective of this work is to develop a conceptual model for the formation of particulate matter (PM) in the California San Joaquin Valley in the fall and winter seasons. A systematic approach was used to compile the findings of the 1995 Integrated Monitoring Study (IMS 95). Quantitative information is used as much as possible to build the conceptual model, whose framework is based on the chemical characteristics of PM and the physical processes responsible for the accumulation of PM.

The analysis of the chemical composition was based primarily on the chemical mass balance (CMB) work by Magliano (1997). Several primary sources were identified, including vegetative burning, mobile sources, and geological material (dust). Ammonium nitrate (NH_4NO_3), secondary organic aerosols (SOA), and ammonium sulfate composed the secondary fraction of PM. Each of these components was associated with precursor gases (e.g., ammonia (NH_3), nitric acid (HNO_3), volatile organic compounds (VOC), sulfur dioxide (SO_2)) and atmospheric oxidants (e.g., hydroxy radical (OH), ozone (O_3), and nitrate radical (NO_3)). We sought to identify the chemical pathways (gas-phase or aqueous-phase) leading to the formation of each component, and the limiting reagent in each case, so that further field work can be focused on the most important chemical processes and precursors.

The physical transport processes analyzed were associated with mass fluxes of PM and precursors into and out of the atmospheric system of the San Joaquin Valley, including horizontal transport (surface and aloft), vertical mixing, wet deposition, and dry deposition. Ground-level transport was limited due to low surface wind speeds. The effects of aloft transport were dependent on both the upper air wind speeds and the exchange of air between the surface and aloft. Rain was not associated with the PM episodes in the fall and winter seasons, so the wet deposition process of concern was the removal of PM by the settling of fog droplets. Dry deposition pertained to both particles and precursor gases.

Key aspects of the conceptual model are summarized in Table E-1.

Table E-1. Summary of Conceptual Models

	Winter (PM-2.5)	**Fall (PM-10)**
Chemical Composition and Transformations	Ammonium Nitrate (46%) ▪ Nitric Acid Sensitive ▪ Nitric Acid Formation Possibly Limited by Oxidants (OH, O_3, NO_3) Availability ▪ Oxidants May be VOC-Sensitive Rather Than NO_x-Sensitive Organic Compounds (34%) ▪ Primary (e.g., Vegetative Burning and Mobile Sources) ▪ Secondary (Anthropogenic or Biogenic Precursors)	Geological Material (57%) Ammonium Nitrate (16%)
Transport Processes	Limited Ground-level Transport ▪ Calm Winds Aloft Transport Possible Limited Vertical Mixing Wet Deposition (Fog) Dry Deposition Unknown Urban Influences (Primary Sources) on Regional Distribution (Secondary NH_4NO_3, SOA)	Limited Ground-level Transport Aloft Transport Possible PM Build-up Correlates with Reduced Mixing Height Limited Wet Deposition (Mild Fog) Dry Deposition Unknown Local Influences (Geological Material) on Sub-regional Distribution (Secondary NH_4NO_3)

In the winter, PM-2.5 accounted for 70% to 80% of the PM mass measured in the rural and urban areas of the San Joaquin Valley. The dominant component of PM-2.5 was NH_4NO_3, contributing an average of 46% to the PM-2.5 mass. Of the two precursors of NH_4NO_3, NH_3 and HNO_3, NH_3 was found to be abundant in the study area of IMS 95. Therefore, the conversion of NO_x to HNO_3 was of interest. There are two pathways for HNO_3 formation that involve the oxidants OH (gas phase only) and O_3 / NO_3 (gas and aqueous phases), respectively. The relative importance of these pathways is uncertain, although daytime production of nitrates likely involved OH. Since only a small fraction of NO_x is converted to HNO_3 (Kumar et al., 1998), it was possible that the oxidation system was limited by the availability of oxidants. During wintertime, these oxidants may be sensitive to VOC rather than NO_x. However, these inferences need to be confirmed.

Primary and secondary organic compounds constituted a significant portion of PM in the San Joaquin Valley, contributing on average 34% of the PM-2.5 mass. Primary components, such as mobile sources and vegetative burning, were strong contributors in urban areas such as Fresno and Bakersfield (up to 35%). The contribution of secondary organic aerosols was typically determined by the difference of total and apportioned organic mass. Schauer and Cass (1998) determined that a regional concentration of about 4.5 $\mu g/m^3$ existed for secondary organic compounds in the San Joaquin Valley. This regional background can contribute 10% to 15% of the total PM-2.5 mass observed at the rural sites (e.g., Kern Wildlife Refuge).

Sulfates were a relatively small component of PM (6%) during the winter. Sulfates were produced as sulfuric acid either in the gas phase or in the aqueous phase. In the urban areas, precursor SO_2 was abundant (about 3 ppb). Daytime, gas-phase production could be a significant venue for the production of sulfate, although aqueous-phase production in fog was the focus of IMS 95. Aqueous-phase oxidizing agents include O_3, H_2O_2, and O_2 (reaction catalyzed by Mn^{2+} or Fe^{3+}). Of the three reactions, the O_3 and O_2 reactions are self-limiting. Their rates decrease with decreasing pH, which may result from the production of sulfates. Analyses of IMS 95 data revealed that the O_3 route was the most important of the three pathways (Collett et al., 1998a).

Stagnation was the single most important factor for the accumulation of PM within the San Joaquin Valley. During a stagnation event, the ground-level wind speed was typically less than 2 m/s, and, on some occasions, diffusion dominated over advection as the mode of pollutant dispersion. Ground-level transport was not a likely mechanism for distributing PM and precursors. Wind speeds aloft were typically higher (up to 10 m/s) and long-range transport aloft was a possible mechanism for pollutant dispersion. Vertical mixing was generally limited to less than 100 m at night and from 125 to 1100 m during the day. Midday vertical mixing of aloft air could be responsible for introducing precursors, transported aloft from upwind areas, to the southern part of the San Joaquin Valley.

Fog was prevalent in the valley during the winter season. In addition to serving as aqueous reactors for the production of secondary sulfate and possibly nitrate, fog droplets also facilitate the wet removal of PM ammonium, sulfate, and nitrate when they settle to the ground. Pandis et al. (1998) concluded that the net effect of fog episodes was the removal of nitrate and ammonium. Sulfates were removed at some sites while produced at others (e.g., Bakersfield).

Dry deposition was not studied during the winter study of IMS 95.

The fall study of IMS 95 was held in the Corcoran vicinity. The fall PM issue differed from the winter one in several aspects: (1) PM-10 exceeded the 24-hour average National Ambient Air Quality Standard, (2) geological material was the dominant component (57%) while NH_4NO_3 only accounted for 16% of PM-10, (3) vegetative burning was not a significant source, (4) fog was patchy. Fewer details were available for the fall analysis. It was expected that the production of NH_4NO_3 would be sensitive to HNO_3, based on results from the winter IMS 95 and a previous analysis of summer photochemistry (Lu and Chang, 1998). However, further research is needed to understand the production of oxidants during the fall season and to assess the sensitivity of oxidants and HNO_3 to VOC and NO_x precursors. Excess organic compounds (OC) (unapportioned primary OC and SOA) contributed 10% to the PM-10 mass. A CMB analysis using tracer-based profiles may decipher this category further.

PM build-up in the Corcoran area correlated well with the 850 mb (1500 m or 5000 ft) temperature at Oakland airport, indicating that meteorology was responsible for the build-up of PM-10. A sub-regional build-up theory was supported by the zone-of-influence study, which identified a 5 to 15 km spatial distribution scale. Geological material was likely to be generated locally (a neighborhood scale of influence of 1 km was also identified), and contributed to higher PM measurements at the industrial sites relative to the residential and agricultural sites. However, no meteorological data were available at the monitoring sites to confirm the contribution of local wind-blown dust. The ground-level wind speed was typically less than 2 m/s, indicating the lack of surface transport. Aloft transport could not be evaluated without aloft wind speed, concentration, and mixing height data. Since fog was patchy, wet deposition was expected to be limited. Dry deposition of gases and PM was not investigated during the IMS 95 fall study.

The following key gaps in current knowledge were identified in the formulation of the conceptual model:

- Abundance of NH_3 with respect to HNO_3 in areas other than the IMS 95 monitoring domain in the San Joaquin Valley and during spring, summer, and fall
- Production route of HNO_3 and key oxidants (OH or O_3 / NO_3)
- Sensitivity of the oxidants to VOC and NO_x
- Precursors (anthropogenic and biogenic) of SOA
- Production route(s) of sulfate
- Buffering capacity of fogs and oxidant concentrations in fog
- Composition profiles of key San Joaquin Valley PM sources (geological material, vegetative burning, mobile sources)
- Aloft transport as a dispersion mechanism for PM and precursors
- Dry deposition of PM and precursors

1. Introduction

1.1 National Ambient Air Quality Standards (NAAQS) for Particulate Matter (PM)

The U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM) in 1997. The standards pertain to particles with aerodynamic diameter of less than 10 μm and those with aerodynamic diameter of less than 2.5 μm:

- Annual average PM-10: Three-year arithmetic average of the annual arithmetic average PM-10 concentrations not to exceed 50 $\mu g/m^3$ at any monitoring site.
- 24-hour average PM-10: Twenty-four hour average PM-10 concentrations not to exceed 150 $\mu g/m^3$ for a three-year arithmetic average of annual 99th percentiles at any monitoring site.
- Annual average PM-2.5: Three-year arithmetic average of the annual arithmetic average PM-2.5 concentrations not to exceed 15 $\mu g/m^3$ for a single community-oriented monitoring site or the spatial average of eligible community-oriented sites.
- 24-hour average PM-2.5: Twenty-four hour average PM-2.5 concentrations not to exceed 65 $\mu g/m^3$ for a three-year arithmetic average of annual 98th percentiles at any population-oriented monitoring site.

Limited PM-2.5 measurements from central California indicate that the annual 15 $\mu g/m^3$ standard will probably be exceeded in several populated areas, especially in the San Joaquin Valley (Watson et al., 1998). These annual average concentrations are dominated by elevated concentrations that occur primarily during fall and winter. In addition, the 24-hour standard value for PM-2.5 (65 $\mu g/m^3$) was exceeded several times during the Integrated Monitoring Study of 1995 (IMS 95) and the 24-hour standard value for PM-10 (150 $\mu g/m^3$) was exceeded twice during IMS 95.

1.2 1995 Integrated Monitoring Study

IMS 95 was the planning study of the comprehensive data collection and modeling effort titled California Regional PM-2.5 and PM-10 Air Quality Study (CRPAQS). Under IMS 95, two studies were undertaken during the fall and winter of 1995 to understand the formation of PM in the San Joaquin Valley. The study domain of IMS 95 is shown in Figure 1-1.

Fall Study: The fall study was performed in the ~~city~~ vicinity of Corcoran, CA, with one core site (community-representative / community-oriented site) and 22 satellite sites. The satellite sites were set up to collect ambient samples in agricultural, industrial, and commercial/residential neighborhood areas. Twenty-four hour average PM-10 samples were acquired daily from 11/1/95 to 11/14/95 at all locations. Daily 24-hour average measurements of ammonia (NH_3), light absorption, and PM-10 mass were also reported. Detailed component analyses (including PM elements, Cl^-, NO_3^-, SO_4^{2-}, volatilized NO_3^-, K^+, NH_4^+, OC, EC, and artifact OC) were performed on 9 daily samples from selected sites.

Winter Study: The winter study featured high-resolution three-hour average measurements for PM-10, PM-2.5, nitric acid (HNO_3), and NH_3 at four locations: Bakersfield, Chowchilla (northern boundary site), Fresno, and Kern Wildlife Refuge (non-urban site). Daily 24-hour average NH_3, PM-2.5, and PM-10 measurements were taken at selected sites. In addition to PM-2.5 and PM-10, size resolved-samples were collected at Bakersfield using a Multi-Orifice Uniform Deposit Impactor (MOUDI). Limited continuous (hourly) PM-2.5 and PM-10 mass measurements were obtained using tapered element oscillating microbalances (TEOM) and beta-attenuation monitors (BAM), respectively. Hourly measurements of light scattering were also conducted using nephelometers. Component analyses were performed for samples on episode days. Supporting gas-phase measurements included hourly NO / NO_x (NO_2 by difference) and SO_2 (all days), and three-hour or 24-hour average samples of hydrocarbon and carbonyl compounds at the urban sites (episode days).

A second component of the winter study was conducted at Walnut Grove, California in the northern San Joaquin Valley to characterize the vertical variations in fog/cloud chemistry and

Figure 1-1. Study Domain of the 1995 Integrated Monitoring Study

physics. Three-hour average measurements of fog composition were obtained at three different heights (ground level, 140 m, and 230 m above ground level). Limited droplet size-resolved data (e.g., pH) were also taken.

1.3 Objectives of this Study

The objective of this analysis is to formulate a conceptual model for fall and winter PM concentrations in the San Joaquin Valley using primarily the information obtained during IMS 95. This conceptual model is a qualitative description of the physical and chemical processes that govern the formation of PM, which, to the extent possible, is supported by quantitative information. IMS 95 is the planning study for the comprehensive field program CRPAQS. Therefore, the conceptual model is an important link between the planning study and the comprehensive field program because it identifies the major characteristics of the meteorology and atmospheric composition of the area that are relevant to PM. The conceptual model is a valuable tool (1) to guide data collection priorities of CRPAQS and (2) to aid future model development and evaluation activities. The planning study approach being implemented in the San Joaquin Valley has been recommended for the general design of field program experiments used for PM model performance evaluation in other areas (Seigneur et al., 1998a).

1.4 Outline of the Report

We first describe the methodology used in the analysis. The applications of the methodology to typical winter and fall PM episodes are described in Sections 3 and 4, respectively. When appropriate, we provide some preliminary remarks regarding additional measurements that would be useful to complete our understanding of PM pollution in the San Joaquin Valley. However, a more elaborate discussion of data needs will be developed in a subsequent report. Finally, we conclude by addressing the questions we set out to answer in our work statement.

2. Methodology

Our methodology is based on a data-driven approach that uses the composition and physical characteristics of PM as the starting point. Working backwards in time, we use a structured approach to understand the chemical transformations and physical transport processes leading to the observed PM. PM precursors and oxidants may be transported over great distances to produce PM at a given location. Therefore, the transport processes of both PM and PM precursors are considered in formulating the conceptual model. By understanding what compounds contribute to PM formation and how PM episodes come about, we may begin to shape a general understanding about the specific chemical compounds and emissions sources that are the most influential for PM pollution in the San Joaquin Valley.

Figure 2-1 shows the framework for analyzing PM by chemical composition. The categories used in this work were identified by chemical mass balance (CMB) (Magliano, 1997). Several of these categories are primary emissions, including geological material (dust), primary mobile sources, and vegetative burning. Excess organic compounds (OC) consist of organic compounds that are not apportioned to specific sources. They may be primary emissions from sources that are not used in the CMB analysis, such as meat cooking, or secondary organic compounds formed in the atmosphere. Other categories are secondary compounds. The formation of nitrates, sulfates, and secondary organic compounds are analyzed further to identify important chemical reactions responsible for their production and the limiting reagents of the reactions.

Ammonium nitrate in the ambient atmosphere is produced by the combination of ammonia and nitric acid. Ammonia is emitted in the San Joaquin Valley primarily by livestock whereas nitric acid is formed in the atmosphere. The formation of nitric acid involves both NO_2 and oxidants, which are in turn formed from precursors, volatile organic compounds (VOC) and NO_x. Information regarding the limiting reagent in each of the transformation steps of this chemical system may be used to develop control decisions for particulate nitrate.

Sulfate is produced by the oxidation of SO_2. The gas-phase oxidation process by OH radicals has a lifetime of about one week (Seinfeld and Pandis, 1998). Aqueous pathways are especially

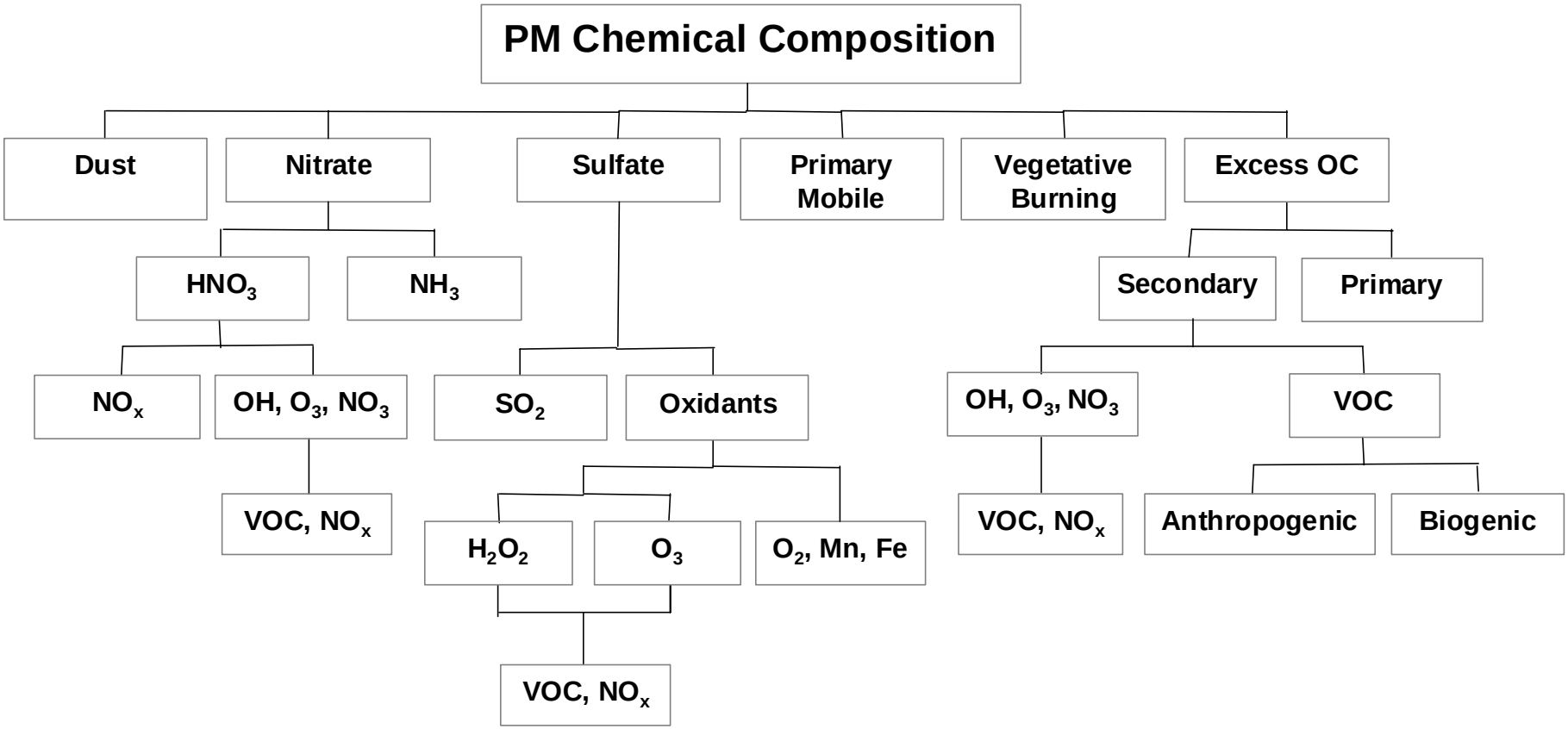

Figure 2-1. Breakdown of PM by Chemical Composition from CMB Analysis (Data Source: Magliano, 1997). Precursors to PM components are also listed.

important during fog episodes in the San Joaquin Valley (Pandis et al., 1998). In the aqueous phase, O_3, H_2O_2, and O_2 (catalyzed by Fe^{3+} or Mn^{2+}) are the main oxidizing agents for dissolved SO_2. The abundance of O_3 and H_2O_2 is determined by the photochemical reactivity of the system. Therefore, it is important to understand the relative abundance of SO_2 and the oxidants, and the dominant reaction(s) responsible for the formation of sulfates to inform the choices of control strategies for this PM component.

Secondary organic aerosols (SOA) are formed via atmospheric reactions of biogenic and anthropogenic VOC with oxidants, such as OH, O_3, and NO_3. Anthropogenic SOA precursors include aromatic compounds, and high molecular weight alkanes and alkenes. Monoterpenes and oxygenated compounds are examples of biogenic emissions that form PM. Therefore, a solid understanding of all VOC emissions within the San Joaquin Valley is essential. In addition, understanding the formation of oxidants (i.e., whether the system is in a VOC- or NO_x-sensitive regime) is also important for a proper assessment of SOA chemistry.

The transport processes that are important on the regional scale include horizontal advection, vertical mixing, wet deposition, and dry deposition (as shown in Figure 2-2). Because there is a secondary component in PM, transport processes for PM precursors (such as HNO_3, NH_3, NO_x, VOC, oxidants) also need to be considered. Horizontal advection is a function of wind flow, both at the surface and aloft, which carries gaseous and particulate pollutants from one location to another. The effect of upper-air transport depends upon vertical mixing. As the mixed layer grows during the day, aloft air is entrained into the surface layer system. If the upper air wind speed is high, an air parcel from an upwind location will be mixed in. Wet deposition removes pollutants and particles by scavenging during a rain or fog episode. Dry deposition pertains to the transfer of gaseous and particulate compounds to the surface where they are removed.

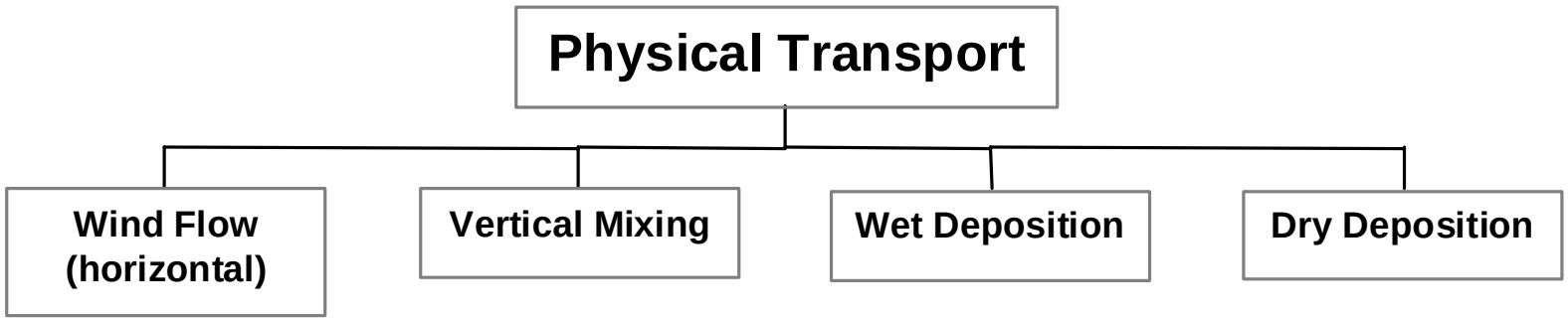

Figure 2-2. Transport Processes Important for the Formation, Accumulation, and Removal of PM.

3. Analysis of Winter PM-2.5 Episodes

3.1 PM-2.5 Problem in the Winter Episodes

The PM-10 24-hour average standard of 150 μg/m^3 was not exceeded during the IMS 95 winter study in December, 1995 and January, 1996. Elevated PM concentrations in the winter were a direct result of increased PM-2.5 concentrations, which constituted on average 70-80% of PM-10 concentrations. PM-2.5 exceeded the new 24-hour average standard of 65 μg/m^3 at the urban sites of Fresno (five times) and Bakersfield (once). Hence, we focus on the PM-2.5 problem within the San Joaquin Valley in the analysis of the winter episodes.

Figure 3-1 shows the PM-2.5 mass concentrations observed at the core sites during the winter study of IMS 95. The trends of PM were very different during the episodes observed on December 9-10, December 25-28, and January 4-6. The characteristics of PM and the associated meteorology are summarized in Table 3-1. Some of the differences may be explained by a combination of meteorological and emissions factors. For the early December episode, PM-2.5 peaked at Fresno and Bakersfield on December 10. On the same day, a reduction in PM-2.5 was observed at the northern boundary site of Chowchilla. However, PM continued to accumulate at Kern Wildlife Refuge until December 11. Warm temperatures aloft, particularly at Vendenberg (15 °C) indicated a strong stagnation event. Fog was also prevalent during this episode, with the daily averaged relative humidity (RH) close to 90% in both cities. A large drop in the 850 mB (1500 m or 5000 ft) temperature was observed at the Oakland airport between December 9 and December 10. A drop in the 850 mB temperature was recorded from December 10 to December 12 at Vendenberg (Lehrman et al., 1998). These records suggested a meteorological event moving through the San Joaquin Valley from NW to SE during the PM episode, which may partly explain the observed temporal variations of PM observed at different sites. During the Christmas episode, Fresno experienced peak 24-hour average PM-2.5 concentration of over 100 μg/m^3 on December 26. The other sites exhibited trends that were similar to one another, with maximum concentrations on December 27. PM concentrations at Bakersfield were about 15 μg/m^3 higher than the rural sites on December 27 and 28. Of the three episodes studied in the

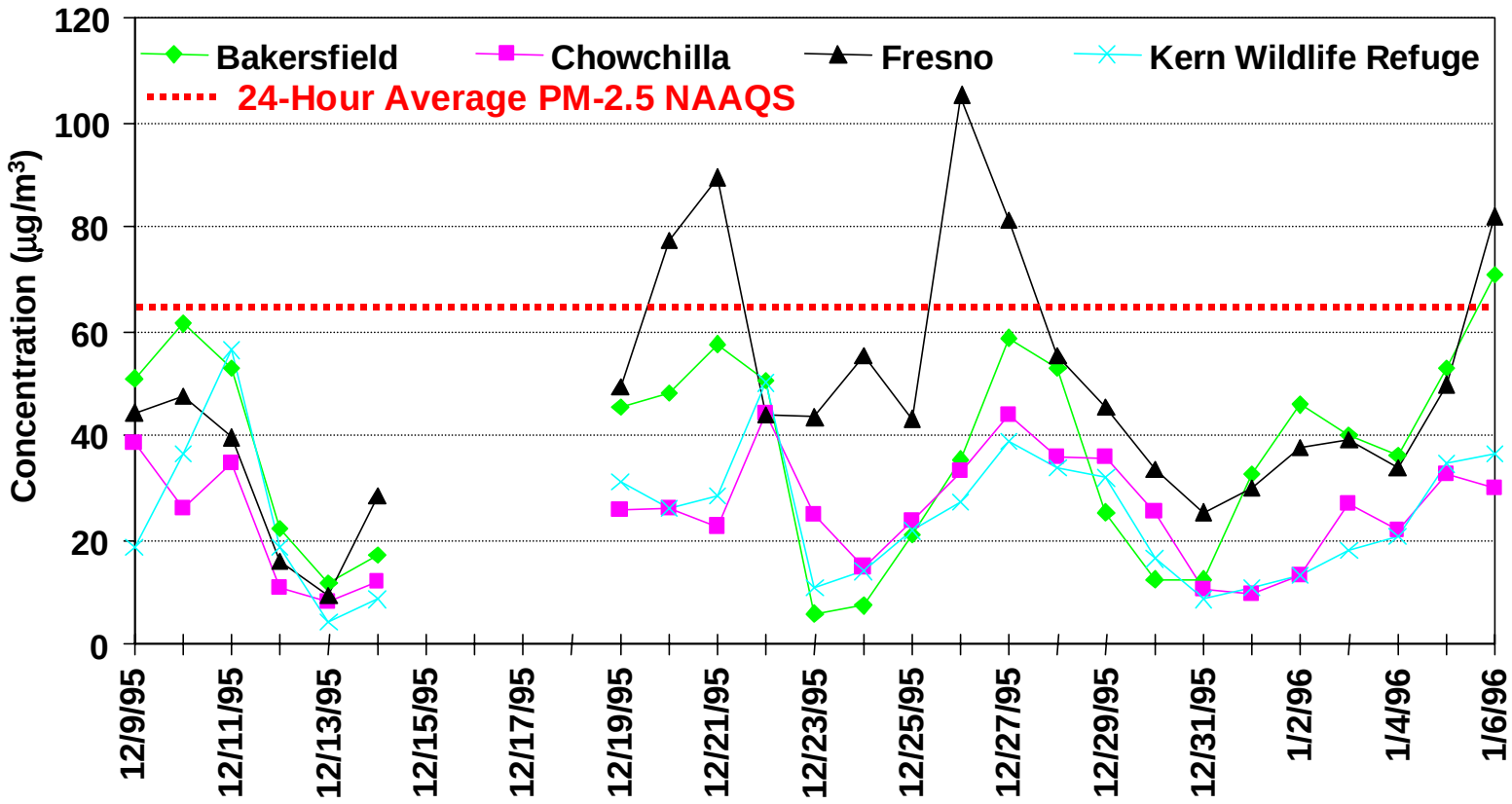

Figure 3-1. Temporal Variations of PM-2.5 Mass Concentrations during the IMS 95 Winter Study (Source: CARB, 1998)

Table 3-1. Characteristics of the Winter PM Episodes in the San Joaquin Valley
(Data Source: Chow and Egami, 1997; Lehrman et al., 1998)

Episode	December 9 – 10, 95	December 25 – 28, 95	January 4 – 6, 96
PM2.5 Observations	None of the core sites exceeded 24-hr PM-2.5 or PM-10 standard	PM-2.5 exceeded 65 $\mu g/m^3$ on two days at Fresno, but not at the other core sites	PM-2.5 exceeded 65 $\mu g/m^3$ on 1/6/96 at Bakersfield and Fresno, but not at the other core sites
Peak Time / Site	Peak concentrations observed at different sites on different days (Chowchilla 12/9, Fresno/Bakersfield 12/10, Kern Wildlife Refuge 12/11 Bakersfield on 12/10/95 (60 $\mu g/m^3$ PM-2.5, 75 $\mu g/m^3$ PM-10) Peak 3-hr concentration: 9 p.m. to midnight	PM peaked on December 26 (Fresno) or 27 (other sites), then decrease until December 31 Fresno on 12/26/95 (105 $\mu g/m^3$ PM-2.5, 125 $\mu g/m^3$ PM-10) Peak 3-hr concentrations: midnight to 6 am. (Lower peaks next two nights.)	PM concentrations on the rise at the 2 urban sites when monitoring period ended on 1/6/96; but rural sites same 24-hour PM on 1/5-1/6 Fresno on 1/6/96 (80 $\mu g/m^3$ PM-2.5, 100 $\mu g/m^3$ PM-10) Peak 3-hr concentration: 9 pm to midnight
Wind Speed	43 – 60% data* < 1 ms^{-1}	36 – 49% data < 1 ms^{-1}. SE winds at low levels	39 – 52% data < 1 ms^{-1} NW winds during the day at ground level. SE winds aloft at Bakersfield
Temperature (ground / upper air)	Ground level: 10 – 15°C; Warm aloft temperatures: 14 – 15 °C	Ground level: 0 – 15 °C Aloft temperature: 7 - 9 °C	Ground level: 7 - 15°C;Aloft Temperature: 10 – 15 °C
Mixing Height at 4 pm	125 – 175 m	250 – 900 m	450 – 1100 m
Fog	10 – 20 fog hours per day at Fresno and Bakersfield	5 – 10 fog hours per day at Fresno and Bakersfield	10 – 15 fog hours per day at Fresno and Bakersfield

* based on hourly-average vector wind at 42 sites in the San Joaquin Valley

winter, the Christmas episode was associated with the lowest temperatures aloft (about 8 °C) and lowest RH (80%). Pressure gradients from San Francisco to Las Vegas and Reno were negative. High pressure over the San Joaquin Valley resulted in low wind transport. The observed patterns of build-up were likely a result of reduced transport and increased anthropogenic emissions during the holiday season. Clear differences in PM-2.5 concentrations were observed between the urban sites and the rural sites during the January episode. Both Fresno (80 $\mu g/m^3$ PM-2.5) and Bakersfield (70 $\mu g/m^3$) exceeded the 24 hour-average PM-2.5 NAAQS of 65 $\mu g/m^3$ on January 6. An Alberta low pressure system preceded this episode (Lehrman et al., 1998). The pressure front may have transported pollutants from the Pacific coastal cities into the San Joaquin Valley. During the episode from January 4 to January 6, the temperature aloft increased while the pressure gradient weakened. Moderate fog was observed (average RH was 85%). PM concentrations at Chowchilla and Kern Wildlife Refuge were 50% lower than the urban sites. PM-2.5 accumulated slowly, if at all, at the rural sites during the last two days of the episode. These observations show that the spatial and temporal patterns of PM-2.5 vary among the episodes.

Diurnal profiles of PM were measured by collecting three-hour average samples in the winter IMS 95 study. Figure 3-2 shows the observed temporal behavior of PM-10 during the Christmas episode. Sharp peaks were observed in the evening at Fresno; weaker evening peaks were observed at Bakersfield on two of the episode days. The rural sites exhibited lower diurnal variability relative to day-to-day fluctuations, with higher PM concentrations during the day. These observations are generally consistent with the conclusions drawn using the visibility data obtained by nephelometers. Since measurements of light scattering could be made at time resolutions of less than one hour, they were used to assess the adequacy of the three-hour average PM samples for capturing changes in PM. Main et al. (1998) analyzed one-hour average nephelometer measurements (transformed to correct for RH effects) and concluded that three-hour samples adequately characterized the diurnal variations in light scattering and PM. Transformed data showed higher PM in the urban areas than in the rural areas. For Fresno and Bakersfield, higher transformed scattering values were observed at night than during the day. Main et al. (1998) also identified 4-7 p.m. as the time frame for increased scattering at Bakersfield, and 9 a.m. to 12 noon as the period of decrease scattering at Fresno. However,

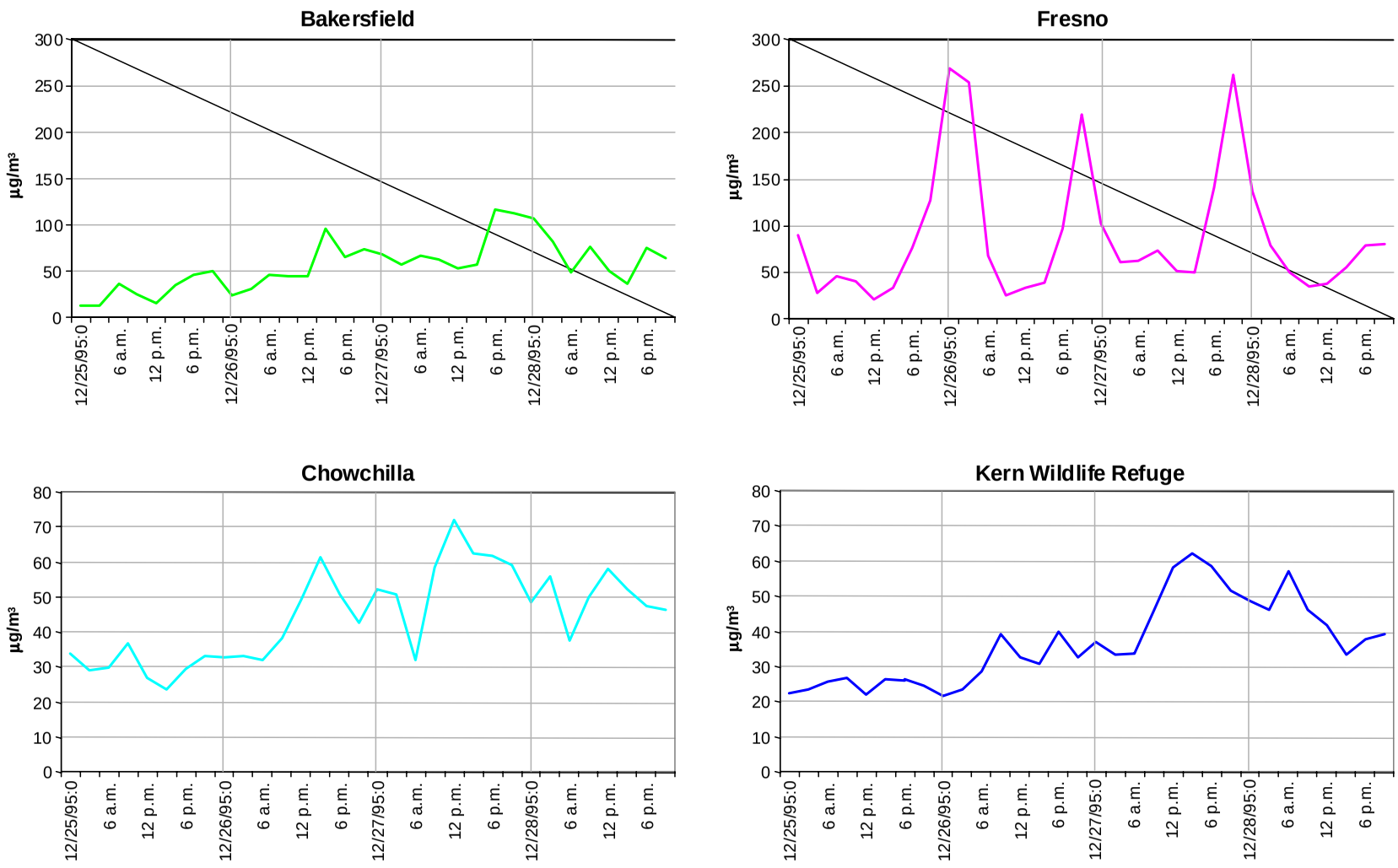

Figure 3-2. Three-hour Average PM-10 Measurements (Source: CARB, 1998)

during the Christmas episode, PM reductions took place earlier in the morning. The transformed readings at the rural sites were less reliable indicators of diurnal PM because fog was prevalent and the RH was too high for the application of the correction term. Main et al. (1998) observed little variation in the light scattering efficiency during the day at Kern Wildlife Refuge, which is consistent with lower PM observed at that site.

Richards et al. (1998) analyzed collocated nephelometer and PM-2.5 measurements and concluded that a heated nephelometer could provide readings that correlate very well with PM-2.5, even under high RH and foggy conditions. The scattering efficiency for PM-2.5 was ~3.7 m^2/g, with higher efficiency from ammonium nitrate and sulfate (~4.2 m^2/g) and lower efficiency from other compounds (~2.9 m^2/g). The good correlation may be a direct result of the dominant fraction of ammonium nitrate, which also contributed significantly to scattering. McDade (1997) verified the extinction of the San Joaquin Valley particles using the observed data on the size distribution and composition of particles. Ammonium nitrate was found to be the largest contributor to light extinction.

3.2 Chemical Composition and Transformations

Table 3-2 shows the contributions of major sources to the concentration of PM-2.5 during the winter episodes. The PM-2.5 composition is displayed in a pie chart in Figure 3-3. Significant variability of the source contributions was observed at the core sites. Table 3-3 shows typical contributions of key components at urban and rural sites. PM at urban sites typically showed higher contributions from primary sources, while higher contributions from secondary compounds were observed at the rural sites. The chemical composition breakdown of the San Joaquin Valley winter PM-2.5 is shown in Figure 3-4, using the CMB categories reported by Magliano (1997).

~~Ammonium Nitrate~~

~~Ammonium nitrate was the most dominant compound found in PM-2.5 during IMS-95 winter episodes. At the non-urban sites, ammonium nitrate can contribute 50% or more to the total mass of PM-2.5. As indicated in Figure 3-2, ammonium nitrate is formed by the combination of ammonia and nitric acid. Ammonia is emitted mainly from farming operations, while nitric acid~~

~~is typically formed in the atmosphere. Kumar et al. (1998) showed that the formation of ammonium nitrate within the San Joaquin Valley was limited by the availability of nitric acid in the winter, as ammonia sources were abundant. The formation of nitric acid, either in the gas phase (as a product of NO_2 + OH), or by the hydrolysis of N_2O_5 (product of NO_2 + NO_3) in water droplets, may either be NO_x-sensitive or oxidant-sensitive. Although information regarding the dominant reaction was not available, indirect evidence from the diurnal profile of total nitrate (peak concentrations in the afternoon) seemed to indicate that the NO_2 + OH reaction was an important nitric acid production route. The analysis of Carr and Gray (1998) indicated that only a small fraction of the available NO_x was converted to nitric acid and nitrate during a typical episode. They concluded that the conversion of NO_x to nitric acid might be limited by the availability of oxidants. Thus, to understand which primary pollutants govern the formation of ammonium nitrate, we need to address the oxidation potential of the atmosphere and determine which pollutants (i.e., NO_x or VOC) are the most influential for the formation of oxidants in the system.~~

Table 3-2. Chemical Mass Balance Analysis of PM in Winter in the San Joaquin Valley (Data Source: Magliano, 1997)

Episode	Component	Contribution (Range at Core Sites)
Winter PM-10	Nitrate	40% (8 – 54%)
	Vegetative Burning[a]	12% (4 – 22%)
	Mobile Sources[b]	12% (4 – 21%)
	Geological material[c]	10% (6 – 16%)
	Excess OC[d]	8% (1 – 25%)
	Sulfate	6% (1 – 10%)
Winter PM-2.5 (70-80% of PM-10 mass)	Nitrate	46% (10 – 69%)
	Vegetative Burning	15% (5 – 35%)
	Mobile Sources	12% (7 – 19%)
	Excess OC	7% (0 – 23%)
	Sulfate	6% (1 – 12%)
	Geological material	0.6% (0.1 – 1 %)

(a) Vegetative Burning: based on combustion PM samples from fireplaces and agricultural burning.

(b) Mobile Sources: based on SCAQMD and Phoenix dynamometer profiles.

(c) Geological material: soil dust profiles determined from samples of soil and (paved and unpaved) road dust from Visalia, Bakersfield, and Taft.

(d) Excess OC: organic compounds not accounted for by the other source categories, including primary and secondary components.

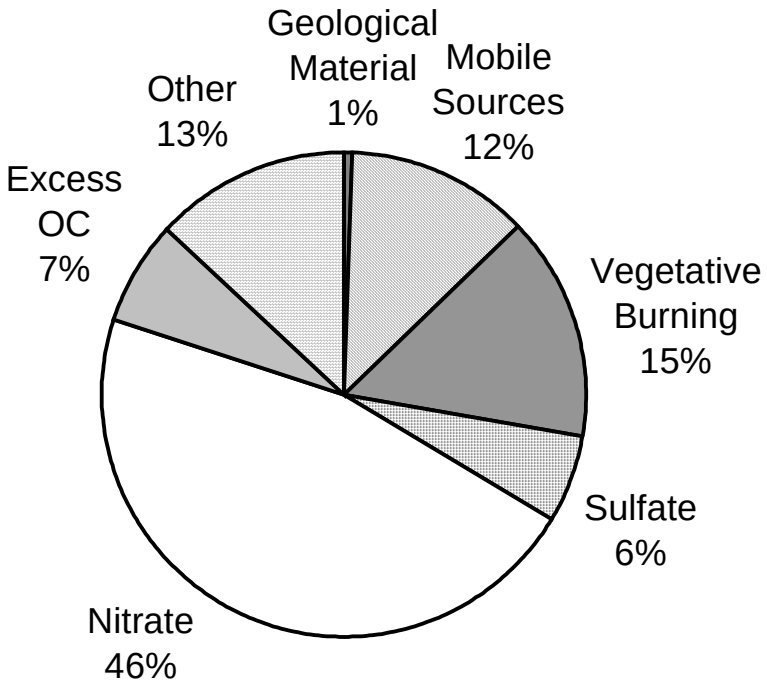

Figure 3-3. Source Contributions Based on Chemical Mass Balance Analysis of Winter PM-2.5

(Data Source: Magliano, 1997)

Table 3-3. Differences in PM-2.5 Compositions at Urban and Rural Sites

(Data Source: Magliano, 1997)

	Urban	**Rural**
Average Mass on Episode Days	57 $\mu g/m^3$	31 $\mu g/m^3$
Nitrate	30%	50%
Vegetative Burning	21%	9%
Mobile Sources	14%	10%

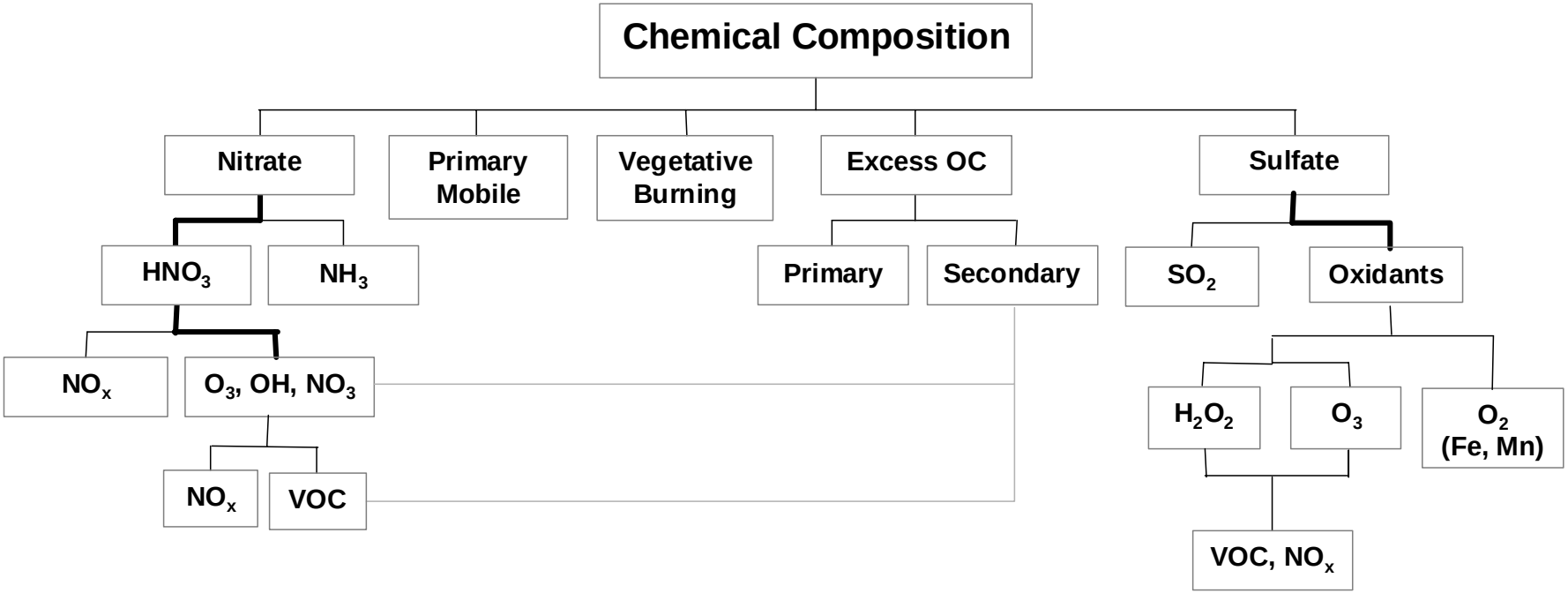

Figure 3-4. Breakdown of PM by Chemical Composition for a Typical Winter Episode (bold lines represent the influential variables for the formation of secondary PM, to the extent that sufficient information is available to determine which variables are the most influential).

Ammonium Nitrate

Ammonium nitrate was the most dominant compound found in PM-2.5 during IMS 95 winter episodes. The ranges of concentrations observed were 9.6 to 24 $\mu g/m^3$ at rural sites and 10.6 to 29.5 $\mu g/m^3$ at urban sites. At the non-urban sites, ammonium nitrate can contribute 50% or more to the total mass of PM-2.5. As indicated in Figure 3-4, ammonium nitrate is formed by the combination of ammonia and nitric acid:

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 . \tag{3.1}$$

Ammonia (NH_3) is emitted mainly from dairies / livestock / poultry feedlots and natural soils (Haste et al., 1998), while nitric acid (HNO_3) is typically formed in the atmosphere. Kumar et al. (1998) showed that the formation of ammonium nitrate (NH_4NO_3) within the study area of IMS 95 was limited by the availability of HNO_3 in the winter, since 75 to 82% of the total nitrate was present in the particle phase. NH_3 sources were abundant, and 40-50% of the ammonia remained in the gas phase after neutralizing the particulate-phase nitrate. The ratio of NH_3 to HNO_3 was greater than 1.05 in 93% of the winter samples. The abundance of NH_3 relative to HNO_3 needs to be confirmed for areas west of Interstate 5 (Phil Roth, Personal Communication, 1998). The formation of HNO_3 may take place either in the gas phase or in water droplets. Gas-phase reactions that form HNO_3 are:

$$OH + NO_2 \longrightarrow HNO_3 \text{, and} \tag{3.2}$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 . \tag{3.3}$$

The hydrolysis reaction also takes place in the aqueous phase, with increased reaction rate. N_2O_5 is formed when NO_2 and nitrate radical (NO_3) combine:

$$NO_2 + NO_3 \longrightarrow N_2O_5 . \tag{3.4}$$

NO_3 is formed when O_3 oxidizes NO_2:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 . \tag{3.5}$$

During the day, the lifetime of NO_3 is usually short because the photolysis reaction of NO_3 is fast, and, consequently, the concentration of N_2O_5 is expected to be low.

The ambient formation of HNO_3 may be either NO_x-sensitive or oxidant-sensitive (OH in Reaction 3.2, NO_3 in Reaction 3.4, and O_3 in Reaction 3.5). Although information regarding the dominant reaction was not available, indirect evidence from the diurnal profile of total nitrate (peak concentrations in the afternoon) seemed to indicate that the NO_2 + OH reaction was an important nitric acid production route. Magliano (1997) also noted an increase in the NH_4NO_3 mass during the day (starting at 9 a.m.). At urban sites, NH_4NO_3 accounted for 20-25% of the evening mass and 40-45% of the midday PM-10 mass. The percentage contribution was relatively constant at rural sites. The analysis of Carr and Gray (1998) indicated that only a small fraction (12% in cities, 30% in rural areas) of the available NO_x was converted to nitric acid and nitrate during a typical episode. They concluded that the conversion of NO_x to nitric acid might be limited by the availability of oxidants. Thus, to understand which primary pollutants govern the formation of ammonium nitrate, we need to address the oxidation potential of the atmosphere and determine which pollutants (i.e., NO_x or VOC) are the most influential for the formation of oxidants in the system.

Organic Compounds

Organic compounds accounted for a substantial fraction (35%) of the PM-2.5 particle mass at the urban sites of Bakersfield and Fresno. In the San Joaquin Valley winter, sources of organic particles included mobile vehicles, vegetative burning (e.g., household wood burning), and other (excess) organic compounds (e.g., primary compounds from meat cooking or secondary organic compounds). The contribution from hardwood and softwood combustion was especially pronounced in the December 26-28 episode at Fresno, where wood combustion surpassed ammonium nitrate as the largest contributor of PM-2.5. (The contribution of vegetative burning

was 35% according to Magliano, 1997; combined hard and soft wood burning contributed close to 50% according to Schauer and Cass, 1998.) The vegetative burning contribution profile exhibited, not surprisingly, peaks in the evening samples at the urban sites, corresponding to domestic fireplace usage. On the other hand, in rural areas, the percentage contribution remained essentially constant throughout the day. The influence of the vegetative combustion source was weak at the Kern Wildlife Refuge core site (see Table 3-3). Motor vehicle particles also exhibited higher contributions at urban sites than rural sites.

Excess OC represents the fraction of OC that is not apportioned to any source in the CMB analysis. The large amounts of excess OC in many CMB runs may be an indication of the inadequacy of the current source profiles, which can result in mis-allocation amongst the various carbon-containing sources using the traditional CMB approach. Nonetheless, a fraction of excess OC corresponds to secondary organic aerosol. At present, there are no direct measurement techniques that allow the experimental distinction of primary vs. secondary organic compounds. Better source profiles or tracer compounds (e.g., Schauer and Cass, 1998) may increase the resolution of the CMB technique in that respect. With sufficient sensitivity, CMB or tracer techniques are tools to apportion ambient organic aerosols to their primary sources; and the amount of secondary organics may be determined by the difference of total organics and the primary fraction. Schauer and Cass (1998) reported that the fine organic compound mass that could not be attributed to direct particulate emissions averaged about 4.5 $\mu g/m^3$ at both urban and rural sites in the winter. The un-apportioned mass was interpreted as a uniform regional background of secondary organic aerosols in the San Joaquin Valley during two different episodes. The secondary organic aerosol background contributed to a maximum of 16% of PM-2.5 to Fresno in the January, 1996 episode. Similar high contributions were also calculated at the Kern Wildlife Refuge, where secondary organics were the second largest contributor to PM-2.5 behind ammonium nitrate. The analysis and modeling results of Strader et al. (1998) were generally consistent with Schauer and Cass (1998), indicating that secondary organic aerosols should not be ignored in the apportionment of the PM concentrations.

Oxidant Chemistry

Oxidant chemistry may be VOC-sensitive or NO_x-sensitive. The sensitivity regime affects the response of the atmospheric system towards control measures placed on the precursors. A possible photochemical indicator (e.g., Sillman, 1995; Lu and Chang, 1998) is the ratio of HNO_3 (or HNO_3 + particulate nitrate) and H_2O_2 concentrations. These chemical species are produced by radical termination reactions and their relative importance sheds some light on whether the chemical system is VOC- or NO_x-sensitive. Figure 3-5 depicts the major chemical pathways of the VOC/NO_x/O_3 system. When NO_x is low, HO_2 radicals preferentially recombine to form H_2O_2 (left-hand side of Figure 3-5). When VOC is the limiting reagent, OH reacts preferentially with NO_2 to form HNO_3 (right-hand side of Figure 3-5). Consequently, the ratio of H_2O_2 and HNO_3 concentrations is a good indicator of the relative extents of NO_x and VOC sensitivity in the atmospheric system.

Lu and Chang (1998) investigated the summer ozone chemistry in the San Joaquin Valley, CA, and determined that much of the domain was sensitive to NO_x, or both VOC and NO_x. However, Jacob et al. (1995) reported a seasonal transition from NO_x-limited conditions during summer to VOC-limited conditions during winter for ozone production over the eastern United States. Therefore, the results of Lu and Chang (1998) may not be directly applicable to the winter conditions in the San Joaquin Valley. Typical concentrations of HNO_3 (1.5 ppb at urban sites, 2.4 ppb at rural sites) and H_2O_2 (0.2 ppb at urban sites, 0.3 ppb at rural sites) suggest that the oxidant chemistry of the San Joaquin Valley may be in the VOC-sensitive regime during the winter season. This result is preliminary because the indicator approach (i.e., HNO_3/H_2O_2 ratio) has not been evaluated for the type of meteorological conditions prevalent in the San Joaquin Valley winter.

Ammonium Sulfate

Although ammonium sulfate only accounted for 6% ($\leq 3.4\ \mu g/m^3$ at Kern Wildlife Refuge; $\leq 3.7\ \mu g/m^3$ at Bakersfield) of the PM-2.5 measured during IMS 95 in the San Joaquin Valley, it was the third largest component at the rural site of Kern Wildlife Refuge. The concentration of SO_2 in the urban areas averaged about 3 ppb during the winter episodes, and accounted for almost 80% of the total sulfur (18% sulfur in fine particles, 4% in coarse particles). Therefore, it was

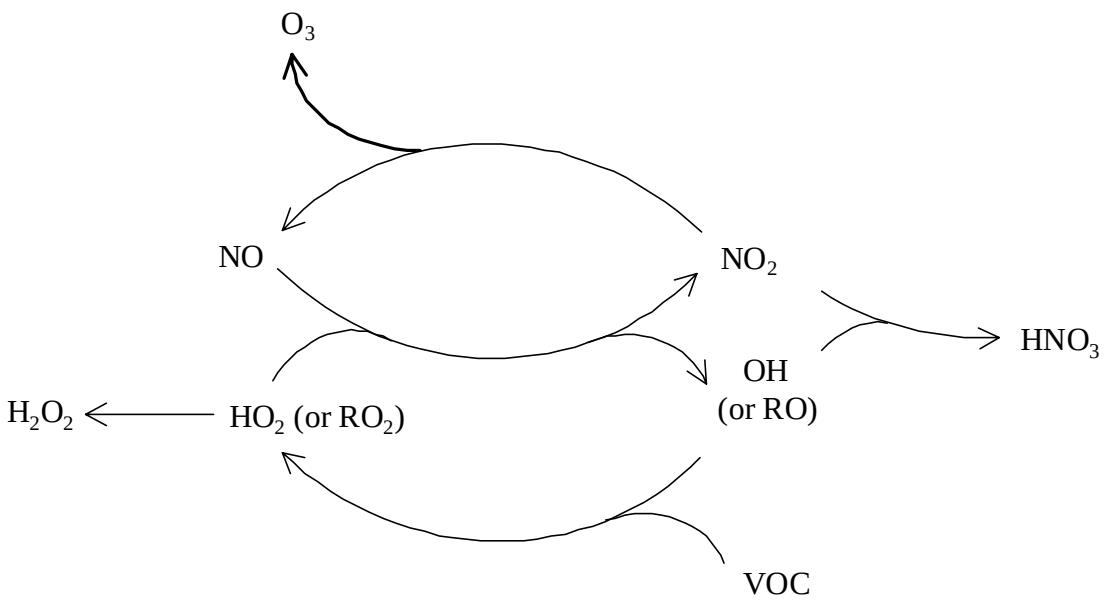

Figure 3-5. Simplified Description of Photochemical Smog Formation Showing the Two Major Interacting Cycles (NO/NO_2 and OH/HO_2 or OH/RO_2 and the Two Major Sinks for Radical Chain Termination: H_2O_2 (NO_x Sensitive) and HNO_3 (VOC Sensitive).

Source: Seigneur et al., 1998b

likely that the conversion of SO_2 to sulfates in urban areas was limited by the availability of oxidants. The situation at the rural areas was not as clear. The concentration of gaseous SO_2 was significantly lower in the rural areas (0.1 ppb, 20% of total sulfur), and fine and coarse sulfate accounted for 56% and 22% of the total sulfur, respectively. In-situ production of sulfate was probably limited. Therefore, transport of particulate sulfate was a factor to consider at rural locations.

Midday peaks observed at the rural sites (Magliano, 1997) and the abundance of sulfates in the PM-2.5 fraction (aqueous production of sulfates typically take place in coarse particles) seemed to be consistent with day-time gas-phase production of sulfate rather than production in fog droplets. Nonetheless, much effort was invested during IMS 95 to understand the aqueous-phase chemistry leading to the formation of ammonium sulfate during a fog episode. There are three major oxidation pathways for dissolved SO_2: oxidation by ozone, catalytic oxidation (dissolved Fe or Mn as catalysts) by oxygen, and oxidation by H_2O_2. Of these three pathways, only the H_2O_2 oxidation reaction is insensitive to pH. The other two reactions have kinetic rates that decrease as the pH decreases; therefore, they tend to be self-limiting since sulfate formation decreases the pH. Therefore, it was postulated that the kinetics of the SO_2 oxidation reaction(s) responsible for sulfate production may change because of pH changes within the fog droplets due to the production of acids.

According to the analysis of Collett et al. (1998a), ozone was the dominant oxidizing agent in 98% of the IMS 95 fog samples. This conclusion was reached based on two main assumptions: (1) dissolved Fe(III) comprised one quarter of total aqueous iron concentration, and (2) the gaseous concentration, from which the aqueous concentration was calculated, was assumed to be equal to the instrument's detection limit (DL) when it fell below DL. Sensitivity studies showed that if these assumptions were relaxed, all three pathways would be important for the formation of sulfate at urban sites, although sulfate production at the rural site will still be dominated by the ozone reaction. Therefore, it is important to have accurate measurements of the oxidants at the ppb level. Collett's group (1998b) found that at urban sites, there was some unexplained buffering capacity within the fog droplet such that the ozone reaction remained highly competitive throughout the fog episode. The fog drop buffering capacity, due to some dissolved

agent, could not be explained by the usual buffering agents, such as carbonate, acetate, and formate. Several phenol candidates were analyzed, but their concentrations did not explain the observed buffering. The authors postulated that a dissolved organic acid, such as humic acid, might be responsible for the buffering of fog droplets. This buffering capacity should be understood for accurate prediction of the chemical reaction pathways that govern sulfate production.

3.3 Transport Processes

Typical transport scales may be inferred by the spatial distribution of PM. For example, Table 3-3 shows that the primary sources, such as mobile sources and vegetative burning, contributed more to PM in the cities, where they are generated, than to PM in the rural areas. On the other hand, nitrate, a surrogate secondary compound, displayed relatively uniform distribution. Therefore, both urban-scale (primary sources) and rural-scale (secondary compounds) influences were observed for PM-2.5 in the winter.

Blanchard et al. (1998) analyzed the spatial representativeness of monitoring stations and the zone of influence of emissions sources. The spatial representativeness, defined as the fraction of the monitoring domain having concentrations within ± 20% of the measurement, of the core sites was variable. For example, the Fresno core site was representative of the monitoring domain only 27% of the time, the Bakersfield core site 60%. However, the spatial representativeness increased to 90% by using two additional sites. Spatial representativeness is also a function of the PM component. Relative to primary components, secondary compounds were more uniformly distributed within each network, as indicated by the large area with similar concentrations. Representativeness was typically high when concentrations were high; however, representativeness and concentration do not necessarily track. Differences in mixing and transport conditions could explain some of the observations of increasing or decreasing spatial representativeness at peak concentration during an episode. Available data seem to indicate higher average spatial representativeness in the rural network (73%) than the urban ones (61% at

Bakersfield, 54% at Fresno) for PM-10. This is consistent with the urban sources at the cities and the dominance of the secondary compounds in the rural areas.

The zone of influence analysis (Blanchard et al., 1998) confirmed the observations of urban (10 km) and regional-scale dispersion (20 km). A mean urban background of 40 $\mu g/m^3$ PM-10 was inferred. Collins (1998) concluded that the regional background averaged about 25 $\mu g/m^3$ for PM-2.5. Concentrations measured at the boundary sites at the valley floor were very similar to the rural sites. Elevated boundary sites usually recorded concentrations lower than or similar to the background sites on the valley floor. For example, 24-hour PM-2.5 measurements recorded at the elevated boundary sites were between 10 to 20 $\mu g/m^3$ on December 26 when the rural concentrations were 30 to 40 $\mu g/m^3$. On January 5, when the rural PM-2.5 concentrations were about 35 $\mu g/m^3$, the elevated boundary sites measured concentrations between 25 and 50 $\mu g/m^3$. Despite the availability of concentration measurements at the boundary sites, fluxes across the boundary sites were poorly defined because of low and variable winds.

Fog and stagnation were typically the dominating features of the meteorological conditions. The temporal and spatial distribution of fog was observed using a network of Optec nephelometers. The light scattering measurements indicated the non-uniform pattern of fog. Fog was more frequent and longer in duration at the rural sites. Of the urban sites, Fresno tended to be foggier than Bakersfield. During the IMS winter study, ground level transport was limited to a length scale of about 4 km during a stagnation period of 3 to 5 hours (Carr and Gray, 1998). Advective transport gave way to diffusion during some periods of stagnant conditions. Carr and Gray observed both regional and local influences on nitrate production, although it was unclear whether the so-called regional influence was due to advective mixing, diffusion, or widespread / area sources.

As shown in Table 3-1, during the winter episodes, the maximum daily mixing height ranged from 125 m to 1100 m. The low mixing heights during several episodes were likely conducive to pollutant build-up within the valley. Dye et al. (1997) indicated that there were typically three layers within the San Joaquin Valley: the surface layer, the upper mixed layer, and the decoupled layer. The heights of the layers varied with time and location. The surface layer depth ranged

from a few hundred meters to about 1000 m. At night, the surface layer was further divided into an inversion layer of 50 – 100 m and a decoupled surface layer. The decoupled layer was roughly 2000 m above ground level. During two of the winter episodes, the mixed layer extended beyond the surface layer at some locations in the afternoon. Since the wind speeds aloft (up to 10 m/s) were typically higher than in the surface layer (0 – 300 m wind generally < 2.5 m/s) (Lehrman et al., 1998), transport of pollutants aloft and subsequent mixing into the surface layer may be a mechanism of distributing pollutants within the valley in a multi-day episode.

With reduced mixing heights of a few hundred meters and reduced length scales for horizontal transport, much of the pollutants were trapped within the San Joaquin Valley. The dominant sink processes were, therefore, wet and dry deposition. Wet deposition is likely to be a significant removal process because of the solubility of ammonium nitrate, nitric acid, and ammonia gas. During fog episodes, a fraction of the particles are activated to grow by absorbing water. As fog droplets settle more quickly than smaller particles, PM is removed as fog. Measurements were taken of wet deposition at Fresno during the early December PM episode. The observed removal fluxes were 169 $\mu g/m^3$ for sulfate, 1018 $\mu g/m^3$ for nitrate and 1291 $\mu g/m^3$ for ammonia. Therefore, the concentration of PM typically diminished after a major fog event, although the effect of wet deposition may be balanced by aqueous production of sulfate during patchy / local fog events. Model predictions of wet deposition fluxes were sensitive to assumptions used in the model. For example, when the wet deposition velocity was reduced by a factor of 2, the removal of nitrate was reduced by 25%. Pandis et al. (1998) calculated with their fog simulation model that the San Joaquin Valley scavenged nitrate and ammonium, but may produce or remove sulfate.

Dry deposition was not studied during IMS 95, although it may be a significant sink for both particles and precursor gases. For instance, nitric acid deposits fairly rapidly (compared to other nitrogen species such as NO or NO_2) because it has high affinity towards surfaces. Russell et al. (1985) determined that 75% of the atmospheric nitric acid could be removed in the California South Coast Air Basin in 24 hours via dry deposition.

4. Analysis of Fall PM-10 Episodes

4.1 PM-10 Problem in the Fall

Figure 4-1 shows the 24-hour average PM-10 mass concentrations observed at Corcoran (core and satellite sites) during the fall study of IMS 95. The spatial average PM-10 concentration in the Corcoran vicinity exceeded 150 $\mu g/m^3$ on November 8 and 14. Table 4-1 summarizes the PM-10 observations and the associated meteorological conditions. Two episodes were monitored during the fall of 1995, separated by the passage of a low pressure system on November 8 and 9 through the valley. The chemical mass balance, with dominating contribution (> 50%) from dust and significant contributions from nitrates (16%) and excess organic compounds (10%) (see Table 4-2 and Figure 4-2), indicated the influence of both primary and secondary components on the PM-10 problem during the fall episodes (November 6-8, November 11-14). The chemical composition breakdown for the fall episodes is shown in Figure 4-3.

The key differences between the winter and the fall episodes are as follows:

- PM-10 concentrations were higher in the fall (maximum PM-10 was 180 $\mu g/m^3$) than in the winter (Maximum PM-10 was 125 $\mu g/m^3$).
- Geological material (dust) dominated the composition of the fall PM-10 (57%), but was a relatively minor component of PM-10 (10 %) and PM-2.5 (0.6%) in the winter.
- Secondary ammonium nitrate was the dominating component of PM-10 (40%) and PM-2.5 (46%) in the winter but not in the fall (16%).
- PM from vegetative burning contributed significantly (15%) in many sites, especially urban ones (21%), in the winter, but not in the fall.
- Fog was patchy and mild in the fall.

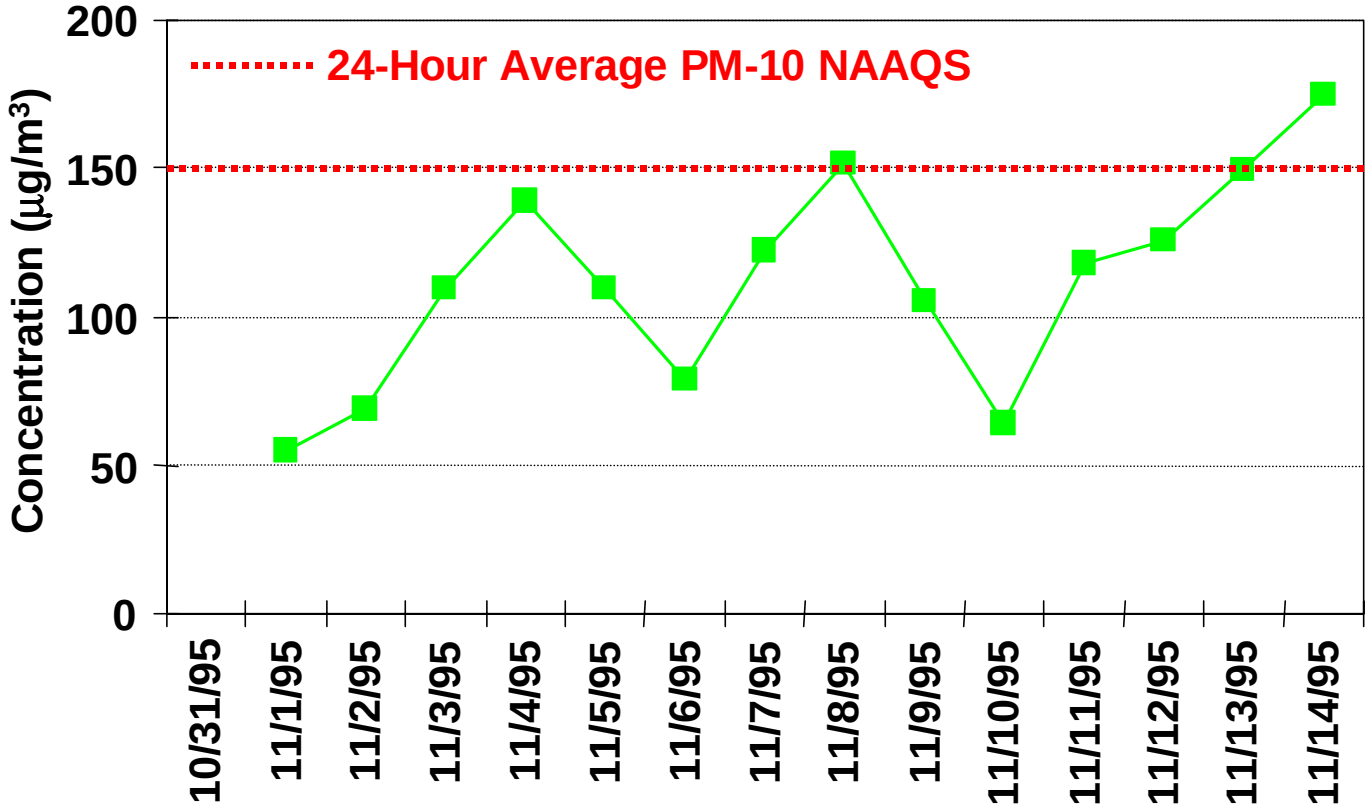

Figure 4-1. Temporal Variations of PM-10 Mass Concentrations during the IMS 95 Fall Study (Source: CARB, 1998)

Table 4-1. Characteristics of the Fall PM Episodes in the San Joaquin Valley

(Data Source: Chow and Egami, 1997; Lehrman et al., 1998)

Episode	November 6 – 14, 1995 (2 episodes, each 3-4 days; decrease in PM observed on November 9, 10)
PM-10 Observations	Concentrations correlate among sites. Corcoran core site and 20 satellite sites exceeded 150 $\mu g/m^3$ 24-hr PM-10 on 11/14/95 Several sites exceeded 150 $\mu g/m^3$ 24-hr PM-10 on four other days
Peak Time / Site	11/14/95, (time unknown, no hourly data available) Peak concentration at an industrial site next to railroad tracks
Wind Speed	Light winds (< 2 ms^{-1})
Temperature (ground / upper air)	Ground temperature: 20 °C; Aloft temperature: 11 – 15 °C
Mixing Height at 4 pm	No report of mixing height 500 mB height of 5820 m (stable condition)
Fog	Bakersfield: no fog (RH = 60%). Fresno: 1-5 fog hours nightly (RH = 70%) Corcoran day-time RH < 50%; 80% at night

Table 4-2. Chemical Mass Balance Analysis of PM in the Fall in the San Joaquin Valley (Data Source: Magliano, 1997)

Episode	Component	Contribution
Fall PM-10 (core site)	Geological Material[(a)]	57%
	Nitrate	16%
	Excess OC[(b)]	10%
	Mobile Sources[(c)]	7%
	Vegetative Burning[(d)]	5%
	Sulfate	3%

(a) Geological Material: soil dust profiles determined from samples of soil and (paved and unpaved) road dust from Visalia, Bakersfield, and Taft.

(b) Excess OC: organic compounds not accounted for by the other source categories, including primary and secondary components.

(c) Mobile Sources: based on SCAQMD and Phoenix dynamometer profiles.

(d) Vegetative Burning: based on combustion PM samples from fireplaces and agricultural burning.

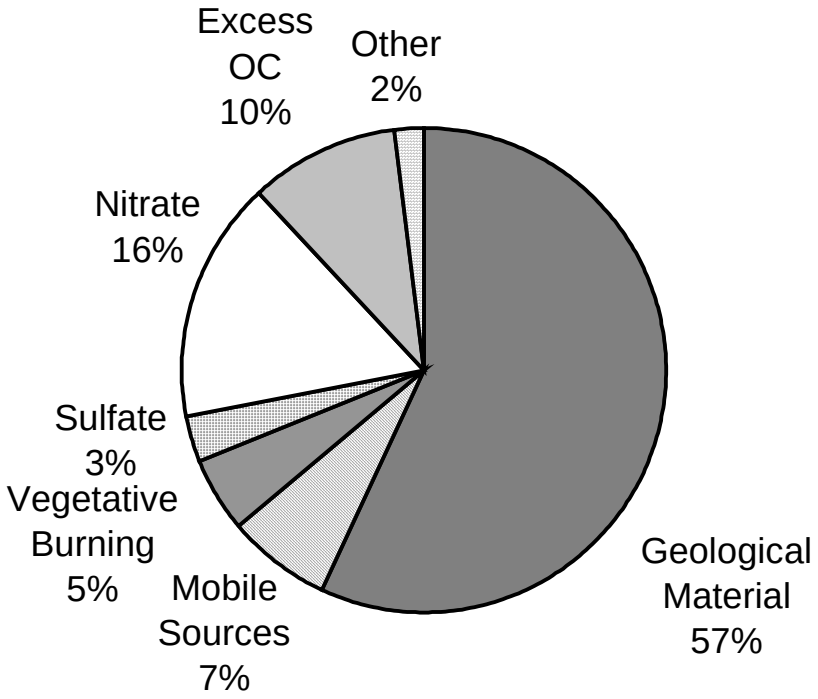

Figure 4-2. Source Contributions Based on Chemical Mass Balance Analysis of Fall PM-10

(Data Source: Magliano, 1997)

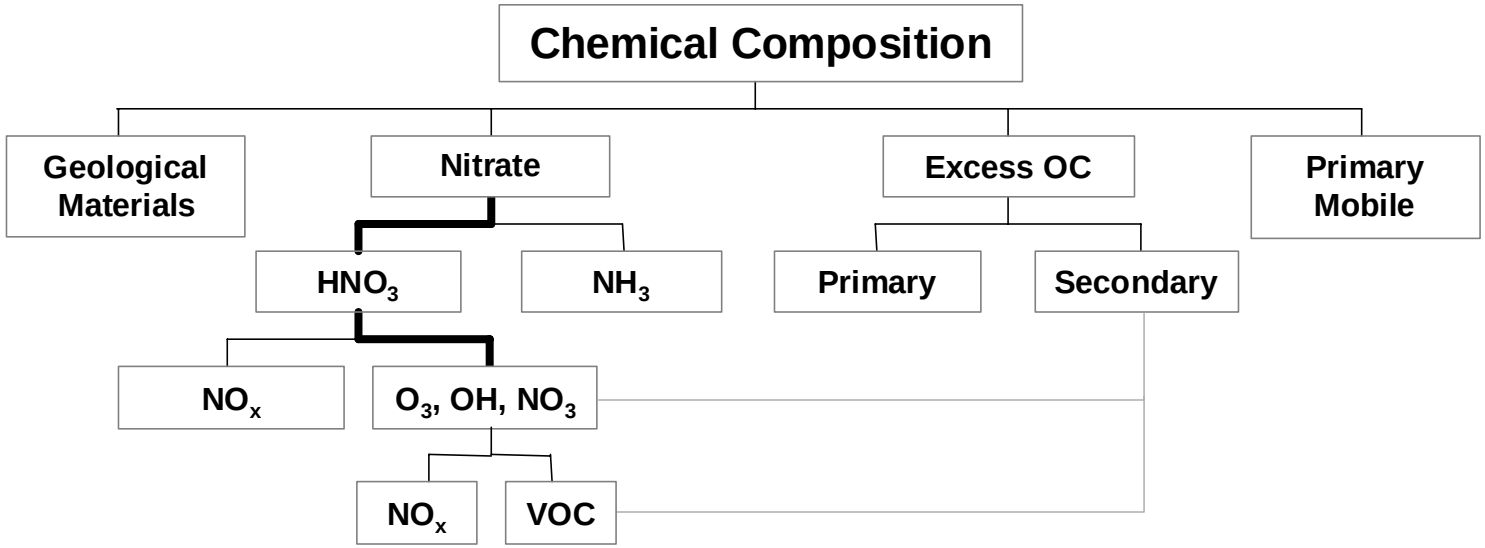

Figure 4-3. Breakdown of PM by Chemical Composition for a Typical Fall Episode
(bold lines represent the influential variables for the formation of secondary PM,
to the extent that sufficient information is available to determine which variables are the most influential)

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4.2 Chemical Composition and Transformations

Geological Material

The largest component of PM-10 in November 1995 was geological material, i.e. dust (57%). Since dust is a primary component, it will be discussed further under transport processes in Section 4.3.

Ammonium Nitrate

Ammonium nitrate was the second most important component of PM-10 in the fall, accounting for about 16% of the mass at the Corcoran core site. The formation of ammonium nitrate warrants further discussion. One key question is whether the formation of nitrate is limited by the availability of nitric acid or ammonia. Kumar et al. (1998) showed that the atmosphere in the monitoring domain within the southern part of the San Joaquin Valley was ammonium rich in the winter. It is likely that the system is also more sensitive to nitric acid than to ammonia during the rest of the year, especially in the summer when the oxidant chemistry is NO_x-sensitive (Lu and Chang, 1998) and, therefore, not conducive to the formation of nitric acid. The nitric acid sensitivity should be confirmed for fall conditions, which have different reaction rates (due to different temperature and solar radiation), mixing conditions, and emissions. Fog was not prevalent during the fall and the atmosphere was relatively dry; therefore, it is postulated that the OH reaction (Reaction 3.2) may be more important than the N_2O_5 hydrolysis route (Reactions 3.4, and 3.3) in the production of HNO_3 in the fall. In order to confirm the important nitrate formation reactions, a better understanding of oxidant chemistry is needed for the fall season in the San Joaquin Valley, CA. Emphasis should be placed on studying the gas-phase oxidation pathways of NO_x to HNO_3, and the sensitivity of oxidants (OH, O_3, and NO_3) to NO_x and VOC.

Excess OC

Another PM component needing further investigations is the excess OC. These are the organic compounds that were not accounted for by the source profiles explicitly included in the CMB study. Excess OC includes both primary (e.g., from meat cooking) and secondary organic components. Tracer-based receptor modeling, similar to that described in Section 3.2, may be used to analyze the source of excess OC, and determine whether these are primary or secondary organic compounds.

4.3 Transport Processes

The spatial representativeness of the Corcoran core site was 87%, i.e., 87% of the area in the monitoring domain recorded PM-10 concentrations within ± 20% of the core site (Blanchard et al., 1998). The average spatial representativeness over all sites in the Corcoran vicinity was 74%. During PM-10 episodes, the spatial representativeness tended to increase, indicating the sub-regional nature of the PM build-up, driven mostly by meteorology. The meteorological conditions are summarized in Table 4-1. As expected, secondary components were more uniformly distributed (87% spatial representativeness averaged over all sites) than primary components (the spatial representativeness of dust is 65%). The source zone of influence study revealed the presence of neighborhood scale influence (~ 1 km) and a 5 to 15 km sub-regional influence. The mean PM-10 background in the vicinity of Corcoran was 100 $\mu g/m^3$. Boundary conditions could not be determined from the Corcoran network (Collins, 1998).

There is little direct evidence from which to infer the dominant physical transport processes affecting the concentrations of PM in the San Joaquin Valley in the fall. Collins (1998) showed that PM concentrations are generally highest during periods of light and variable winds which tend to come from the southeast. Lower PM concentrations were associated with stronger northeasterly winds. As shown in Figure 4-4, PM-10 concentrations correlate well with the aloft temperatures measured at Oakland, CA (850 mB temperature at about 1500 m or 5000 ft), indicating reduced mixing as a major cause of the observed PM episodes. Furthermore, both primary (e.g., dust) and secondary components (e.g., nitrates) increased during the fall episodes. These observations tended to support a sub-regional build-up of PM as the culprit of the pollution episodes under the particular fall conditions.

The dominance (57%) of dust or geological material in the PM composition also supported the sub-regional build-up hypothesis, as coarse materials are generally not transported over great distances. The correlation of PM-10 concentrations among the core and satellite sites (i.e., the fact that the concentrations at all sites increase and decrease together) indicated that meteorology

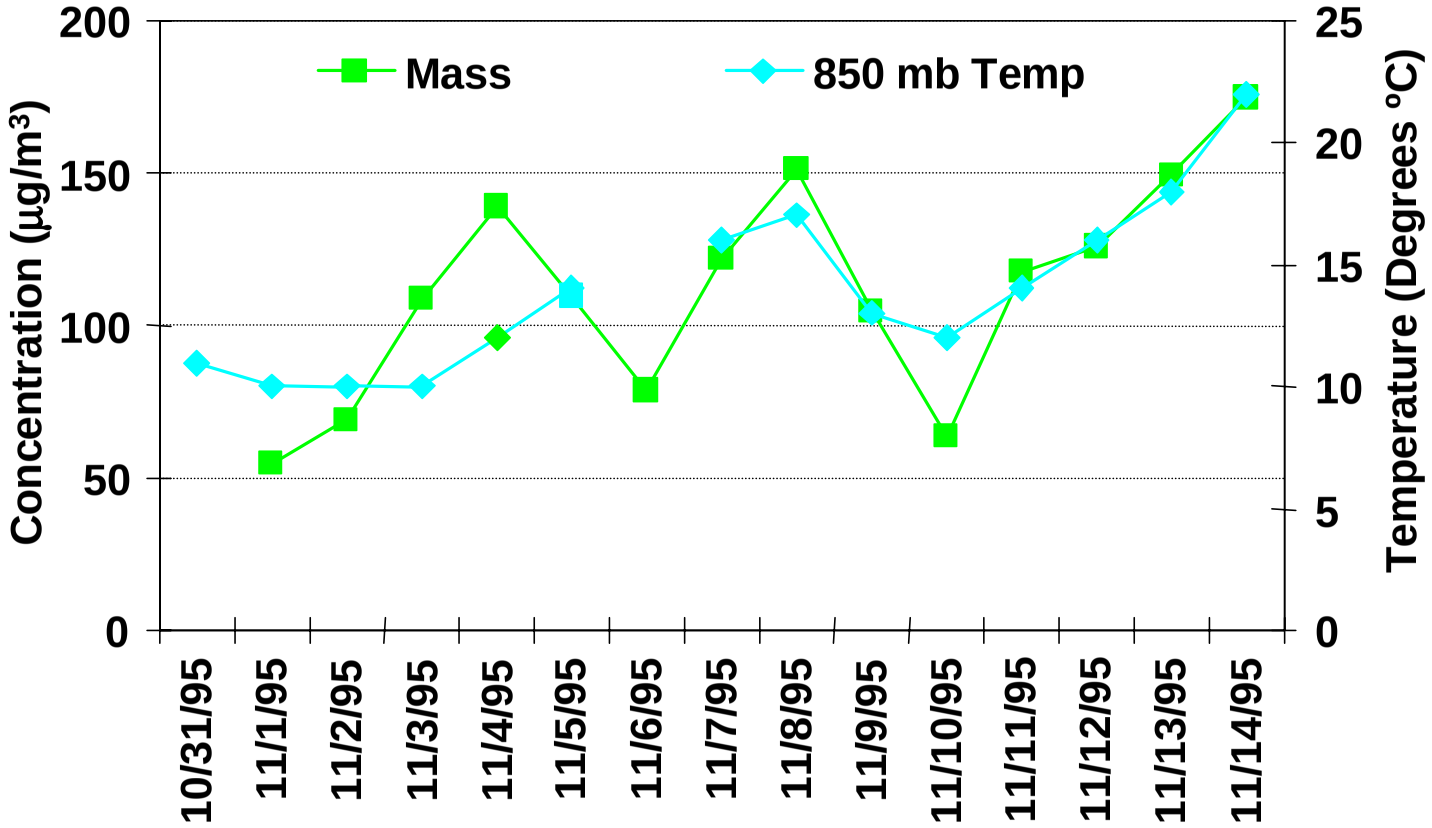

Figure 4-4. Fall PM-10 Mass at Corcoran and 850 mB Temperature (Source: CARB, 1998)

was the driving force behind episodes in the Corcoran area. Spatial variability recorded by the network was attributed to local influences. It was found that industrial sites tended to record higher concentrations than the residential sites. Average PM-10 concentrations were 134 $\mu g/m^3$ at the industrial sites, 113 $\mu g/m^3$ at the agricultural sites, and 112 $\mu g/m^3$ at the commercial / residential sites (Chow and Egami, 1997). However, because of the intermittent nature of the many PM-generating activities, observations of activities did not correlate well with the 24-hour data that were collected (Coe and Chinkin, 1998). No meteorological data were available at the monitoring sites to evaluate the contribution of local wind-blown dust.

Long-range surface transport from upwind pollutant sources to Corcoran was unlikely, as the surface wind speed was typically less than 2 m/s during the fall episodes in Corcoran. Mixing height, upper air winds, and concentration data are necessary to evaluate the impact of vertical mixing and long-range transport of precursors and PM aloft.

Wet deposition probably played a minor role in the dissipation of PM during the fall episode. No rain was reported during the PM monitoring period in November, and only patchy evening fog was reported in Fresno.

No information was available from IMS 95 to determine whether dry deposition provides a dominant sink for PM and PM precursors in the San Joaquin Valley in the fall. Depending on the size of the coarse material, e.g., dust, dry deposition could play a role in the PM balance at the Corcoran location.

5. Discussion

5.1 Synthesis of Winter Episodes

In the winter, PM-2.5 dominated PM in the San Joaquin Valley. Secondary ammonium nitrate was an important component of PM. It was shown that nitric acid limited the yield of this secondary compound, as ammonia was abundant within the IMS 95 study area. To control nitric acid formation effectively, it is necessary to develop a better understanding of the NO_x/VOC/oxidant chemistry for the San Joaquin Valley. To that end, it may be desirable to conduct an extensive gas-phase measurement program to characterize speciated VOC, NO, NO_2, O_3, H_2O_2, HNO_3, and, if feasible, OH, NO_3, HO_2, and RO_2 within the San Joaquin Valley during winter. In particular, the formation of nitric acid should be studied in detail. Two chemical reactions are of interest: NO_2 + OH and N_2O_5 + H_2O. Since N_2O_5 is formed from the reaction of NO_2 with NO_3, this reaction may be important in the evening or during a fog episode when NO_3 accumulates due to the lack of photolytic dissociation. N_2O_5 cannot be measured directly, but the formation rate of nitric acid via N_2O_5 hydrolysis may be inferred from measurements of NO_3. Other oxidized nitrogen species, including HNO_3, particulate nitrates, HNO_2, PAN, and other organic nitrates, may also be measured to improve the understanding of nitrogen chemistry.

Secondary organic aerosols are another component that requires further study. During IMS 95, the relative contribution of secondary organic aerosols to PM was significant at the rural site. In addition to the transport and transformation of anthropogenic emissions from urban areas, the atmospheric reactions of biogenic compounds are also a source of secondary organic aerosols. The modeling results of Strader et al. (1998) may be useful in understanding the atmospheric organic-oxidant reactions in the foggy winter climate encountered in the San Joaquin Valley. Unfortunately, their implementation of the state-of-the-art secondary aerosol formation processes cannot be considered fully reliable for predicting PM in the San Joaquin Valley, because of some generic input data used in their simulation and uncertainties in the model formulation. In order to understand the formation of secondary organic aerosols, a better understanding of the VOC emissions inventory and oxidant chemistry is needed for both anthropogenic and biogenic

emissions, such as monoterpenes and oxygenated hydrocarbons. IMS 95 provided no information on the magnitude of biogenic emissions within the San Joaquin Valley. VOC emissions inventories, both anthropogenic and biogenic compounds, should be a focus of the forthcoming field campaign.

Sulfate seemed to be a minor (6%) component of San Joaquin Valley PM in the fall and winter. However, with abundant SO_2 in the southern part of the valley and the sensitivity of sulfate production to changes in oxidant concentrations, it is prudent to examine more closely the mechanisms for sulfate formation to assure that changes in precursor (NO_x or VOC) emissions designed to reduce ozone and other components of PM will not have adverse effects on the sulfate problem.

Oxidant production may be sensitive to NO_x or VOC. There is some evidence that ozone formation in the summer is sensitive to NO_x (Lu and Chang, 1998). However, data from IMS 95 seemed to indicate that the formation of oxidants and HNO_3 during the winter season was sensitive to VOC, although the indicator approach (Sillman, 1995; Lu and Chang, 1998) has not been verified for the cooler and foggier winter conditions. Oxidant chemistry should be further investigated to confirm the precursor (NO_x or VOC) sensitivity in the winter season. This basic understanding of the atmospheric system is important because any reduction of NO_x (e.g., for controlling summer O_3) may increase the abundance of HO_2 radicals and enhance the production of H_2O_2 (see Figure 3-5). Since ozone and H_2O_2 are both oxidizing agents of SO_2, the trade-off between the different reaction pathways needs to be understood.

Two areas of research needs identified by IMS 95 researchers are the source of fog buffering capacity and the sensitivity of ambient ozone measurements at the ppb levels. Modern ozone instruments with sub-ppb detection limit and sensitivity (Seigneur et al., 1998a and references therein) may need to be considered in future field studies. Accurate RH measurements are also needed to understand the importance of various aqueous-phase processes. Furthermore, McDade's finding (McDade, 1997) that light extinction was sensitive to particulate water confirmed the need for such measurements for determining light scattering by PM.

The accumulation of pollutants, e.g., NO_2, HNO_3, was associated with stagnant conditions with limited surface transport. Under these conditions, the regional uniformity of secondary pollutants (e.g., ammonium nitrate and secondary organic aerosols) within the San Joaquin Valley is intriguing. Was the time scale of reaction and deposition slower than the time scale of transport (advective or diffusive) under stagnant conditions? Or were widespread sources responsible for the regional scale concentrations of pollutants? In the fall episode, and in some winter episodes, the influence of regional sources was evident (Blanchard et al., 1998). It should be useful to better characterize the meteorological conditions that are associated with enhanced regional influence.

One question that IMS 95 did not sufficiently address because of its limited scope was the magnitude of above-ground transport. There is some evidence that transport of pollutants aloft and subsequent mixing into the surface layer (in the middle of the afternoon) may be a mechanism of distributing pollutants within the valley in a multi-day episode. Aloft measurements of concentrations will be needed to determine the magnitude of this mixing process.

Wet deposition is mostly a function of fog in the San Joaquin Valley PM episodes studied. The effects of fog are two-fold. First, particles that become fog droplets by absorbing water vapor are subsequently removed by gravitational settling. Second, fog droplets provide the aqueous medium for the production of sulfates. The net effect of a fog event depends on the length of the event, the availability of precursors, oxidants, and catalysts, and the composition of the original PM. It is probably advisable to study the wet deposition phenomenon further, and to understand if any recycling of PM and gaseous pollutants occurs through volatilization at the conclusion of the fog event.

Dry deposition information is needed to complete our understanding of major mass fluxes in the system. Direct measurements of dry deposition fluxes by the eddy correlation technique over a variety of land-use types are needed for both PM and precursor gases, including O_3, HNO_3, NH_3, and other nitrogen-containing compounds.

5.2 Synthesis of Fall Episodes

A primary component of the fall PM-10 is geological material (dust), which accounted for over 50% of the mass according to CMB analyses. Limited information is available regarding the source of the dust particles. Given that wind speeds were typically less than 2 ms^{-1}, it seems unlikely that wind blown dust was a significant contributor to PM-10. Other sources of mechanically generated aerosols, such as paved and unpaved roads and farming activities, may be addressed by tracer experiments. Ammonium nitrate (16%) was the second most common component, followed by excess OC (about 10%), which included both primary and secondary components. Accurate geological material profiles and tracer-based organic profiles are needed for major San Joaquin Valley primary sources to increase the resolution of the CMB methods and to elucidate the importance of secondary organic compounds.

A sub-regional build up in the vicinity of Corcoran seemed to be a reasonable hypothesis during a multi-day episode. Although local sources were postulated to explain the spatial variability, there was no direct evidence to link observations of local emissions to elevated 24-hour PM measurements. The atmospheric lifetimes of particles due to settling are functions of particle diameters. The range of PM transport may be estimated if particle size measurements are available. This information may be used to infer the mechanism of sub-regional buildup of PM in the San Joaquin Valley during the fall season. To evaluate the effects of transport, upper level wind and mixing height data are required. Measurements of dry deposition of particles and precursor gases may be needed to refine estimates of areas of influence.

6. Conclusions

6.1 Summary of Conceptual Model

In the formulation of a conceptual model for PM during IMS 95, a data driven approach was used. Available information was systematically compiled into a framework based on the chemical characteristics of and transport processes associated with the observed PM. The key features of the conceptual models for the fall and winter PM episodes in the San Joaquin Valley are summarized in Table 6-1.

Table 6-1. Summary of Conceptual Models

	Winter (PM-2.5)	**Fall (PM-10)**
Chemical Composition and Transformations	Ammonium Nitrate (46%) ▪ Nitric acid Sensitive ▪ Nitric acid Formation Possibly Limited by Oxidants (OH, O_3, and NO_3) Availability ▪ Oxidants May be VOC-Sensitive Rather Than NO_x-Sensitive Organic Compounds (34%) ▪ Primary (e.g., Vegetative Burning and Mobile Sources) ▪ Secondary (Anthropogenic or Biogenic Precursors)	Geological Material (57%) Ammonium Nitrate (16%)
Transport Processes	Limited Ground-level Transport ▪ Calm Winds Aloft Transport Possible Limited Vertical Mixing Wet Deposition (Fog) Dry Deposition Unknown Urban Influences (Primary Sources) on Regional Distribution (Secondary NH_4NO_3, SOA)	Limited Ground-level Transport Aloft Transport Possible PM Build-up Correlates with Reduced Mixing Height Limited Wet Deposition (Mild Fog) Dry Deposition Unknown Local Influences (Geological Material) on Sub-regional Distribution (Secondary NH_4NO_3)

6.2 Comparison with the Conceptual Models of Watson et al. (1998)

Compared to previous conceptual models, ours place a stronger focus on understanding the chemical processes behind the formation of secondary compounds and, therefore, should provide a better balance between meteorology and chemistry in the analyses of the PM episodes. Watson et al. (1998) discussed the primary compounds in terms of their sources and secondary PM in terms of their precursors: NH_3, SO_2 for sulfate, NO_x (HNO_3) for nitrate. We added another facet to the analysis of the secondary compounds and pointed out the need to address the availability of oxidants, which govern the chemical transformation of precursors to PM. Indeed, there was evidence to support that the oxidation of NO_x to HNO_3 was limited by the availability of oxidants, as was the oxidation of SO_2 to sulfate. In addition, different reactions, involving different oxidants, may contribute to the formation of secondary sulfate and nitrates depending on the time of day, the presence of fog and clouds, the amount of available light, relative humidity, etc. To understand these chemical systems, and to design effective control strategies, further work is needed to measure key oxidants accurately and to improve the understanding of the oxidant chemistry, particularly its sensitivity to NO_x or VOC. The effectiveness of any controls placed on the precursors will be dependent on the limiting reagents. In addition, it is important to coordinate the efforts to control oxidants in the summer (O_3) and in the winter (PM). Summer oxidants may be sensitive to NO_x. However, NO_x controls must be accompanied by methods to address VOC concentrations if the oxidants involved in the wintertime formation of secondary PM are more sensitive to VOC than NO_x.

Another component that was not analyzed in detail in Watson's approach is secondary organic aerosol (SOA) formation. Limited analyses seem to indicate that it could be a non-negligible contributor at the rural sites and at the urban sites under some circumstances. Better emissions inventories / profiles and measurements of ambient VOC at urban and rural sites may be useful in deciphering the importance of this component.

Watson et al. (1998) narrated the events that led to PM formation that involve (1) the accumulation of PM and precursors over night, (2) mixing with aloft air in the morning and early afternoon (reduction in PM and precursors), (3) photochemical production and accumulation

aloft (clear sky) of oxidants, nitric acid, and secondary aerosol, (4) entrainment of secondary aerosol by stratus cloud droplets (5) aqueous oxidation of sulfur, (6) radiation inversion separating pollutants aloft and those accumulating at the surface, and (7) mixing of ammonia and nitric acid by upper air transport. This analysis seems to be consistent with available information. However, some components of their analysis are hypotheses that, at this point, cannot be confirmed with available evidence. Aspects of this conceptual model that require verification include the aloft production of oxidants and secondary compounds, the role of cloud droplets, and upper air transport as a mechanism of pollutant dispersion. The removal processes of wet and dry deposition were not addressed in the conceptual model of Watson et al. (1988). Our analysis of the physical transport and removal processes, based loosely on mass balance arguments, confirmed the lack of ground level advection and reduced vertical mixing as the principal meteorological conditions associated with PM build-up. We acknowledged the possibility of aloft transport as a mechanism for pollutant dispersion under apparently stagnant conditions, and pointed out the possibility of widespread sources of precursors and diffusion as explanations of the regional distrubution of pollutants. To complete our understanding of the mass fluxes within the valley, there is also a need to understand the wet and dry removal processes.

Watson et al. (1998) proposed a separate conceptual model for the fall. We concur with the basic features of the fall conceptual model, with primary sources responsible for local influences and secondary compounds responsible for the "subregional influence." The key differences between the fall and the winter conceptual models are the contribution of dust and the lack of fog. Watson et al. (1998) also proposed that the stronger along-valley flows transport particles into the Mojave Desert, although IMS 95 was too limited in its geographical scope to evaluate the full range of transport. Several measurements should be taken to verify several aspects of Watson's model: particle size distribution information will aid the determination of particle lifetimes and the distance of dust dispersion; and measurements of photochemical oxidants will be useful in determining the sensitivity of the oxidant system for nitric acid production.

6.3 Answers to Specific Questions on PM Episodes in the San Joaquin Valley

In the statement of work, several questions were raised. We now address these questions based on the results of our analysis. Where appropriate, quantitative descriptions are provided based on the data from specific episode days, January 5 (winter) and November 14 (fall).

What are the causes of excessive PM-10 and PM-2.5 concentrations in the SJV?

The chemical components that contributed to PM build-up were identified. In the fall, PM-10 contained a significant amount of geological material (see Table 4-2). Ammonium nitrate and organic compounds also contributed to the accumulation of PM. On November 14, the relative contributions from geological material, ammonium nitrate, and organic compounds (mobile sources + vegetative burning + excess organic compounds) were 58%, 21%, and 14%, respectively. In the winter, ammonium nitrate was the major component of PM-2.5 (see Table 3-2). Nitrate contributions averaged 41% at the urban sites and 64% at the rural sites on January 5. Primary organic sources such as vegetative burning and mobiles sources also contributed to fine particles, particularly at the urban sites (30% on January 5, 60% on December 26 in the Fresno area). Contributions of sulfates to PM-2.5 were observed in rural areas (10% on January 5).

What is the influence of meteorology, emissions, chemistry, and deposition on PM concentrations?

Meteorology: In both the fall and winter seasons, stagnant conditions (i.e., lack of advective transport) seemed to be the major cause of high PM in the sub-regional or regional scale. Warm aloft temperatures (15 to 20 °C in the fall; 10 to 15 °C in the winter) curtailed vertical mixing. Ground-level transport was an unlikely mechanism for pollutant distribution. The effects of upper-level transport were not clear, because of the lack of ambient concentration data aloft.

Emissions: The effects of urban-scale emissions were observed in the winter where primary emissions typically contributed to more PM at the urban sites than at the remote sites. For example, on January 5, mobile sources and vegetative burning combine to account for 30% or 15 $\mu g/m^3$ PM at urban sites, but only 16% or 5 $\mu g/m^3$ at rural sites. No direct link was found

between a locally observed emission activity and high PM at a single monitoring site in the fall, although higher average concentrations observed at the industrial sites than residential and agricultural sites may be attributable to local emissions.

Since secondary PM components were prominent in the fall and winter seasons, the emissions of gaseous precursors also need to be addressed, including NH_3, NO_x, SO_2, and VOC. Improvements in the emission inventories for VOC are also important for understanding the production of oxidants in the San Joaquin Valley.

Chemistry: Ammonium nitrate was the top component of PM-2.5 during the winter study. On average, 40 to 50% of the total ammonia was in the gas phase during IMS 95. The average phase partition of ammonia during the January, 1996 episode was as follows: 43% in PM-2.5, 10% in PM-10, 1% in fog droplets, and 46% as gaseous ammonia. Because of the abundance of NH_3 in the area, the formation of ammonium nitrate seemed to be limited by the availability of HNO_3, a secondary compound. A large fraction of nitrates were associated with the particulate phase; only 18-25% of nitrate existed in the gas phase as nitric acid. An oxidant study is recommended to understand the oxidation pathways of NO_x to HNO_3, and the sensitivity of key oxidants (OH or O_3/NO_3) to NO_x and VOC. A comprehensive understanding of the availability of oxidants will also be beneficial in the analysis of secondary organic aerosols and secondary sulfates.

Deposition: Fog episodes caused a net removal of PM by wet deposition, especially for ammonium and nitrate, removing 40 to 46 % (by mass) of ammonia and 15 to 29% of the nitrate present before the fog episode at Bakersfield and Fresno in the early December episode (Pandis et al., 1998). Sulfate formation in fog was estimated to exceed sulfate removal by fog settling at some sites (e.g., Bakersfield on December 10, 1995) but not all. Dry deposition was not studied during IMS 95; dry deposition may be a significant removal pathway for HNO_3 and other PM precursors.

What differences are observed for PM and PM components and precursor species among urban, rural, and industrial areas?

Winter: Episodes during the winter IMS study showed that PM concentrations were higher at the urban sites than the rural sites. During the January episode, PM averaged 51 $\mu g/m^3$ at the urban sites, and 32 $\mu g/m^3$ at the rural sites. In general, the urban sites contained larger contributions from anthropogenic primary sources, such as wood burning and mobile vehicle emissions, than rural areas. The average ammonium nitrate (NH_4NO_3) over all episode days was 18.7 $\mu g/m^3$ at urban sites, and 17.8 $\mu g/m^3$at rural sites. Although the concentrations of NH_4NO_3 are similar, PM at rural sites was always dominated by NH_4NO_3 (> 50%). Contributions from secondary organic compounds and sulfates could also be non-negligible (20%) according to the analysis of Schauer and Cass (1998) and Magliano (1997). Due to the predominance of secondary compounds in the winter, which tended to be regionally distributed, conclusions regarding the distribution of PM between industrial and residential sites were not clear. There was some evidence that within the winter saturation network at Bakersfield, the residential and transportation sites recorded higher PM (70 $\mu g/m^3$ PM-10) than the industrial sites (45 $\mu g/m^3$). Larger contributions were observed of mobile sources, vegetative burning, and geological material (possibly road dust) at these sites, potentially reflecting the proximity to sources. However, more analyses in more areas are needed to confirm these observations.

Precursors to secondary PM include HNO_3 (NO_x), NH_3, SO_2, and VOC. The concentrations of HNO_3 at the urban sites were lower than or equal to those at the rural sites. For example, during the January episode, the urban sites recorded 1.1 to 1.2 $\mu gN/m^3$ HNO_3 (4.4 to 4.5 $\mu gN/m^3$ in the PM phase) while the Kern Wildlife Refuge site recorded 1.2 $\mu gN/m^3$ of HNO_3 (3.9 $\mu gN/m^3$ in the PM phase). Although total oxidized nitrogen was higher in the urban areas, NO_x was also 10 times more abundant than in the rural areas. Total oxidized nitrogen was 29% (by mole) at Kern Wildlife Refuge, compared to only 10 to 13% at the urban sites, indicating the aged nature of the air parcel at the rural site. Ammonia seemed more abundant in Bakersfield than at the other core sites, possibly due to area sources southwest of the city (Haste et al. 1998). SO_2 was also more abundant in the cities than at Kern Wildlife Refuge. The distribution of sources again explained the difference. Gas-phase organic concentrations exhibited strong diurnal fluctuations in the urban areas, with about 400 $\mu gC/m^3$ in the morning and only 250 $\mu gC/m^3$ in the afternoon. No

specific information is available regarding the gas-phase concentrations of organics at the rural sites.

Fall: During the fall episodes, higher PM-10 was observed in industrial areas than at the other sites. On November 14, an industrial site near railroad tracks recorded the highest concentrations of PM (273 $\mu g/m^3$), while the average PM-10 in the Corcoran area was only 180 $\mu g/m^3$ (Magliano, 1997). The absolute contribution of secondary components, such as ammonium nitrate, was fairly constant. For example, on the same day, the contribution of secondary ammonium nitrate ranged from 35.2 to 40.4 $\mu g/m^3$. Therefore, the site-to-site variability was attributed to changes in impacts due to primary emissions of geological material (83 to 146 $\mu g/m^3$) and organic compounds (mobile sources + vegetative burning + excess organic compounds accounted for 9.6 to 55.4 $\mu g/m$) (Chow and Egami, 1997; Magliano, 1998).

What are the chemical processes for the formation of secondary aerosols, especially during foggy conditions when the photochemical processes may be limited?

Nitrate: Ammonium nitrate is formed by the combination of NH_3 and HNO_3. Ammonia was found to be abundant in the San Joaquin Valley; therefore, the formation of this secondary compound was limited by the availability of nitric acid. Nitric acid is formed when NO_2 reacts with OH or O_3 (with subsequent reaction of NO_3 with NO_2 to form N_2O_5, followed by reaction of N_2O_5 with water). The dominant reaction (i.e., NO_2 + OH or NO_2 + O_3) cannot be identified with the available data. The fact that total nitrate peaked in the afternoon suggests that the NO_2 + OH reaction may be dominant. The sensitivity of oxidants to VOC and NO_x needs to be evaluated. The abundance of NO_x relative to oxidized nitrate seems to provide evidence that wintertime conditions may be conducive to a VOC-sensitive oxidant system. However, more data are needed to confirm these hypotheses.

Sulfate: Sulfate was fully neutralized as ammonium sulfate. In addition to the gas-phase oxidation of SO_2 by OH, aqueous reactions in the fog could be an important source of sulfate in the San Joaquin Valley. Of the reaction pathways with O_3, H_2O_2, and O_2 (catalyzed by Fe or Mn), model simulations and data analyses based on IMS 95 results indicated that the O_3 reaction dominated within fog droplets. However, because of uncertainties in the gas-phase oxidant

concentrations, this finding should be re-evaluated when accurate measurements of oxidants are available at the ppb level.

Organics: Secondary organic aerosols (SOA) may contribute to a significant fraction of PM (e.g., 8% of PM-2.5 in Bakersfield, 13% in Kern Wildlife Refuge during the January 4-6 episode). SOA is formed in the oxidation of anthropogenic and biogenic VOC. Strader et al. (1998) found aromatic compounds to be efficient SOA producers in their model. However, a more thorough understanding of the contributions of the various VOC categories to the formation of SOA would require better information on the emissions inventories of biogenic and anthropogenic VOC. Strader et al. (1998) also found that clouds and fog reduced the photochemical production of secondary organic aerosols by a factor of 2 or 3 from the maximum clear sky conditions because of reduced availability of photons. The thermodynamic interactions between fog droplets and SOA are unknown.

What is the influence of fog on PM concentrations?

The influence of fog is two-fold. First, it serves as an aqueous reactor for the formation of sulfate and nitrate. Second, fog drops settle to the ground and remove PM with them. The net effect of a fog episode depends on the pre-fog concentrations, duration of fog, and the availability of oxidants. Nitrate and ammonium are typically removed, while sulfate may be produced or removed. During the December 10 episode, fog was found to remove 29% and 46% of the nitrate and ammonia that were present in the atmosphere before the fog occurrence in Bakersfield. However, with sulfate production over-balancing the wet removal, a 7% by mass increase of sulfate after the fog was predicted by the computer model (Pandis et al., 1998).

What is the spatial influence of primary emissions and secondary aerosol precursors during each conceptual model scenario relevant to the IMS 95 fall and winter sampling periods?

In the fall, spatial variability observed among different site types supported a local scale of influence of primary emissions, although a link between locally observed, often intermittent, emission activities and high 24-hour average PM measurements at a specific site was not identified. Blanchard et al. (1998) identified a 1-km neighborhood scale for primary sources and

a 5 to 15 km sub-regional scale for the distribution of secondary PM. In the winter, elevated primary source contributions of wood combustion in the CMB analysis in the urban areas indicated an urban-scale primary source influence. HNO_3, a secondary gaseous pollutant, was fairly uniformly distributed in urban areas, and tended to increase as a percentage of total nitrogen at the rural site of Kern Wildlife Refuge where the air parcels were more aged (Kumar et al. 1998). Relatively high levels of NH_3 were detected at urban sites far from emission sources (Haste et al., 1998). Haste et al. (1998) used a 25-km radius when comparing ambient NH_3/NO_x ratios to inventory values. On the other hand, Pandis et al. (1998) noted a SO_2 plume in Bakersfield on December 19, 1995, indicating that this precursor was not as well-mixed as ammonia and nitric acid.

References

Blanchard, C.L., Michaels, H.M., Tanenbaum, S.J., and Fine, J., 1998. Spatial Representativeness of Monitoring Sites and Zone of Influence of Emission Sources. Draft Final Report for Tasks 4.2.1 and 4.5.6. Contract Number 97-1PM. California Air Resources Board, Sacramento, CA.

CARB, 1998. ftp://themis.arb.ca.gov/pub/temp/ondov/A-IMS95

Carr, E.L. and Gray, H.A., 1998. Draft Final Report. 1995 Integrated Monitoring Study Data Analysis. Work Element 4.6.3: Time and Length Scales for Mixing Secondary Aerosols During Stagnation Periods. SYSAPP-98/08. California Air Resources Board, Sacramento, CA.

Chow, J.C. and Egami, R.T., 1997. San Joaquin Valley 1995 Integrated Monitoring Study: Documentation, Evaluation, and Descriptive Data Analysis of PM_{10}, $PM_{2.5}$, and Precursor Gas Measurements. Final report. DRI Document No. 5460.1F1. California Air Resources Board, Sacramento, CA.

Coe, D.L. and Chinkin, L.R., 1998. Emission Source Activity Detection: Analysis of CMB Model Results and Daily Activity Data for IMS 95. Draft Final Report STI-997212-1775-DFR. California Air Resources Board, Sacramento, CA.

Collett Jr., J.L., Hoag, K.J., and Pandis, S.N., 1998a. Final Report: IMS 95 Data Analysis Work Element 4.6.7, The Influence of Drop Size-Dependent Fog Chemistry on Aerosol Production and Deposition in San Joaquin Valley Fogs. California Air Resources Board, Sacramento, CA.

Collett Jr., J.L., Hoag, K.J., and Pandis, S.N., 1998b. Final Report: IMS 95 Data Analysis Work Element 4.6.8, How Does Acidification of Drops due to Aqueous Phase Acid Production Limit Aerosol Formation in Fog Drops? California Air Resources Board, Sacramento, CA.

Collins, J.F., 1998. Characterization of Boundaries and Backgrounds in the San Joaquin Valley Integrated Monitoring Study 1995. Draft Final Report. California Air Resources Board, Sacramento, CA.

Dye, T.S., Kwiatkowski, J.J., MacDonald, C.P., Ray S.E., Chinkin, L.R., and Lindsey, C.G., 1997. Measurement Methods Validation: Adequacy and Validation of Meteorological Measurements Aloft During IMS95. Draft Final Report. STI-997218-1766-DFR. California Air Resources Board, Sacramento, CA.

Haste, T.L, Chinkin, L.R., Kumar, N., Lurmann, F.W., and Hurwitt, S.B., 1998. Use of Ambient Data Collected During IMS 95 to Evaluate a Regional Emission Inventory for the San Joaquin Valley. Draft Final Report, STI-997211-1800-DFR. California Air Resources Board, Sacramento, CA.

Jacob, D.J., Horowitz, L.W., Munger, J.W., Heikes, B.G., Dickerson, R.R., Artz R,S., and Keene, W.C., 1998. Seasonal Transition from NO_x- to Hydrocarbon-limited Conditions for Ozone Production over the Eastern United States. *J. Geophys. Res.* **100**: 9315 - 9324

Kumar, K., Lurmann, F.W., and Pandis, S., 1998. Analysis of Atmospheric Chemistry During 195 Integrated Monitoring Study. Draft Final Report STI-997214-1791-DFR. California Air Resources Board, Sacramento, CA.

Lehrman, D.E., Smith, T.B., and Knuth, W.R., 1998. Final Report. Work Element 2.2.2 – Meteorological Representativeness; Work Element 2.2.3 – Fog and Low Cloud Characteristics. California Air Resources Board, Sacramento, CA.

Lu, C.H. and Chang, J.S., 1998. On the Indicator-Based Approach to Assess Ozone Sensitivities and Emissions Features. *J. Geophys. Res.* **103**: 3453-3462

Main, H.H., Richards, L.W., Hurwitt, S.B., Chinkin, L.R., 1998. Characterization of the Spatial and Temporal Patterns of Visibility in the San Joaquin Valley During IMS 95. Draft Final Report. STI-997217-1778-DFR. California Air Resources Board, Sacramento, CA.

Magliano, K.L, 1997. Chemical Mass Balance Modeling of Data from the 1995 Integrated Monitoring Study. Draft Final Report. California Regional PM10/PM2.5 Air Quality Study.

McDade, C.E., 1997. IMS 95 Data Analysis Work Elements: 7.3 Contribution of Chemical Constituents to Visibility Reduction, 7.4 Contribution of Chemical Constituents to Light Extinction Budget, 7.5 Contribution of Emission Sources to Light Extinction Budget. Draft Final Report. Contract Number 97-7PM. California Air Resources Board, Sacramento, CA.

Pandis, S., Lillis, D., Collet, Jr., J., and Richards, L.W., 1998. Final Report. 1995 Integrated Monitoring Study Data Analysis. Fog Effects on PM Concentration and Composition in the SJV. California Air Resources Board, Sacramento, CA.

Richards, L.W., Hurwitt, S.B., Main. H.H., Chinkin, L.R., 1998. Characterization of the Validity of Light Scattering Measurements During the 1995 Integrated Monitoring Study. Draft Final Report. STI-997216-1796-DFR. California Air Resources Board, Sacramento, CA.

Russell, A.G., McRae, G.J., and Cass, G.R, 1985. The Dynamics of Nitric Acid Production and the Fate of Nitrogen Oxides. *Atmos. Environ.* **19**: 893-903

Schauer, J.J and Cass, G.R., 1998. Source Contributions to Airborne Particles in the San Joaquin Valley during the IMS95 Study. Contract 97-6PM; Draft Final Report. California Air Resources Board, Sacramento, CA.

Seigneur, C., Pun, B., Pai, P, Louis, J.-F., Solomon, P., Emery, C., Morris, R., Zahniser, M., Worsnop, D., Koutrakis, P., White, W., and Tombach, I., 1998a. Guidance for the Performance Evaluation of Three-Dimensional Air Quality Modeling Systems for Particulate Matter and Visibility (Draft). Document Number CP033-98-1. American Petroleum Institute, Washington, D.C.

Seigneur, C., Pun, B., and Zhang, Y., 1998b. Review of Methods for Source Apportionment in Three-Dimensional Air Quality Models for Particulate Matter (Draft). Document Number CP030-98-1. EPRI, Palo Alto, CA.

Seinfeld, J.H. and S.N. Pandis, 1998. Atmospheric Chemistry and Physics, Wiley, NY, NY.

Sillman, S., 1995. The Use of NO_y, H_2O_2, and HNO_3 as Indicators for Ozone-NO_x-Hydrocarbon Sensitivity in Urban Locations. *J. Geophys. Res.* **100**: 14175-14188

Strader, R., Pandis, S., and Lurmann, F, 1998. Final Report. 1995 Integrated Monitoring Study Data Analysis 6.5. Evaluation of Secondary Organic Aerosol Formation in Winter. California Air Resources Board, Sacramento, CA.

Watson, J.G., Dubois, D., Roth, P.M., McDade, C., Hackney, R., Niccum E., Magliano, K., Ranzieri, A., et al., 1998. Field Program Plan for the California Regional $PM_{2.5}/PM_{10}$ Air Quality Study. DRI Document #9801.1D3. California Regional $PM_{10}/PM_{2.5}$ Air Quality Technical Committee.

APPENDIX II

A CONCEPTUAL MODEL FOR OZONE FORMATION IN THE SAN JOAQUIN VALLEY

A CONCEPTUAL MODEL FOR OZONE FORMATION IN THE SAN JOAQUIN VALLEY

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EXECUTIVE SUMMARY

A conceptual model is formulated for the formation and accumulation of ozone (O_3) in the San Joaquin Valley based on the chemical characteristics of the ambient atmosphere and the physical transport and removal processes observed during the San Joaquin Valley Air Quality Study (SJVAQS) / Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) of 1990.

Exceedances of the one-hour National Ambient Air Quality Standard (NAAQS) of 120 ppb were observed during the field program in urban areas. Based on the data from the SJVAQS / AUSPEX, both urban and rural areas will have difficulty meeting the 8-hour average O_3 NAAQS of 80 ppb that was promulgated in 1997.

O_3 concentrations are typically higher in the southern part of the San Joaquin Valley. VOC sources are also more abundant in the southern part of the San Joaquin Valley. Vehicular emissions are observed at the San Francisco Bay Area sites and biogenic influences are observed at the rural sites. NO_x concentrations tend to be more variable because of local emissions. High concentrations of O_3 and VOC are also observed aloft. During the night, O_3 aloft (up to 100 ppb) is preserved because the formation of the inversion layer insulates the aloft O_3 from the titration effects of surface NO emissions. The VOC mix aloft also tends to be more chemically aged than the surface mixture, especially in the morning. Aloft concentrations of NO_x are frequently below instrument detection limit, especially in areas of high O_3.

The key transport process seems to be aloft transport during the night, as surface winds are weak (< 2 m / s). The nocturnal jet (100 – 400 m a.g.l.) carries pollutants towards the Southeast at speeds of up to 30 m / s. Tracer studies show that materials released in the San Francisco Bay Area reach the southern tip of the San Joaquin Valley in 20 to 30 hours. The mountains prevent any significant ventilation of the valley air. Therefore, O_3 and precursors tend to be carried over from one day to the next, especially in the southern part of the valley, where the carry-over burden can reach up to 70 to 100 ppb O_3 (aloft concentrations at night).

The mixing layer grows during the day, entraining aloft O_3 carried over from the night before. However, the large-scale subsidence that characterizes the O_3 episode

meteorology limits the mixing layer height, enhancing further buildup of pollutants during an episode.

Dry deposition of O_3 was studied in the California Ozone Deposition Experiment (CODE). O_3 deposition velocity is highest during the day, and dry deposition may remove up to 3000 tons O_3 per day. The significance of dry deposition for precursors and products is unknown at this point. Wet deposition is not expected to be an important flux in the San Joaquin Valley during summer due to the dry weather associated with O_3 episodes.

The high O_3 concentrations observed in the San Joaquin Valley result both from the transport of O_3 and precursors from upwind locations, and the local production of O_3 in urban areas within the valley. Upwind areas, including the San Francisco Bay Area and the Sacramento Valley, may contribute to same-day O_3 in the northern part of the San Joaquin Valley. In addition, efficient aloft transport by the nocturnal jet distributes pollutants from these upwind source areas throughout the San Joaquin Valley. VOC and NO_x emitted from urban areas within the San Joaquin Valley also add significantly to the O_3 concentrations observed downwind from Fresno and Bakersfield.

One of the key questions that need to be addressed is the sensitivity of O_3 to precursors VOC and NO_x in different parts of the San Joaquin Valley. Current information indicates that O_3 tends to be VOC-sensitive in the San Francisco Bay Area and NO_x-sensitive in most of the San Joaquin Valley. Such analyses need to be repeated to study the sensitivities of 8-hour average O_3 concentrations. Further development and evaluation of three-dimensional models will be useful for determining the influences of point sources and the possible interactions between O_3 and particulate matter.

1.0 BACKGROUND

1.1 The Ozone Problem in the California Central Valley

Summer ozone (O_3) air pollution is a serious problem in the California San Joaquin Valley. With the exception of the Los Angeles area, the San Joaquin Valley records some of the highest O_3 concentrations in the United States. For example, between 1984 and 1986, the San Joaquin Valley exceeded the National Ambient Air Quality Standard (120 ppb, averaged over 1 hour) an average of 75 times per year. In 1997, EPA established a new NAAQS for O_3 of 80 ppb, 8-hour running average. Based on the data from the O_3 episodes during SJVAQS/AUSPEX, several sites in the San Joaquin Valley are out of compliance with the new O_3 NAAQS (Chow et al., 1998).

1.2 SJVAQS / AUSPEX

The San Joaquin Valley Air Quality Study (SJVAQS) and Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) were two components of a comprehensive study to address the issue of poor air quality in the California San Joaquin Valley. The comprehensive study involved: (1) a large-scale air quality measurement program, (2) analyses of the causes of poor O_3 air quality, and (3) the development and application of a regional scale air quality model (SAQM). The SJVAQS focused on determining the causes of the exceedances in the San Joaquin Valley of the O_3 NAAQS. AUSPEX was intended to develop a comprehensive model addressing O_3, aerosol, visibility, and acid deposition issues and to obtain a high-quality data base for model evaluation and application (Blumenthal, 1993). To support these objectives, a field program was conducted during an eight-week period from July 9, 1990 to August 24, 1990. 14 intensive days, which corresponded to high O_3 episodes, were selected for detailed measurements. The technical objectives of the field program are listed as follows (Blumenthal et al., 1997):

- Characterize the three-dimensional meteorological transport within the San Joaquin Valley, between the San Joaquin Valley and surrounding air basins, and among the surrounding air basins on the days leading up to and during O_3 episodes.
- Characterize the spatial and temporal patterns and frequency distributions of O_3, O_3 precursors, and PM concentrations in the study area
- Characterize pollutant fluxes
- Characterize emissions
- Characterize dynamic atmospheric processes in the study region
- Provide input and evaluation data for air quality and meteorological models, including initial and boundary conditions
- Develop an improved understanding of key chemical processes and intermediate species

Figure 1-1 shows the SJVAQS / AUSPEX study domain (Ranzieri and Thuillier, 1994). The SJVAQS provided for a dense monitoring network within the domain of the San Joaquin Valley, which ended just south of Sacramento. The AUSPEX study extended the spatial coverage to the coastal cities of San Francisco, Monterey, and San Luis Obispo and to the Pacific Ocean. The northern and southern boundaries were extended to Sutter Butts (north of Sacramento) and the Tehachapi mountains, respectively. The Mojave desert was also included in the southeastern part of the AUSPEX domain.

Surface air quality data were collected at 59 sites to supplement routine data from over 70 stations. 41 of these sites measured O_3, nitric oxide (NO), nitrogen oxides ($NO_x = NO + NO_2$), winds (speed and direction), and temperature. The remaining sites measured at least O_3 and winds. Peroxyl acetyl nitrate (PAN) was measured continuously at 10 sites. Two to four samples of volatile organic compounds (VOC) (including carbonyl compounds) were taken at 36 sites and analyzed in laboratories. 10 of the O_3 sites also measured PM mass and PM-2.5 and PM-10 chemistry. Light scattering and light absorption were measured at two sites. In total, air quality and / or

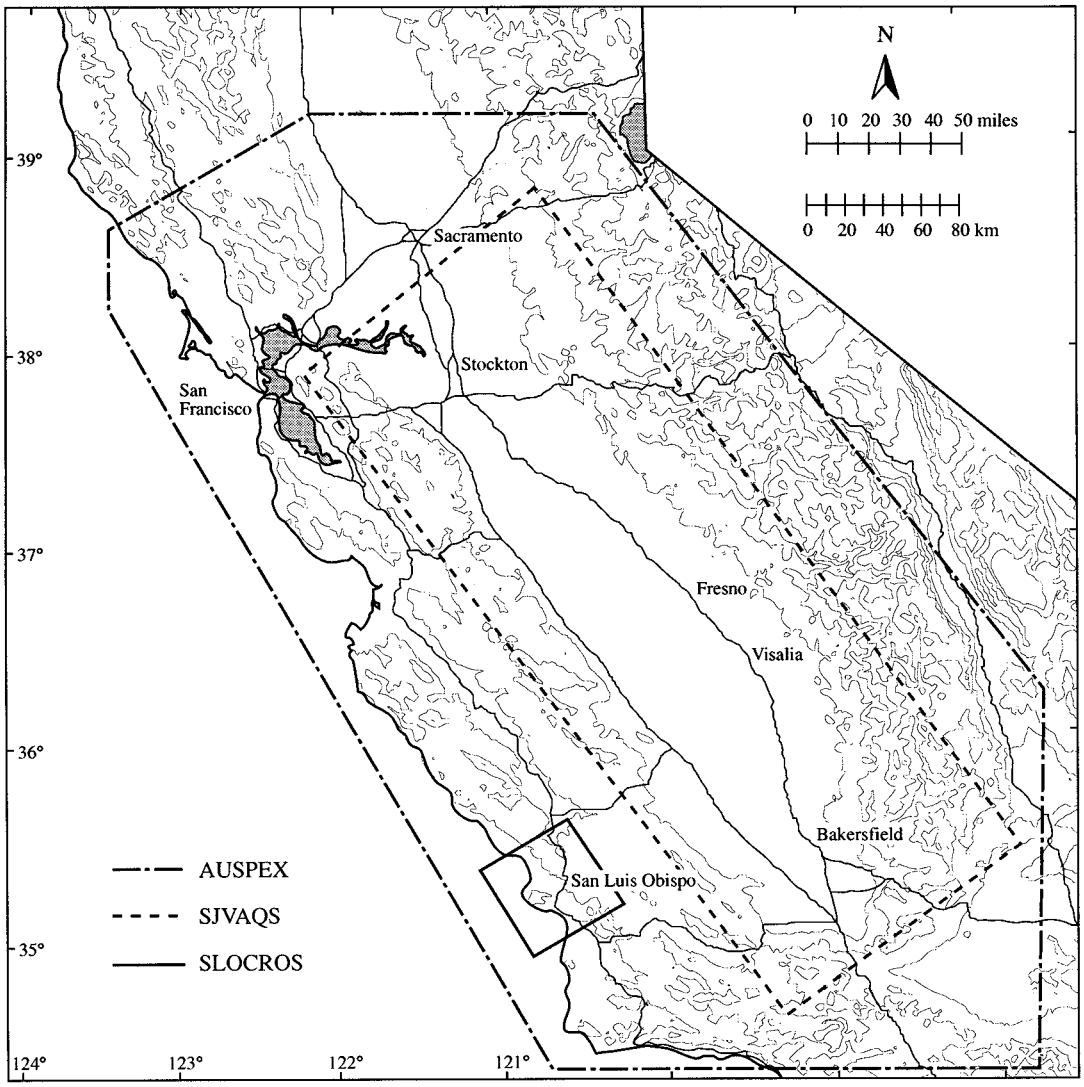


Figure 1-1. The Study Domain of SJVAQS / AUSPEX. (Source: Ranzieri and Thuillier, 1994)

meteorological data were collected at over 300 surface sites. Measurements that require collection of samples and subsequent laboratory analyses (e.g., VOC, PM chemistry) were only obtained on intensive episode days.

Point measurements of upper air meteorology were obtained from 49 sites. Continuous (hourly-averaged) upper wind measurements were taken using radar profilers (7) and Doppler acoustic sounders (14) throughout the study period. The range of the radar profilers was 2 km a.g.l., while that for the sounders was 500 m. 29 balloon sounding sites were also set up to take 4 to 8 (typically 6) soundings per day of winds and temperature during O_3 episodes.

On intensive days, up to 9 instrumented aircraft measured both meteorology and air quality aloft. Each aircraft made two to three flights per episode day. Different aircraft carried different instruments. Measurements of O_3, NO, NO_x, NO_2, VOC, light scattering, temperature, and dew point were obtained within the San Joaquin Valley to document the distribution of pollutants and offshore to characterize the boundary conditions.

Tracer studies were performed on intensive days to characterize the transport patterns from major source areas within and upwind of the San Joaquin Valley. Perfluorocarbon gas tracers were released from Bakersfield, Fresno, Hayward, Modesto, Pittsburg, and San Jose and measured with a surface monitoring network. The data obtained in tracer studies were also valuable for evaluating the performance of meteorological models.

1.3 Objectives of This Study

The main objective of this study is to develop a conceptual model for O_3 formation, transport, and accumulation in the California San Joaquin Valley using primarily the information obtained during SJVAQS / AUSPEX of 1990. This conceptual model is a qualitative description of the physical and chemical processes that govern the formation of O_3, which, to the extent possible, is supported by quantitative information. Through the identification of the key processes and key knowledge gaps, the conceptual

model for O_3 serves as a tool for guiding future research and mathematical model development.

1.4 Organization of This Report

Section 2 contains a discussion of the methodology used in the development of the conceptual model. The chemical transformations that govern the formation of O_3 in the San Joaquin Valley are presented in Section 3. Section 4 summarizes the relevant transport and removal processes. The conceptual model is synthesized in Section 5. In the conclusion (Section 6), answers are provided to the key questions raised in the scope of work. Several recommendations are also presented in Section 6.

2.0 METHODOLOGY

The methodology used to develop the conceptual model for O_3 formation in the California San Joaquin Valley is similar to the methodology developed for and applied to the development of the conceptual model for PM in the same area (Pun and Seigneur, 1998). This methodology is data-driven and works backwards in time. The two components of the analysis are:

- An analysis of the chemical transformations
- An analysis of the physical transport processes

The atmospheric concentrations of O_3 and associated chemicals, such as VOC, NO_x, and PAN, provide the starting point for formulating a conceptual model. O_3 precursors may be transported over great distances to produce O_3 at a given location. Therefore, the transport processes of both O_3 and O_3 precursors are considered. The two analyses are then combined into the conceptual model.

Figure 2-1 illustrates the framework of the analysis for chemical transformations. O_3 is produced in the atmosphere from the reactions of VOC and NO_x. These compounds are emitted from anthropogenic and biogenic sources. This differentiation is particularly important for VOC since biogenic sources contribute significantly to the atmospheric burden of VOC at some San Joaquin Valley sites, particularly during summer. A major question is the sensitivity of O_3 concentrations to the availability of NO_x and VOC. Several measurement and modeling techniques are available to examine the relative sensitivity of ozone to its precursors (e.g., Sillman, 1995; Blanchard et al., 1995). Figure 2-2 illustrates the major chemical pathways of the VOC / NO_x / O_3 system. If VOC concentrations are low (VOC-sensitive regime), OH radicals are available to react with NO_2 to form nitric acid (HNO_3). If NO_x concentrations are low (NO_x-sensitive regime), HO_2 radicals tend to recombine to form H_2O_2 rather than to react with NO. Therefore, the ratio of HNO_3 and H_2O_2 may be used as an indicator of the VOC / NO_x sensitivity of

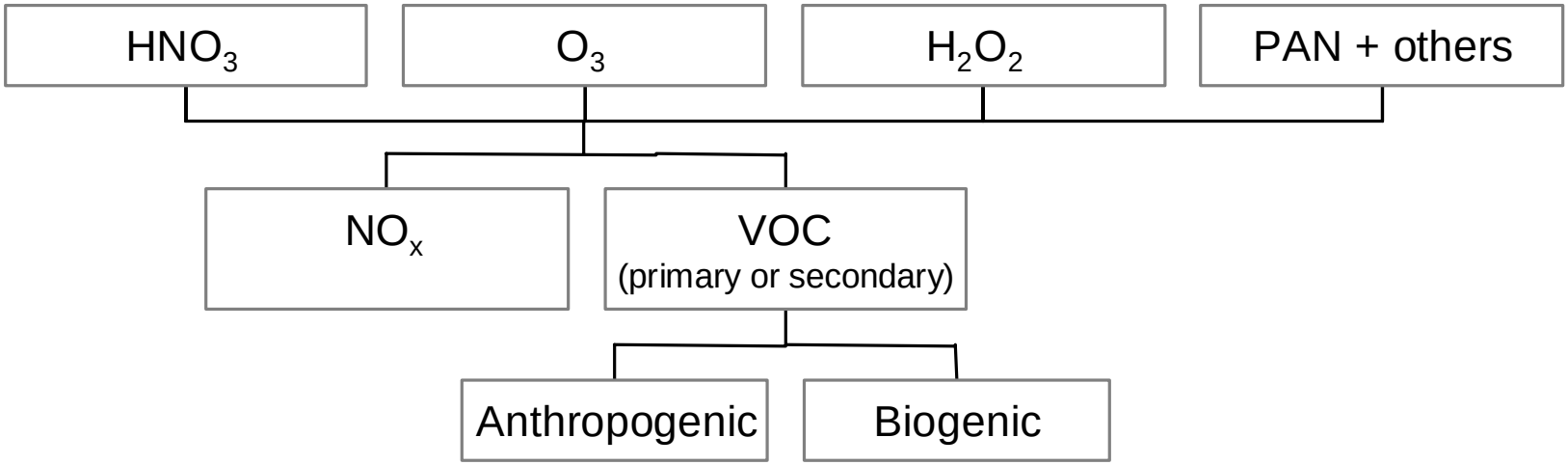


Figure 2-1. Framework for the Analysis of Chemical Transformations Leading to Ozone Formation in the San Joaquin Valley

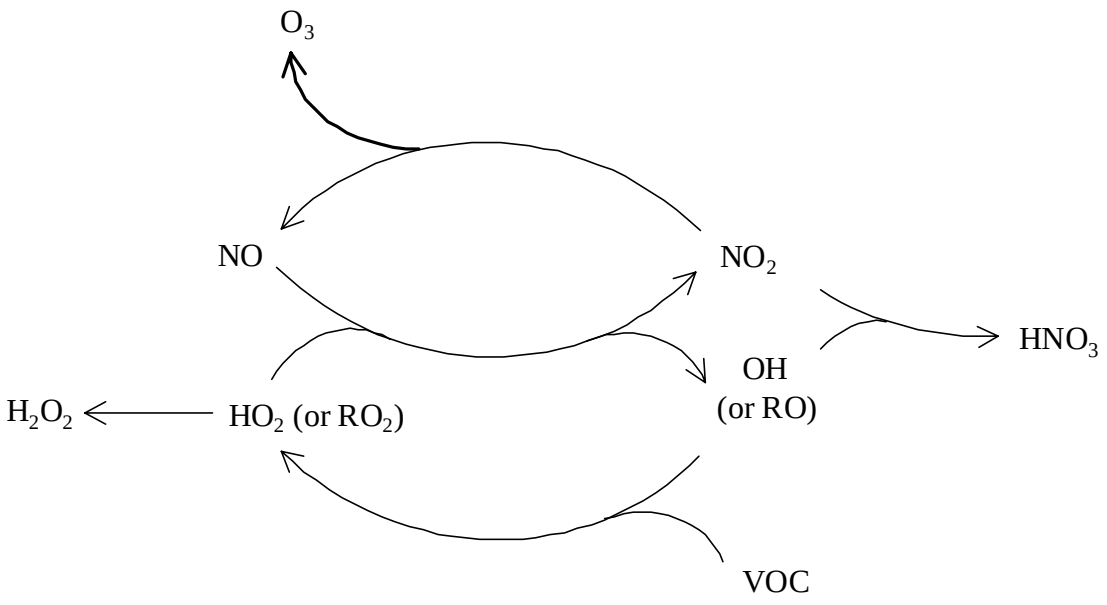


Figure 2-2. Simplified Description of Photochemical Smog Formation Showing the Two Major Interacting Cycles (NO/NO_2 and OH/RO_2 or OH/HO_2) and the Two Major Sinks for Radical Chain Termination: H_2O_2 (NO_x Sensitive) and HNO_3 (VOC Sensitive)

the system. Other indicators that have been used include NO_y, $HCHO/NO_y$, $O_3/(NO_y-NO_x)$, and $(NO_y-NO_x) / NO_y$ (Lu and Chang, 1998). The sensitivity characterization provides information regarding which pollutant could be controlled to obtain the maximum benefits in O_3 reduction. To extrapolate this information to the specific sources to control for O_3 reduction in a particular area, additional information is needed to define the source-receptor relationship of the ozone precursors. At a location mostly affected by local emissions, control of local sources will achieve the desired reductions in precursors and ozone. However, at some receptor locations, upwind sources may need to be targeted for controls. Upwind areas may contribute to ozone at a given location via surface and aloft transport. Since the range of aloft transport is typically farther than surface transport, an upwind source may be hundreds of miles away from a receptor site affected by such transport, and a regional strategy is necessary in this case to address high O_3 concentrations. The sensitivity of O_3 concentrations to NO_x and VOC may differ for local and distant upwind sources; therefore, regional strategies are likely to be more complex than local strategies.

Figure 2-3 presents the framework for the analysis of the physical processes. The transport and removal processes that are important at the scales of the San Joaquin Valley include horizontal advection at the surface and aloft, vertical mixing, dry deposition, and wet deposition. Wet deposition is not very important in the summer in the San Joaquin Valley and can be ignored. Dry deposition is an important removal process for some precursors as well as for O_3. Vertical mixing is a strong function of the diurnal cycle of the boundary layer height and other phenomena such as updraft and convective cells. Advection varies significantly between the surface and the free troposphere. Above 1000 m, the wind flow is governed by synoptic (or sub-synoptic) patterns. Although high mountain ranges lead to some channeling effects, terrain effects are generally limited at this height. Between about 200 m and 1000 m, the wind flow is strongly affected by the local terrain and the related local meteorology. Local pressure gradients, channeling, mountain-valley effects, and land/sea breezes near the coast interact with the synoptic patterns to create wind flows that vary significantly with time and location. This layer is typically decoupled from the surface at night and significant advective transport can take place with little interaction with fresh emissions during the night. The wind flow at the

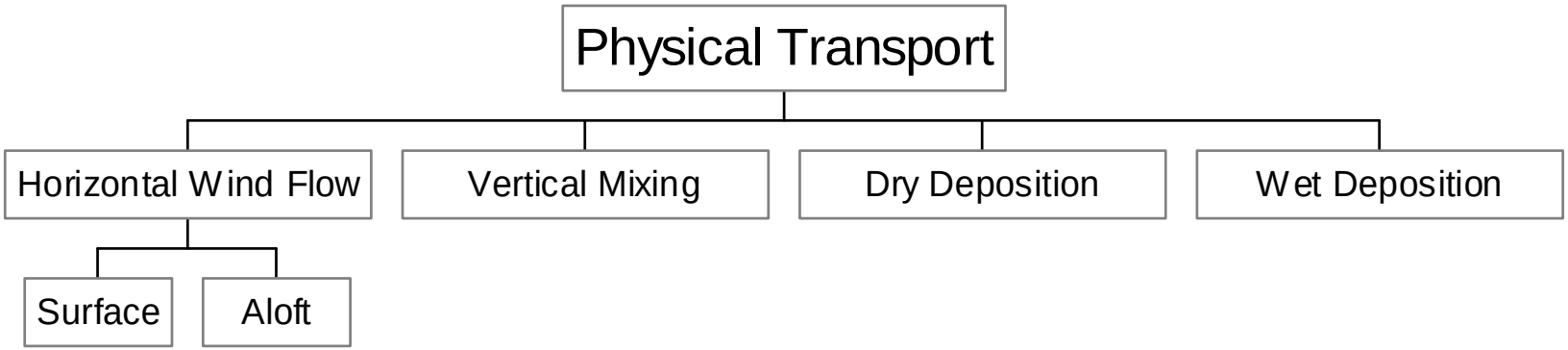


Figure 2-3. Transport Processes Important for the Formation and Accumulation of Ozone in the San Joaquin Valley.

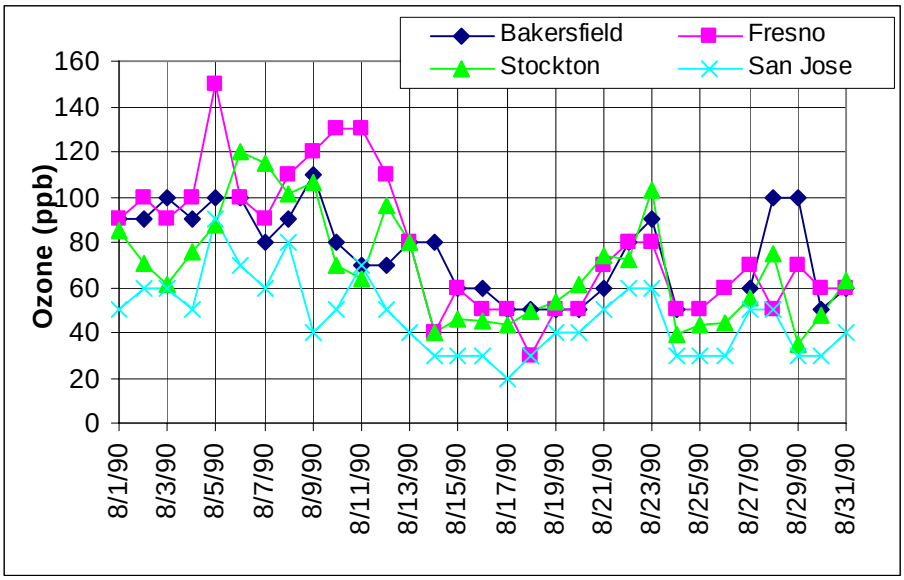
surface is coupled to the 200 – 1000 m layer during the day. However, the surface layer is subject to a strong thermal inversion at night and calm winds and/or drainage flows are common. An analysis of physical transport processes must unravel how these various mechanisms transport O_3 and its precursors to and within the area of interest, i.e., here the San Joaquin Valley.

3.0 CHEMICAL TRANSFORMATIONS

3.1 Temporal Trends

The time series of daily maximum one-hour average O_3 concentrations at a few selected sites are shown in Figure 3-1. There are some variations in the maximum 1-hour concentration time series among monitoring sites. For example, O_3 concentrations decreased at Stockton and Bakersfield after peak concentrations on August 9, while the O_3 concentrations continued to increase in Fresno. On the other hand, O_3 also seems to be a regional problem. This is clearly shown in the daily maximum 8-hour average concentrations in Figure 3-2. Urban and non-urban sites in different parts of the San Joaquin Valley exhibited similarities in time series trends, especially during the second half of August. These similar trends suggest a strong, common meteorological driving force behind O_3 formation. In general, the maximum hourly O_3 concentrations correlate well with the maximum 8-hour average O_3. At urban sites, the 8-hour average concentrations can be 20 to 30 ppb lower than the 1-hour maximum when O_3 concentrations are above 100 ppb (e.g., in Fresno). On the other hand, at rural sites such as Sequoia, the daily maximum 8-hour concentrations of ozone are very similar (< 5 ppb difference) to the daily one-hour maximum concentrations. As a result, while urban areas exceed the old, one-hour average NAAQS of 120 ppb, both urban and rural areas may exceed the new, 8-hour average NAAQS of 80 ppb (Figure 3-2).

The diurnal variations of O_3 at several sites have been analyzed by Chow et al., (1998), as shown in Figure 3-3. At most sites on the valley floor, the build-up process started at 7 or 8 Pacific Daylight Time (PDT). O_3 peaked in the afternoon, and diminished throughout the night. The early accumulation of O_3, at least at some sites, may be due to the carry-over of O_3 from the previous day, as photochemical production of O_3 is expected to be slow early in the morning. The time of maximum O_3 ranged from 2 p.m. to 6 p.m. Early afternoon O_3 maxima were associated with rural locations affected by mixing from aloft and urban locations. Late afternoon O_3 maxima were associated with locations downwind of an urban source of precursors. For example, on August 6, 1990, O_3 peaked at 6 p.m. at Crows Landing, which could be an indication of afternoon



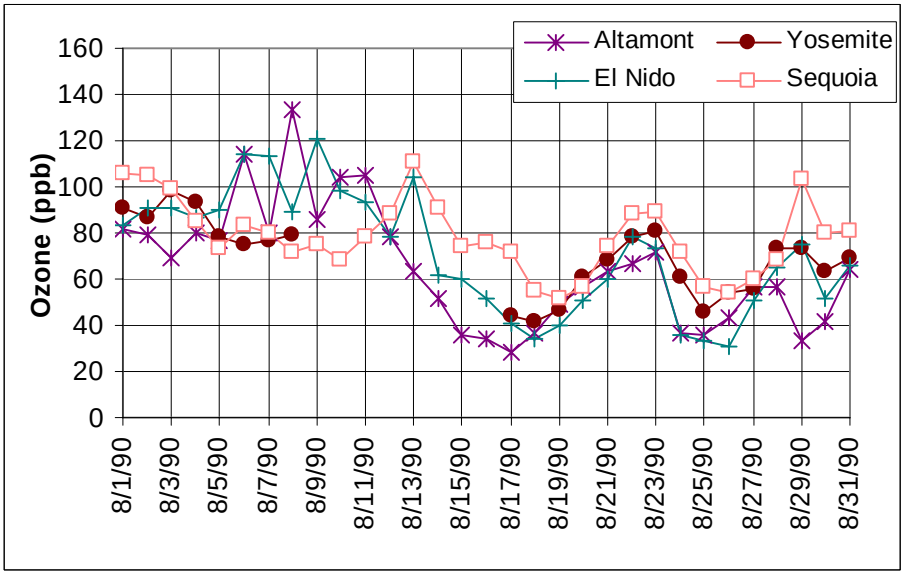
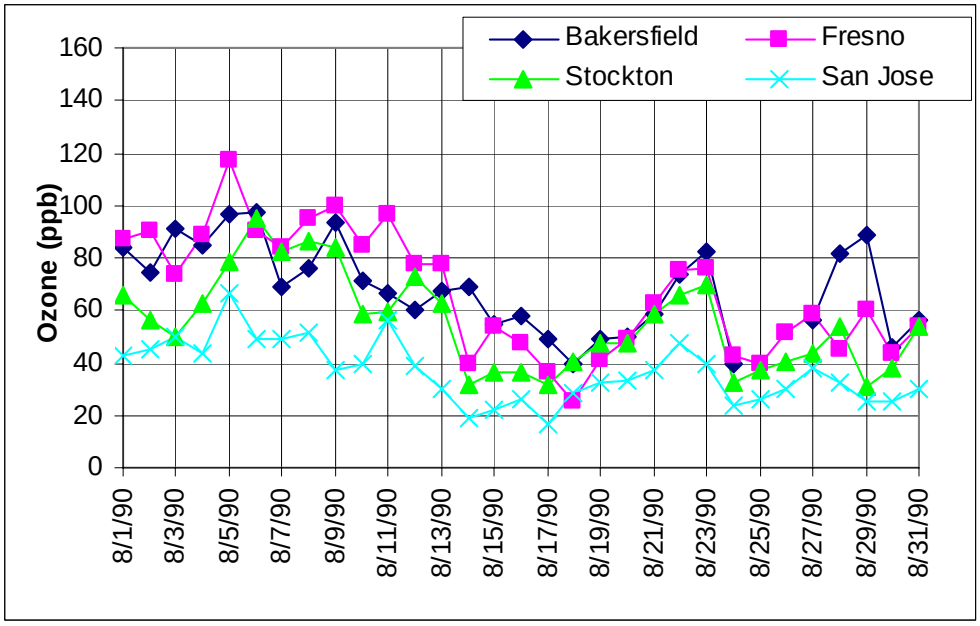


Figure 3-1. Daily Maximum One-Hour Average Ozone Concentrations at Selected Sites. (Data Source: CARB, 1998)



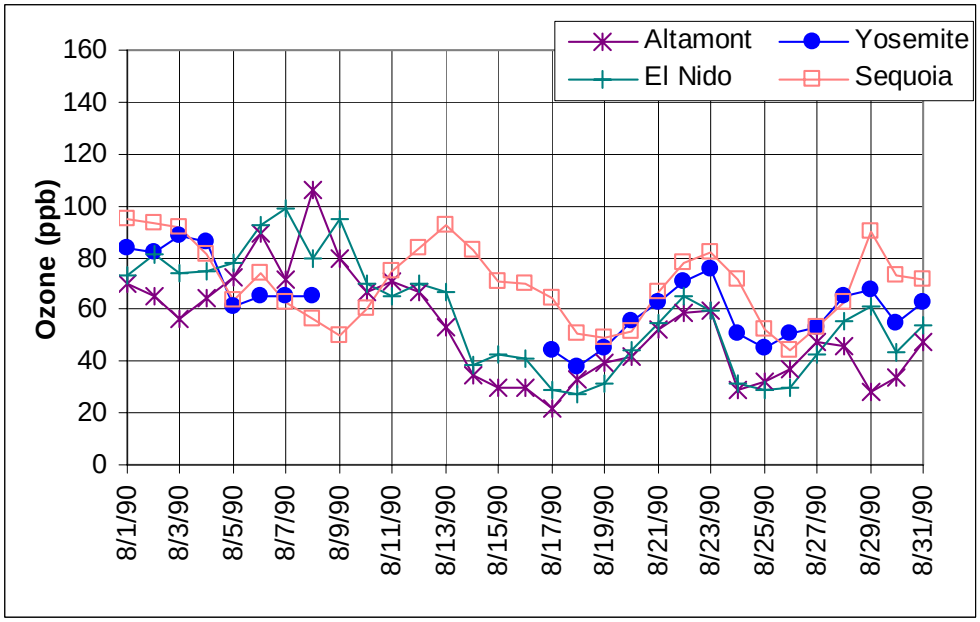


Figure 3-2. Daily Maximum Eight-Hour Average Ozone Concentrations at Selected Sites. (Data Source: CARB, 1998)

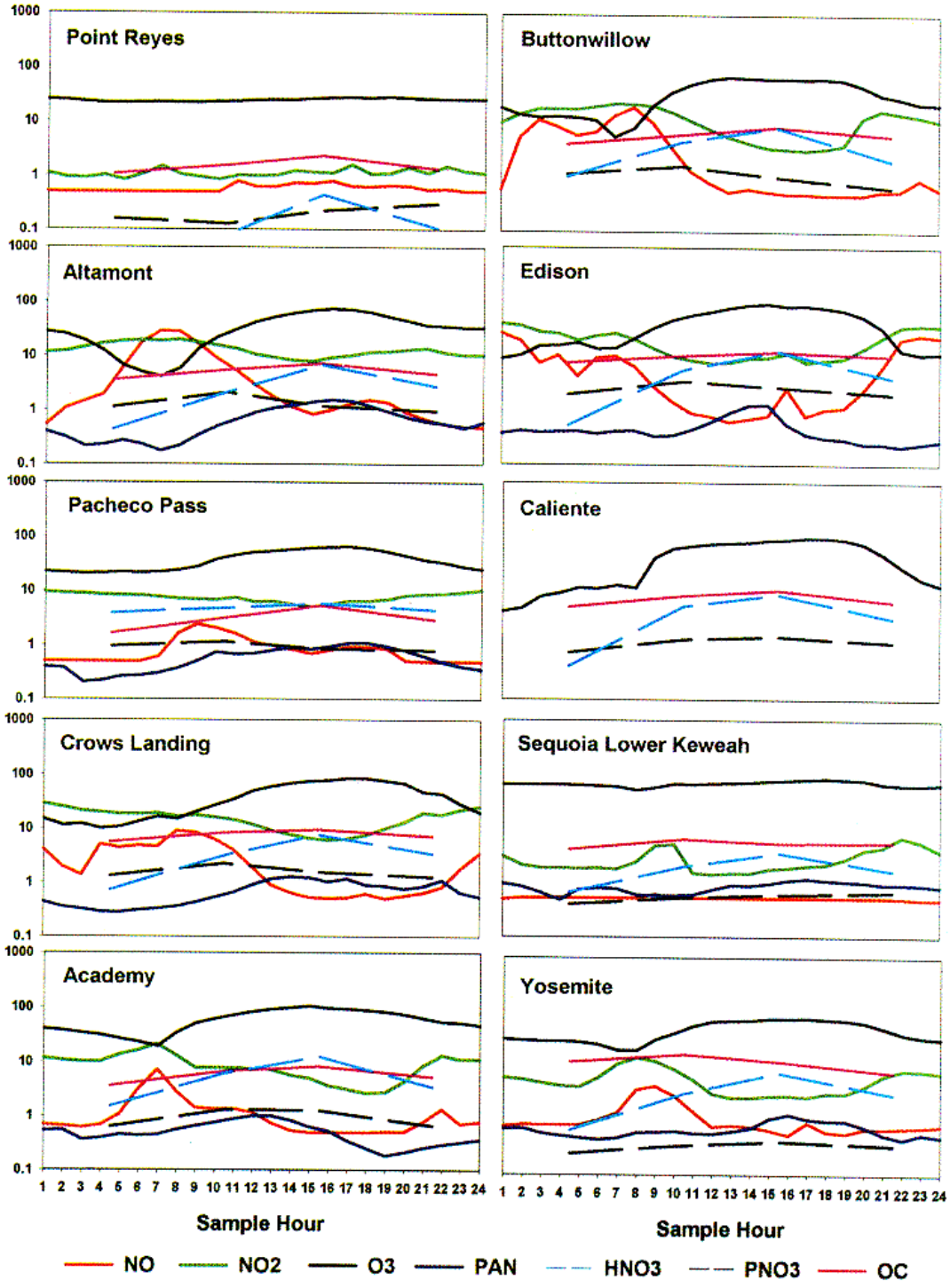


Figure 3-3. Diurnal Patterns of Concentrations of NO, NO_2, O_3, PAN, Total Particulate Nitrate, and OC (Source: Chow et al., 1998; reprinted with permission from Elsevier Science)

transport from the San Francisco Bay Area and northern Valley cities. Ground level O_3 typically decreased throughout the evening due to the lack of photochemical production and continuous scavenging by NO_x emitted within the surface layer.

Due to night-time decoupling of the inversion layer (the bottom 100 m near the surface), O_3 that was produced near the ground may be trapped aloft during the evening. Insulated from the scavenging effects of ground level NO_x emissions, aloft O_3 may be preserved during the night. Figure 3-4 illustrates that the nighttime aloft O_3 concentrations ranged from 60 to > 100 ppb between episode days (Blumenthal et al., 1997). The high nighttime O_3 concentrations observed at the elevated site of Sequoia Lower Keweah may be an indication that this site was sampling air above the inversion layer. As the boundary layer grew during the day, the aloft O_3 may have mixed into the surface layer, thus contributing to the observed ground-level O_3. The O_3 carried aloft generally increased throughout the episode on 3-6 August 1990. In the south end of the valley, the carry-over burden increased from 65 - 75 ppb on August 4 to 80 - 100 ppb on August 6, 1990. On August 5 and 6, the average O_3 concentrations in the morning boundary layer were well below the prior afternoon averages throughout the San Joaquin Valley due either to ventilation of the aloft O_3 overnight or depletion of O_3 in the surface layer.

Compared to O_3, the concentrations of NO_x were more variable and more susceptible to the effects of local sources. Surface levels of NO_x early in the morning are good indicators of stagnation in the source areas. During the early morning hours, the NO_x concentrations (mostly NO_2 due to the titration effect of O_3 from the previous day) were typically 30 to 100 ppb in the urban areas and 10 to 20 ppb in the rural areas (Blumenthal et al., 1997). The NO fraction of total nitrogen was highest during the 0700 – 1200 PST sampling period, when emission rates were high. During the afternoon, NO_x concentrations were generally low, though they probably continued to fuel O_3 production, especially at urban sites where most of the afternoon NO_x was expected to be NO_2. The NO_x measured in downwind areas were postulated to be interference from other oxidized nitrogen species such as PAN and HNO_3 (Blumenthal et al., 1997).

In the morning, most of the NO_x was confined to a surface layer extending up to 300 m above the ground level. Little NO_x was carried over above the surface radiation

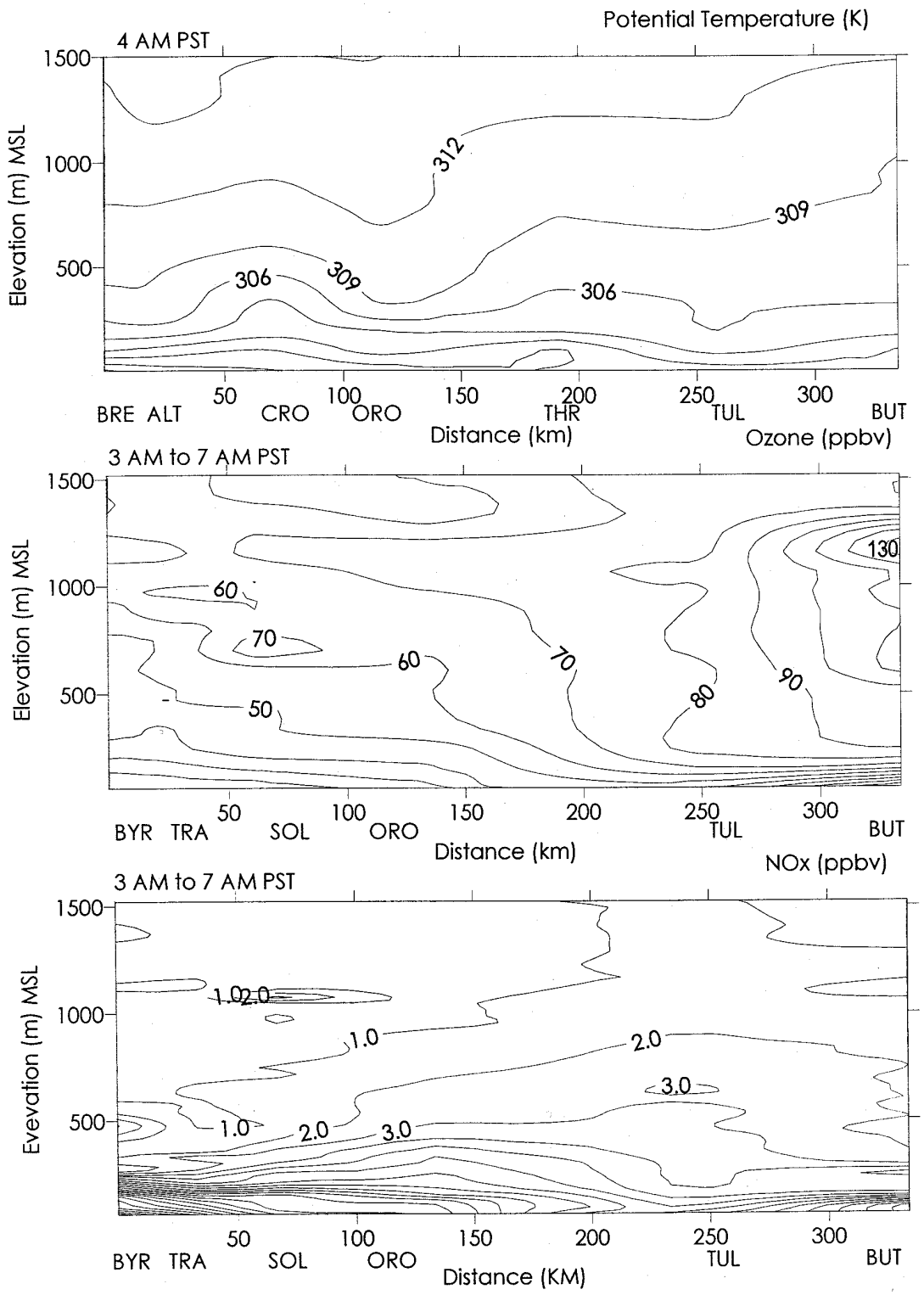


Figure 3-4. West Valley North-South Cross Section from Byron Airport (BYR), Near Brentwood, (BRE), to Buttonwillow (BUT), August 6, 1990, Early Morning. (Source: Blumenthal et al., 1997)

inversion in the morning. Early morning NO_x concentrations were usually 2 ppb or less in the areas of highest O_3 carry-over (Figure 3-4). Since air parcels aloft were expected to be chemically well-aged, the measured morning NO_x aloft was likely to be interference from PAN or HNO_3 (Blumenthal et al., 1997). In the afternoon, the aloft NO_x concentrations could be as high as the surface observations, due to the favorable mixing condition. Therefore, O_3 may be produced aloft as well as near the surface.

PAN and HNO_3 were measured at 10 sites each. PAN was monitored continuously using a Luminol-based chemiluminescence instrument. HNO_3 was collected by a denuder. The concentrations of PAN were lower than those of HNO_3 at most sites, and these compounds typically represented 1 – 9.5% and 1 – 23% of the total measured nitrogen species (NO_y), respectively. HNO_3 typically exhibited peak values at 3 or 4 p.m. PAN also peaked in the afternoon, although the timing of the peak was not as regular. There was no indication that the concentrations of HNO_3 and PAN increased during the multi-day episode (DeMassa et al., 1996). No upper air measurements were made for these compounds.

During the August episode, the VOC concentrations ranged from 40 ppbC at Point Reyes to 785 ppbC at Bakersfield (Magliano, 1996). The temporal patterns of VOC depended strongly on the mixture of sources, and are therefore related to the composition of VOC. In general, urban sites were associated with high aromatic fractions and tended to exhibit high concentrations in the morning due to fresh motor vehicle emissions and low mixing heights. Biogenic emissions, i.e., isoprene (the only biogenic VOC detected), were highest during midday or afternoon. Sites that received much contribution from biogenic emissions exhibited the same diurnal trend. Downwind sites tended to exhibit peak VOC during midday when they received VOC transported from upwind locations. These air parcels were associated with higher levels of formaldehyde and other secondary organic compounds, with sufficient photochemical activity to continue producing O_3 at the downwind sites. No obvious trends were observed for VOC during the O_3 episode in August 1990. However, Blumenthal et al. (1997) noted lower VOC / NO_x ratios on the morning of August 3, 1990 and higher VOC / NO_x ratios on the morning of August 5 during the August 3-6 episode. A possible

explanation is that under a stagnation episode, the VOC/NO_x ratio increases since NO_2 is oxidized to nitrates faster than VOC are oxidized to CO and CO_2.

The VOC concentrations aloft ranged from 14 to 634 ppbC during the August episode. Aloft VOC exhibited less variation from day to day and between morning and afternoon than VOC observations at the surface, possibly because VOC surface concentrations are directly influenced by VOC surface emissions. The composition of the morning and afternoon aloft samples was also similar, with the exception that toluene was more abundant in the morning while the afternoon samples were enriched in formaldehyde, isoprene, ethane, ethene, and propane. A few of the morning samples were taken within the surface layer, while most were collected in the decoupled layer. The morning abundance of toluene was associated with mobile emissions, especially for samples taken within the surface layer. Formaldehyde was more abundant in the afternoon because it is a photochemical reaction product. Isoprene emissions were higher in the afternoon than in the morning due to the effects of temperature on biogenic emissions. Light hydrocarbons, such as ethane, ethene, and propane, are associated with evaporative emissions. Evaporative emissions were probably significant during the afternoon of the San Joaquin Valley summer O_3 episodes because the ambient temperatures were quite high. The results of a chemical mass balance (CMB) (Magliano, 1996) also show that gasoline vapors (evaporative emissions) were contributors to ambient VOC in the afternoon at urban and non-urban sites.

The aloft VOC / NO_x ratios were analyzed (Magliano, 1996) when the concentrations of NO_x were above the detection limit of about 4 ppb. On average, the VOC / NO_x ratios were higher (14) in the morning than in the afternoon (10). Since NO_2 is oxidized to nitrates faster than VOC oxidation to CO and CO_2, the higher morning VOC / NO_x ratios indicated that the morning samples were more aged chemically than the afternoon samples. The aloft air mass was insulated from fresh emissions during the night and early morning, and the night-time reactions of nitrate radical with organic compounds (Smith et al., 1995) played an important role in removing reactive nitrogen species from the air aloft.

3.2 Spatial Trends

During the well-studied August 3-6 episode, two patterns of O_3 distribution were observed. On the first three days, high O_3 values were observed downwind of major Central Valley cities, including Sacramento, Bakersfield, and Fresno. On the last day of the episode, high O_3 concentrations were observed downwind of Bakersfield and in the northwestern part of the San Joaquin Valley in the Tracy / Stockton area later in the afternoon (6 p.m.). Local emissions from the San Joaquin Valley cities (especially on August 3-5) as well as emissions from the San Francisco Bay Area (e.g., August 6) played a key role in the formation of O_3 in these downwind areas. The diurnal profiles varied with locations. Sharp afternoon peaks of very high concentrations were typically observed at urban sites and sites downwind from urban sites, where evening concentrations fell to below 20 ppb. At rural sites, the observed ranges of O_3 values were typically smaller. For example, at Sequoia, daytime peaks were about only 30 to 40 ppb above nighttime concentrations. On some days, the nighttime O_3 concentrations remained as high as 70 ppb (e.g., Sequoia on August 2, 1990), probably due to the lack of local NO emissions for O_3 titration. Because of the site's elevation, these high nighttime concentrations may be indicative of the extent of aloft O_3 preservation during the night. When the nighttime concentrations were high at Sequoia, the day-time peak, as high as 110 ppb, occurred late in the afternoon (6 – 7 pm). On other days, the nighttime concentrations dropped to below 40 ppb, O_3 accumulation started earlier in the day and the peak concentrations occurred between 3 to 6 p.m. These days may represent an alternative (perhaps more favorable) mixing condition. There was very little O_3 diurnal variation at Point Reyes, located upwind of the San Francisco Bay Area. Point Reyes, considered a boundary site, observed lower O_3 concentrations than the sites within the valley.

Some of the afternoon boundary layer average O_3 concentrations appeared to be higher than the surface maxima (e.g., on August 4, 1990). Blumenthal et al. (1997) postulated a different air mass at the surface which had less O_3 production potential than the aloft air mass. Another possible explanation is that O_3 production aloft was more efficient than at the surface. Several investigators (e.g., Dickerson et al., 1997; Jacobson,

1998) have alluded to the role of particles in photochemistry through their effects on UV irradiance. Although PM is generally not considered a severe problem in the summer in the San Joaquin Valley, its role, if any, on the photochemical production of O_3 needs to be investigated.

The day-to-day O_3 carry-over burden increased from the north to the south during the August episode. The aloft O_3 in the north end of the valley was 40 to 60 ppb, slightly over clean air values. These values probably did not contribute significantly to the O_3 concentrations observed in the afternoon, which can be up to 140 ppb. In the south end, the carry-over burden of O_3 increased to 70 – 100 ppb. These concentrations of aloft O_3 were comparable to the observed afternoon O_3 (80 to 100%).

Blumenthal et al. (1997) observed the highest total nitrogen (NO_y) concentrations at Buttonwillow and Edison (40 ppb on average), whereas low total nitrogen concentrations were observed at Point Reyes, Sequoia, Yosemite, and Pacheco Pass (10 ppb on average). NO_x concentrations were typically high at receptor sites of urban primary emissions, e.g., Altamont Pass, Buttonwillow, Crows Landing, and Edison. Secondary nitrogen compounds, such as PAN and HNO_3, dominated the nitrogen balance at Academy (downwind of Fresno), Pacheco Pass, Sequoia, and Yosemite, i.e., sites affected by chemically aged air masses from urban areas.

According to the analysis of Magliano (1996), the highest VOC concentrations were found at the southern San Joaquin Valley sites, including Bakersfiled, Oildale, Taft, and Visalia, and at urban sites in the Bay Area (e.g., Pittsburgh, San Jose, Livermore, Richmond). The southern San Joaquin Valley sites were influenced by hydrocarbon emissions from oil production in the area, and the abundance of alkanes in the observed composition supported that conclusion. Relatively high concentrations of aromatic compounds found in the Bay Area VOC mixture were consistent with vehicular emissions. High isoprene emissions at Sequoia and Yosemite accounted for their high olefin fractions. Carbonyl fractions were typically higher downwind from urban areas than in urban areas, on account of the more chemically-aged air masses that these sites received. Rasmussen (1992) confirmed the abundance of oxygenated species (aldehydes, ketones, alcohols) at these sites.

CMB results (Magliano, 1996) indicated the prevalence of motor vehicle exhaust (35 – 70%) in urban areas at all times. Contributions of oil production at the southern part of the valley were consistent with industrial activities in the area. The presence of oil production contributions outside of the southern San Joaquin Valley reflected the similarity of the profiles used for oil production emissions and those of refinery emissions, liquid petroleum gas, etc. Biogenic fractions (10 – 15%) were much lower from the CMB analyses than the inventory values at Yosemite and Sequoia (> 50%). Possible reasons for the discrepancy may be the efficient chemical removal of biogenic organic compounds due to their high reactivity, transport of anthropogenic and secondary compounds to the forest sites, or uncertainties in the emissions inventories.

The VOC / NO_x ratios were found to be highest (22 to 40) at the southern San Joaquin Valley sites, which had high VOC concentrations, and at the forested sites with low NO_x concentrations. Morning ratios averaged 9.2 at Bay Area sites, 9.6 at rural sites, and 16.5 at southern Valley sites.

During the August episode, many of the highest aloft VOC concentrations were recorded over Lodi at the northern edge of the San Joaquin Valley. The variations among other aloft sites were less than the surface observations. In general, VOC concentrations aloft in the San Francisco Bay Area exceeded those within the Valley. These samples also contained the highest aromatic and unidentified fractions. (Note that on average 39% of the aloft samples contained unidentified hydrocarbons, compared to 27% of the surface samples.) The highest alkane and alkene fractions were found over the southern San Joaquin Valley and over Mariposa, respectively. The most abundant species aloft were similar to the most abundant species at the surface. The findings that 2,4,4-trimethylpentane (Blumenthal et al., 1997) and olefins (Rasmussen, 1992) were present in larger quantities aloft than at the surface is not explained by the current understanding regarding their sources and reactivities. The abundance of ketones aloft was consistent with the assumption that the air aloft was more chemically aged than surface air.

3.3 VOC / NO_x Sensitivity

O_3 concentrations above NAAQS levels are observed in the San Joaquin Valley. Therefore, it is essential to understand the dynamics of the VOC / NO_x / O_3 system in the San Joaquin Valley to determine whether O_3 formation is sensitive to VOC or NO_x concentrations. Since large-scale experiments cannot be performed to alter the ambient VOC / NO_x concentrations and to monitor the resulting O_3 response, the traditional methodology to investigate VOC / NO_x sensitivities involves computer experiments to simulate alternative input scenarios and the resulting O_3 concentrations (e.g., the Empirical Kinetic Modeling Approach or EKMA). Alternatively, indicator species and ratios can be identified from computer simulations (Sillman, 1995) so that ambient measurements of these species or ratios may indicate the sensitivities of the system. Lu and Chang (1998) studied the response of the San Joaquin Valley simulation to 50% reductions in VOC and NO_x using SAQM, and evaluated the indicator approach of Sillman (1995). They found that several indicators may be used to distinguish the NO_x / VOC sensitivity in the San Joaquin Valley. These include NO_y, HCHO/NO_y, H_2O_2/HNO_3, O_3/(NO_y-NO_x), and (NO_y-NO_x)/NO_y. According to the results of the simulations, in over 90% of the model domain, the peak 1-hour O_3 concentrations would be sensitive to NO_x reductions or combined NO_x and VOC reductions for August 5, 1990. (The sensitivities of the so-called "transition areas" have not been determined. These areas are lumped into the combined NO_x and VOC reduction areas.) For example, in areas downwind of Fresno and Bakersfield, where peak O_3 concentrations exceeded 120 ppb, a 50% reduction of NO_x results in a maximum reduction of 30 ppb and 18 ppb of O_3, respectively. On the other hand, VOC-sensitive regions, such as the San Francisco Bay Area, may respond negatively to NO_x reductions. (In a study conducted by the Bay Area Air Quality Management District (Martien and Umeda, 1993), NO_x controls placed on utility boilers in the Bay Area result in an increase in O_3 in the urban area, while O_3 benefits of roughly equal magnitude are observed downwind.) This negative response in the vicinity of the Bay Area may result in violations of the NAAQS if NO_x controls are implemented. Different spatial and temporal O_3 distribution patterns suggested that the meteorology on August 6 may be different from the previous episode days, with more

significant transport from the San Francisco Bay Area resulting in late afternoon O_3 peaks in the northern part of the San Joaquin Valley. The sensitivity of O_3 to its precursors needs to be verified for this meteorology scenario.

Using a different methodology, Blanchard et al. (1995) investigated the VOC / NO_x sensitivity issue by developing a measure for the reaction extent for smog production. The extent of the reaction reaches a maximum of unity when the concentration of NO_2 approaches zero, denoting NO_x-limitation. During the episode days in August 1990, the extent of the O_3 production reaction was frequently unity at Academy (downwind of Fresno). Therefore, the O_3 concentrations at this site would be NO_x-sensitive according to the methodology of Blanchard et al.

The results of the two studies discussed above were consistent with the findings of the Policy Committee of SJVAQS (San Joaquin Valley Air Quality Study Policy Committee, 1996), which were based on modeling simulations conducted at the California Air Resources Board.

It is important to note, however, that the sensitivity of O_3 to precursors may vary both spatially and temporally. For example, there is some preliminary evidence based on data analysis (Altshuler, 1998) and modeling (Ziman, 1998; Lu and Chang, 1998) that O_3 formation in the San Francisco Bay Area (i.e., an upwind area of the San Joaquin Valley) tends to be VOC-sensitive during the summer. Also, an area may switch from a NO_x-sensitive regime during summer to a VOC-sensitive regime during winter. Jacob et al. (1995) demonstrated this pattern for the eastern United States. For the San Joaquin Valley, the analysis of Pun and Seigneur (1998) suggests that the oxidant system may be VOC-sensitive in the winter. Therefore, it may be important to coordinate O_3 control measures between the San Francisco Bay Area and the San Joaquin Valley and to consider O_3 and PM reduction efforts using a holistic approach for different seasons.

4.0 PHYSICAL PROCESSES

The meteorology of SJVAQS/AUSPEX has been extensively studied, especially for the intensive observation periods of the end of July and early August 1990. Detailed descriptions and extensive summaries can be found in Lehrman et al. (1994), Niccum et al. (1995), Seaman et al. (1995), Thuillier (1997), and others. The primary meteorological influences that are conducive to high O_3 episodes are summarized in terms of horizontal transport, vertical mixing, and deposition processes as follows.

4.1 Horizontal Transport

The following brief description of the summertime climatology of the region around the San Joaquin Valley is based primarily on the descriptions of Seaman et al. (1995) and Niccum et al. (1995).

Surface Transport

During the summer, the contrast between the warm continent and the colder Pacific Ocean generates a pressure gradient between a high pressure over the ocean (East Pacific Ridge) and lower pressure over the land. The general low level flow is, therefore, in the southeasterly direction, more or less parallel to the coast. This situation is not static, but is modulated by the synoptic scale perturbations that follow the westerlies north of the region of interest.

The complex topography of the region and the sea/land breezes also influence this general climatology. The normal effect of the surface friction is to make the surface winds slow down and rotate towards the low pressure area. This would give the surface winds a component across the coastline. During the day, the land warms up, inducing a sea breeze that intensifies the surface wind at the coast. The reverse is true at night, when the surface wind dies down and can even be reversed (land breeze). However, this simple picture is complicated by the presence of several orographic ranges that are parallel to the coast line.

The San Joaquin Valley is confined between the coastal Diablo and Tremblor range to the West and the Sierra Nevada to the East. Its southeastern end is defined by the Tehachapi Mountains near Bakersfield while in the northwest the low area continues with the Sacramento Valley. The coastal ranges are not continuous, but have several openings to the sea: the mouths of the San Joaquin and Sacramento rivers at the Carquinez Straight, the Pacheco Pass near the Monterey Bay, and the Cholame Pass near San Luis Obispo.

These openings towards the sea, especially the Carquinez Straight, tend to funnel the sea breeze. The typical low level circulation during a summer day is therefore a fairly strong inflow of marine air in the San Francisco Bay Area, which splits between Sacramento and Stockton, with flow towards the southeast up the San Joaquin Valley and the northwest into the Sacramento Valley. The surface flow brings in VOC, NO_x, and O_3 from the San Francisco Bay Area into the Central Valley (Lehrman et al., 1997). The flow up the valleys is modified by the mountain breezes generated by the heating of the hills all around the valleys. Satellite data indicate that the skin temperature in the bare Sierra foothills can reach 47 - 50ºC (Martien and Umega, 1995), compared to about 35ºC on the valley floor. The result of the mountain breezes is a low level divergence at the bottom of the valley and convergence on the coastal ranges.

Near the surface, the flow in the August episode exhibited the normal pattern of inflow through the Carquinez Straight and up the San Joaquin Valley, with some additional inflow through the Pacheco Pass. This flow was rather weak, however, since it was mainly due to mesoscale pressure patterns, the sea breeze, and the mountain effects, without much synoptic forcing. In fact, the synoptic flow aloft tended to be opposed to the surface flow.

Aloft Transport

In the July episode (July 27-29) the low level winds were generally weak (≤ 2 m/s) at 1500 m above sea level, and the directional patterns not very organized. Nevertheless, the flow was consistently on-shore in the Sacramento river delta area,

entering the San Joaquin valley, and exited the valley through the Cholame pass and the Tehachapis.

Throughout the July 27-29 period the East Pacific Ridge was high and fairly diffuse over California. This pattern precluded any strong synoptic influence on the transport patterns in the lower levels and was favorable to poor dispersion conditions. It was fairly similar to the situation on August 3.

At night, a strong surface inversion develops and the air flows aloft are decoupled from the surface. The strong radiative cooling of the surface generates drainage flows down the mountain slopes and into the valley. However, the pressure gradient usually precludes air from flowing down the valley. Normally, a low level jet of 10 to 30 m/s develops at about 400 m above ground level, roughly parallel to the San Joaquin Valley axis, towards the southeast. In the early morning hours, a local cyclonic circulation often develops in the Fresno area, which has become known as the Fresno eddy. Its causes are not completely understood but it is probably related to blocking of the flow in the upper valley under a low inversion.

It should be noted that the up-valley flux was maximum during the early part of the night, because of the nocturnal jet. The flux between 18:00 and 24:00 PDT was 3 to 4 times larger than between 8:00 and 12:00 PDT (Lehrman et al., 1994). Back trajectory calculations (Lehrman et al., 1997) indicated that air parcels from the San Francisco Bay Area and the Sacramento area could be transported overnight in the jet stream and higher level flows to areas in the southern San Joaquin Valley with high O_3 burden.

Tracer Studies

Tracers released in Pittsburg and San Jose on August 3 indicate that material meandered around the northern part of the San Joaquin Valley until late afternoon when a more organized transport began to move material up the valley (Smith and Lehrman, 1995). It traveled first along the east side of the valley to the neighborhood of Fresno, then moved over to the west side. It took 20 to 30 hours for the tracer to reach the end of the valley, about 500 km from the release points, implying an average velocity of about 4.5 m/s. Rappolt and Teuscher (1995) noted that transport is not well predicted using

only the surface winds, another indication that the nocturnal jet, a few hundred meters above the surface, plays a critical role in the transport.

Even though the releases of tracers on July 27 and August 3 were at different times of the day, in both cases the tracer arrived in Fresno in the morning hours, consistent with most of the transport occurring at night. The maximum concentrations resulting from the evening July 27 release were higher than those resulting from the morning August 3 release since the July 27 transport took place shortly after the release time and was more organized. Once in the upper valley, the tracer remained there for about a day. Several stations recorded a secondary maximum the next day.

Lehrman et al. (1997) noted that the measured concentrations of tracers were generally smaller than would be expected from standard diffusion and transport models. They attributed this difference to the strong wind shear in the nocturnal jet and the complex variability of the mixing height, which could not be taken into account by a simple model.

4.2 Vertical Mixing

The vertical thermal structure of the air in the region is determined by the surface temperature and the general subsidence due to the large-scale anticyclone. Off the coast, the profile is characterized by a strong inversion above a shallow marine boundary layer. The marine inversion is strongest just off the coast where the upwelling of cold deep-ocean water keeps the lower atmospheric layer quite cool. Inversions of up to 20ºC are observed in a layer of 200-300 m, with its top lower than 1000 m above the surface. When this air moves over land, the hot surface rapidly warms the boundary layer during the day. Surface heat fluxes can exceed 1000 Wm^{-2} and the mixed layer can develop to 1200 m in the Sacramento area. Further up in the valley, however, the combination of the large scale subsidence, the low level divergence due to up-slope winds and mid-level warm advection tends to sustain a fairly low (400 to 1200 m) weak stable layer despite the very high surface temperatures (around 40ºC). Lehrman et al. (1997) noted three flow regimes: the synoptically driven flow above 1000 m a.g.l., the locally driven flow aloft from 200 to 1000 m, and the surface layer flow below 200 m. During the day, the

mixing between the layer occurs, because the mixed layer height extends to > 1000 m. At night, however, strong inversions trap emissions within the surface layer.

The general situation during the high O_3 episode of August 3-6, 1990 approximately followed the general climate of the region with one main difference: the position of the high pressure center. On August 3, the 500 mb map showed a weak high pressure center almost exactly over the central San Joaquin Valley. Over the next 3 days, this anticyclone intensified and moved east and north until, on August 6, it was positioned at the boundary between Nevada, Oregon, and Idaho. This large scale pressure pattern induced a stronger than usual advection of warm air aloft from the southwestern desert towards central California, as well as a more intense subsidence than usual. A situation in which the 500 mb East Pacific Ridge is over or to the east of California is conducive to high O_3 values in the San Joaquin Valley (Lehrman et al., 1994). The O_3 episode was, however, not quite as intense as it could have been if the center of the high had traveled further south towards the Four-Corners area.

In both the July and August episodes the subsidence associated with the high pressure and the warm air advection together contributed to high temperatures at mid level in the San Joaquin Valley. The soundings at Oakland show the 850 mb temperature increasing from 22ºC to 27ºC between August 3 and August 5. This was several degrees warmer than the normal average for that period (19.9ºC at Oakland). The mixed layer therefore did not extend very high, despite the strong heating at the surface. This had the effect of trapping any pollutant or precursors in the boundary layer. For example, the height of the mixed layer never exceeded 500 m at Visalia during the whole period and only briefly exceeded 1000 m on one occasion at Mariposa and at Delano.

The sky was mostly clear during the period except for developing convective cloudiness over the Sierra Nevada on August 5 and 6. This cloudiness was due mainly to the advection of moisture from the Gulf of Mexico (so-called “monsoon” situation). This cloudiness reduced insolation in the eastern part of the valley on those days. The surface temperature, however, was not affected much since the clouds developed in late afternoon, and the infrared emission by the increasing moisture aloft tended to partly counteract the reduced solar radiation. Maximum surface temperatures reached 34 to 38ºC throughout the southern part of the valley.

The mixing height during the July intensive period was generally higher than in the August period, sometimes reaching 1500 m. With clear skies throughout the period, maximum surface temperatures, though slightly lower than in August, reached 32 to 36ºC.

4.3 Dry Deposition

The California Ozone Deposition Experiment (CODE) was conducted to support the SJVAQS / AUSPEX field program (Pederson et al., 1995). The main components of CODE were measurements of vertical fluxes of O_3, carbon dioxide (CO_2), water vapor, sensible heat, and momentum at three sites using the eddy covariance technique on both tower-based and aircraft platforms. The three sites were located in a cotton field, grape vineyard, and dry senescent annual grassland, respectively. Measurements were also taken to characterize the state of the vegetation, e.g., stomatal conductance, radiative leaf temperature, leaf wetness, soil temperature and heat flux, soil composition and water content, mean nitrogen oxide and O_3 concentrations, solar and net radiation, photosynthetically active radiation, and vertical profiles of wind, temperature, O_3, and water vapor. Aircraft data included reflected short-wave radiation, surface greenness index, and radiative surface temperature.

The key results of CODE are shown in Figure 4-1 (Pederson et al., 1995). Daytime O_3 deposition velocity was highest at the cotton site, with a maximum value of 0.7–1.0 ms^{-1}. The diurnal patterns were similar at the cotton and vineyard sites: maximum deposition velocities were observed near midday and minimum deposition velocities were observed at night. The deposition velocity observed at the grassland was low, and showed little diurnal variation. Desjardins et al. (1995) found that fluxes measured on the aircraft platform (30 m) were comparable to tower-based measurements (9.4 m). They also demonstrated that diurnal patterns of regional fluxes may be obtained using a combination of tower- and aircraft-based measurements.

With the measured deposition velocities, the removal rates of O_3 could be of the order of kilograms per hour per km^2. Order-of-magnitude calculations of O_3 dry deposition, O_3 flux at the northern end of the valley, and an upper limit of O_3-forming

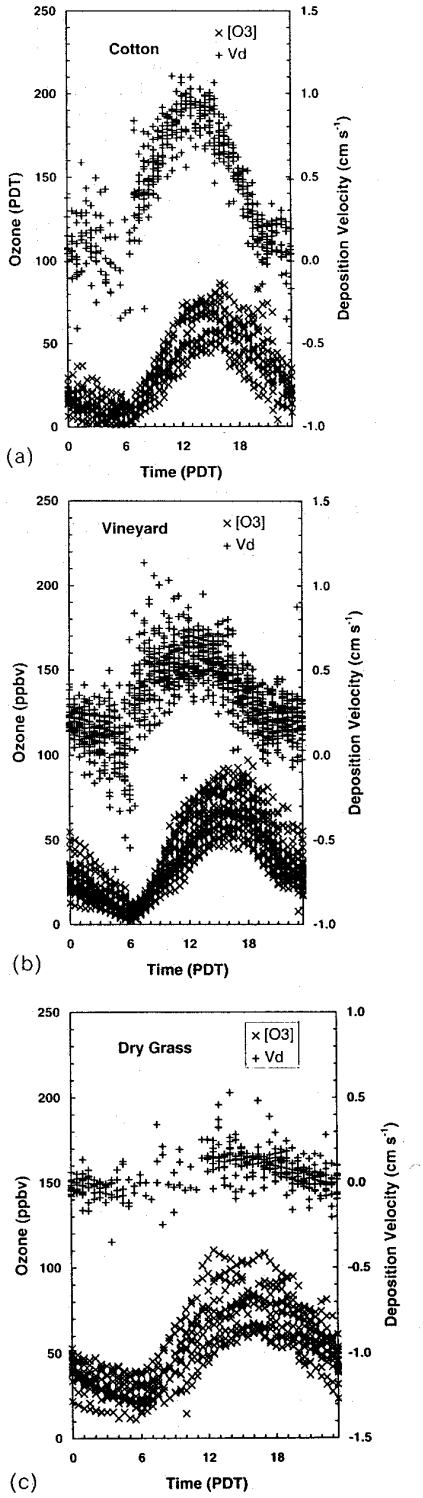


Figure 4-1. Diurnal Variations of O_3 Concentrations and Deposition Velocities for a Composite Day Representing All Observations at the Cotton Site (a), Vineyard Site (b), and Dry Grass Site (c). (Source: Pederson et al., 1995; reprinted with permission from Elsevier Science)

emissions were 3,000, 4,000 and 80,000 tons per day, respectively. Therefore, dry deposition can be an important flux in the O_3 budget. Fluxes of NO_x and VOC were not measured during CODE.

4.4 Wet deposition

Wet deposition was not important during the SJVAQS / AUSPEX study because the study period was relatively dry (Thuillier, 1997) and rain was not associated with high O_3 episodes.

5.0 SYNTHESIS

Two major phenomena appear to lead to O_3 concentrations in excess of the NAAQS in the San Joaquin Valley: (1) transport of O_3 and precursors from upwind areas (primarily, the San Francisco Bay Area) into the San Joaquin Valley leading to high O_3 levels in the northern part of the valley and (2) emissions of precursors, mixing, and atmospheric reactions within the San Joaquin Valley leading to high O_3 levels downwind of urban areas such as Fresno and Bakersfield. The first phenomenon is favored by organized flow from the north/northwest into the valley whereas the second phenomenon is exacerbated by multi-day stagnation periods. Although these two phenomena are neither mutually exclusive nor collectively exhaustive, they help conceptualize the dynamics and chemistry of O_3 pollution in the San Joaquin Valley.

5.1 Transport of O_3 and Precursors from Upwind Areas into the San Joaquin Valley

Pollutants and O_3 precursors from point and area sources accumulate in the mixed layer during the day in the San Francisco Bay Area and are transported or diffuse slowly in the northern part of the San Joaquin valley. Some inflow is also observed through the Pacheco Pass, bringing polluted air from the San Francisco Bay Area to the west side of the San Joaquin Valley. On some episode days, fluxes of O_3 and NO_x that accompanied sea breezes were significant. (VOC fluxes from the Bay Area were not measured.) An example was August 6, 1990 when onshore flows became more dominant after the high pressure system moved away from the San Joaquin Valley. In addition, fluxes from the Sacramento Valley were also important. The combined NO_x fluxes into the northern part of the San Joaquin Valley may exceed the northern valley emissions. Precursor and O_3 transport is especially influential to O_3 in the northern part of the San Joaquin Valley.

5.2 Formation of O_3 from San Joaquin Valley Emissions

Although the transport of O_3 and VOC/NO_x from upwind areas contributed to O_3 accumulation in the San Joaquin Valley, the within-valley production of O_3 was postulated to be capable of generating O_3 levels that exceed the NAAQS (San Joaquin Valley Air Quality Study Policy Committee, 1996). The observations of high ozone downwind from urban centers (Sacramento, Fresno, and Bakersfield) on August 3-5 were evidence of urban-scale O_3 production during stagnant (high pressure) conditions.

Ozone formation in the valley results from a combination of processes including emissions of precursors (NO_x and VOC), aloft long-range transport within the valley, vertical mixing under the large-scale subsidence, and removal processes.

Emissions and concentrations of NO_x and VOC in the San Joaquin Valley

During the day, NO_x and VOC are emitted within the valley. According to the emissions inventories, the major NO_x contributors were mobile sources (Magliano, 1996). The CMB results show VOC contributions from vehicle exhaust, liquid gasoline, gasoline vapor, oil production, and acetone and unidentified / unexplained VOC. The concentrations of NO_x were highest in the morning in urban areas, reflecting the mobile source contributions. Many upwind point sources are highly buoyant or are released aloft. These sources may not contribute to high ground level NO_x close to the source, but result in O_3 production farther downwind. VOC concentrations were highest in the morning samples from the southern San Joaquin Valley, where significant emissions of hydrocarbons occurred from oil production. Motor vehicle exhaust was the main contributor at all time periods in the urban areas, ranging from 35 to 70% of total VOC. The Yosemite and Sequoia sites showed 10-15% VOC contributions from biogenic emissions according to the CMB results. However, the inventory estimates were substantially higher (> 50%). This discrepancy may be due to the transport of VOC (anthropogenic emissions + secondary organic compounds) from urban areas, the high reactivity of isoprene, or uncertainties in the emission estimates. Larger unidentified

fractions and larger acetone fractions were measured in the afternoon samples than the morning samples, reflecting the atmospheric reactions that took place during the day.

Aloft Long-range Transport within the San Joaquin Valley

Ground level winds are generally weak. Long-range transport takes place aloft. This is particularly important at night, when a nocturnal jet develops approximately along the axis of the San Joaquin Valley. The nocturnal jet carries pollutants towards the southern tip of the valley (up valley), including those released aloft above the inversion layer and those that had been mixed upwards from the surface point and area sources during the day. In the morning, the O_3 and VOC precursors reached the upper valley. The carry-over burden of O_3 increased from the northern part of the San Joaquin Valley to the southern part and can be as high as 100 ppb in the downwind area. The carried over VOC represented a chemically aged mixture, with concentrations about a quarter of those measured at the ground level in the morning. The lower-level winds slow down but remain generally up-valley, with some upslope flow developing along the Sierras and the coastal range. Long-range transport appears to be especially important in influencing the O_3 concentrations at rural sites with few precursor sources nearby. High O_3 is preserved aloft at night. With efficient transport by the nocturnal jet, sources hundreds of miles upwind may contribute to high O_3 concentrations in the southern part of the valley when the aloft air is mixed into the surface layer during the next day.

Vertical mixing

The large scale subsidence from the East Pacific Ridge and the advection of warm, rather moist air from the southeast keeps the mixed layer from developing very high. At night, the inversion lowers because of the large scale subsidence. Pollutants emitted during the day and mixed upwards may be trapped above the inversion layer. In addition, point sources may release pollutants above the inversion layer at night. These pollutants are transported downwind by the nocturnal jet. In the morning, under the strong insolation, the temperature rises rapidly, forming a mixed layer that brings

pollutants, transported aloft during the night, to the surface. Since the aloft air is characterized by high O_3 concentrations in many parts of the San Joaquin Valley, the immediate effect of vertical mixing in the morning may be the titration of surface NO by O_3 to form NO_2.

As the mixed layer grows during the day, emissions from the surface combine with those from buoyant or aloft point sources. O_3 production may take place both at the surface and aloft within the mixed layer. The relative efficiency of photochemical reactions at the surface and aloft may be related to the light extinction characteristics of PM. At present, the extent of O_3 production aloft is uncertain.

Upslope circulation along the Sierras and the Coastal Range generates divergence in the valley, strengthening the subsidence and keeping the mixed layer rather shallow. The pollutants are therefore trapped in the valley, without much possibility of escape except over the Chalome Pass and the Tehachapis. Dry deposition, especially over agricultural land, appears to be an important physical removal process for O_3 within the San Joaquin Valley.

5.3 Sensitivity of O_3 to Precursors

Summer O_3 in most areas of the San Joaquin Valley appears to be more sensitive to NO_x controls than to VOC reductions alone. However, there may be areas where NO_x reductions may be counterproductive to O_3 reduction. On August 6, ozone peaks were observed in the northern part of the San Joaquin Valley that could be attributed to downwind transport from the San Francisco Bay Area. The sensitivity of O_3 to its precursors under this meteorological scenario has not been verified. There is some evidence that summer O_3 in the San Francisco Bay Area is VOC-sensitive. Reductions in NO_x may result in an increase in O_3 according to modeling studies performed by the BAAQMD (Martien and Umeda, 1993). As a polluted air mass travels downwind, ozone accumulates from the reactions of VOC and NO_x. Since NO_x is depleted faster than VOC, O_3 production within the air parcel becomes increasingly NO_x-limited without fresh emissions of precursors. In this case, while VOC controls in the San Francisco Bay Area are beneficial for reducing O_3 production in the Bay Area and transported O_3 at the

receptor sites in the northern part of the San Joaquin Valley, NO_x controls are needed within the valley to reduce the O_3 production potential in areas affected by both fresh emissions from within the valley and aged air from the Bay Area.

One final consideration is that it will be beneficial to address the issues of O_3 and PM sensitivities to precursors jointly since NO_x and VOC emission changes will affect both pollutants. In addition to addressing the exceedances of the O_3 NAAQS in the summer and PM NAAQS in the winter, it may also be beneficial to understand if any indirect effects exist between PM and O_3 in the summer. Dreher and Harley (1998) postulated that the weekend increases in O_3 in the San Francisco Bay Area may be related to reduced emissions by trucks. In addition to the reduced O_3 titration by NO, increased photochemical reactivity may result from reduced emission of black carbon by trucks. However, the weekend effect does not seem to be very prominent in the San Joaquin Valley (Altshuler, 1998). Carefully planned experimental field programs, data analyses, and mathematical modeling efforts should help address the PM-O_3 interaction issue effectively.

6.0 CONCLUSIONS

6.1 Questions and Answers

What are the causes of high ozone in the San Joaquin Valley?

Under stagnant conditions, urban emissions of VOC and NO_x within the San Joaquin Valley can cause O_3 exceedances in areas downwind of major cities, such as Fresno, Bakersfield, and Sacramento. During an episode with significant sea breeze, the San Joaquin Valley also receives carry-over pollutants from upwind sources such as the San Francisco Bay Area or the Sacramento Area. The northern part of the valley is the most affected by upwind sources; however, central and southern parts of the valley are also influenced. For example, the carry-over O_3, which is transported aloft at night, can reach concentrations as high as 80 – 100 ppb in Bakersfield.

What is the nature of the regional ozone accumulation? Is it from many local sources or is it due to transport at the surface and / or aloft?

The regional accumulation of O_3 within the San Joaquin Valley is the result of combined urban sources and transport, especially aloft transport in the evening. Urban sources mostly affect areas downwind on the same day of the emissions. During the night, pollutants (O_3 and VOC) trapped above the surface layer may be transported and mixed within the San Joaquin Valley by phenomena such as the nocturnal jet and the Fresno eddy.

What is the contribution to urban and regional ozone from upwind areas and is it due to transport at the surface and / or aloft?

Urban emissions of VOC and NO_x contribute significantly to the O_3 production downwind. This urban-scale O_3 production is supplemented by regional O_3 in the event of an episode. Regional scale O_3 may be a result of O_3 and precursors emitted in the

northern San Joaquin Valley or in the San Francisco Bay Area, which are transported, typically aloft, throughout the valley.

What are the primary meteorological phenomena that contribute to ozone accumulation in the San Joaquin Valley? Are some phenomena more important than others in ozone accumulation at the surface?

Several meteorological phenomena contribute to O_3 accumulation in the San Joaquin Valley. Synoptic high pressure and stagnation help trap pollutants within the San Joaquin Valley. The upper air nocturnal jet along the valley axis transports O_3 and precursors from the northern part of the valley to the southern part of the valley. Daytime sea-breezes help inject fresh pollutants from the San Francisco Bay Area into the Central Valley under particular synoptic conditions.

What is the influence of meteorology, emissions, chemistry, and deposition on ozone concentrations?

Meteorology: Meteorology serves in two major ways to enhance O_3 concentrations within the San Joaquin Valley during an episode. First, the synoptic high pressure and low mixing height trap pollutants within the San Joaquin Valley, allowing the accumulation of pollutants over a period of days. Second, upper air transport takes place at night to move pollutants from one location to another, where they are subsequently incorporated into the boundary layer during the day. This "carry-over" is especially important in the southern part of the San Joaquin Valley. The pollutants from the San Francisco Bay Area may also be transported through the delta and the mountain passes to contribute to high O_3 concentrations in the northern part of the valley in the late afternoon.

Emissions: VOC and NO_x emissions within the valley are very important in the production of O_3 in the central and southern part of the Valley, from Fresno to Bakersfield. Data analyses suggest that VOC emissions in the San Joaquin Valley and upwind source areas may be underestimated in the inventory. Improvements of the

emissions inventories are needed for mobile emissions, biogenic emissions, and uninventoried sources.

Chemistry: The chemistry of O_3 production involves the reactions of VOC to produce radicals that subsequently react with NO to produce O_3. Of the precursors, VOC and NO_x, available information seems to indicate that O_3 is more sensitive to NO_x than VOC in most areas of the San Joaquin Valley. However, reductions in NO_x may be counterproductive to O_3 reduction in some areas.

Deposition: The measured maximum dry deposition flux of 0.5 $\mu g/m^2$/hour leads to an O_3 removal rate of about 3000 tons / day in the San Joaquin Valley. Considering an average O_3 concentration of 80 ppb, this deposition rate leads to a residence time of about 8 hours for O_3. Therefore, dry deposition is a significant flux for the mass balance of O_3 within the San Joaquin Valley. Dry deposition fluxes of precursors NO_x and VOC and products HNO_3, PAN, and PM need to be quantified. Wet deposition is not expected to be important in the summer in the San Joaquin Valley because of the low relative humidity and the lack of rain.

What differences in ozone concentrations are observed among urban, rural, and industrial areas?

Peak O_3 concentrations were frequently observed in areas downwind of major urban areas. Strong diurnal profiles were also observed at these sites with maximum O_3 concentrations during the afternoon and minimum concentrations during the night. Rural locations tended to exhibit less diurnal variability, although the concentrations ranged from close to background values at Point Reyes to ~80 ppb at Sequoia. Some of the highest O_3 concentrations were observed in the southern part of the valley, which is affected by upwind transport and local emissions of NO_x and VOC (oil production).

What is the spatial influence of point sources and what is their influence to downwind receptors?

There is insufficient information available to address this question thoroughly. Tracer releases from Pittsburg, CA provide evidence that emissions from upwind point sources may affect air quality as far downwind as the southern San Joaquin Valley. 14% of the tracer mass was detected at the surface in the southern part of the San Joaquin Valley the morning after the tracer release. Much of the long-range transport takes place at night by the nocturnal jet. Within the Central Valley, point source emissions released into the surface layer during the day may be trapped in the decoupled layer in the evening and transported towards the southeast. Furthermore, fresh emissions from elevated point sources in the path of the nocturnal jet may also be transported downwind and lead to O_3 production the next morning. Due to rapid aloft transport, the relative importance of point sources (that mix upwards) would simply depend on their rates and composition. Mathematical modeling of air quality in the San Joaquin Valley using a three-dimensional model with subgrid-scale treatment of plumes will be needed to properly address this question.

Is the formation of ozone in the San Joaquin Valley sensitive primarily to NO_x or VOC? Does it differ in different parts of the Valley, e.g., urban areas versus rural areas, northern part versus southern part?

Limited analyses indicate that the formation of O_3 in the San Joaquin Valley in the summer is sensitive primarily to NO_x although reductions in both VOC and NO_x may be needed to reduce O_3 in some areas. According to Lu and Chang (1998), VOC sensitivity occurs mainly in the San Francisco Bay Area. There is some additional evidence (Martien and Umeda, 1993; Altshuler, 1998; Ziman, 1998) to support this hypothesis. Purely NO_x-sensitive locations are typically outside of urban areas. Since VOC sources are more abundant in the southern San Joaquin Valley, the chemistry in the southern part of the valley is expected to be relatively NO_x-sensitive compared to areas in the north. The analysis was performed based on maximum one-hour average ozone concentrations, conclusions regarding the sensitivity of the 8-hour average cannot be inferred with certainty at this point. For example, if a receptor site is affected by air parcels from two different upwind locations at different times of the day, O_3

concentrations may be sensitive to NO_x at certain times and to VOC at other times. Moreover, if O_3 concentrations at a receptor within the San Joaquin Valley consist of transported O_3 (e.g., from the San Francisco Bay Area) and O_3 generated from emissions within the valley, some fraction of the total O_3 burden may be sensitive to VOC whereas the other fraction may be sensitive to NO_x. It is conceivable that the area can be NO_x-sensitive with respect to the one-hour standard and VOC-sensitive with respect to the 8-hour standard. A similar sensitivity analysis is recommended for the San Joaquin Valley to analyze the most efficient control strategies for the 8-hour standard.

Is the response of ozone to changes in NO_x and VOC emission changes expected to be similar to the response of PM-2.5 to these same changes during winter?

Winter PM-2.5 is sensitive to the production of HNO_3, a key precursor of ammonium nitrate. Some evidence exists to support VOC sensitivity of oxidant and HNO_3 productions in the winter (Pun and Seigneur, 1998). Therefore, winter PM-2.5 is expected to be more sensitive to changes in VOC levels than changes in NO_x levels. In contrast, O_3 in the summer seems to be sensitive to NO_x concentrations in many areas of the San Joaquin Valley. Jacob et al. (1995) observed a seasonal transition between NO_x- to VOC-sensitivity for O_3 production in the eastern part of the United States. These observations suggest that the same transition phenomenon may occur in the San Joaquin Valley. It may be necessary to carefully coordinate the NO_x and VOC control programs so that measures applied to reduce O_3 in the summer do not adversely affect PM-2.5 in the winter.

Is there a significant difference between week-day and week-end ozone concentrations (for the same meteorology) in the San Joaquin Valley?

Due to the focused attention on the analysis of the August 3-6 episode, no analysis has been performed to address the weekday-weekend effects. Changes in VOC and NO_x emissions result in changes in ozone dynamics during the weekend. In addition, an indirect effect may be caused by reductions in vehicular emissions of PM and

precursors, leading to increased UV radiation and photochemical activity (Dreher and Harley, 1998). However, other analyses suggest that weekday-weekend effects are not very pronounced in the San Joaquin Valley (Altshuler, 1998, private communication).

Are the ambient concentrations of ozone precursors consistent with current emission inventories of these precursors?

Not exactly. The morning ambient VOC / NO_x ratios ranged from 4.2 at San Francisco on August 6, 1990 to 27.5 at Bakersfield on August 5, 1990. The range of VOC / NO_x ratios in the emissions inventory is between 1.7 and 8.6. The emission inventory ratios at Livermore range from 4.8 to 8.2, with higher values on the weekends. The ambient ratios were between 6.1 and 19.3 during SARMAP (Magliano, 1996). In general, the ambient ratios exhibited much higher variability than the current emission inventories indicate. Uncertainties in mobile sources, biogenic, and oil production emissions need to be addressed.

6.2 Recommendations

Several aspects of the O_3 conceptual model are well understood: the combined effects of local and upwind production of O_3 from NO_x and VOC at sites such as Fresno and Bakersfield, the transport (sea breeze) of O_3 from the San Francisco Bay Area affecting primarily areas in the northern San Joaquin Valley, the overnight aloft transport of O_3 and precursors by the nocturnal jet, and the low mixed layer height caused by subsidence and mountain effects. However, some details remain to be thoroughly understood: the sensitivity of the O_3 chemistry at different locations within the San Joaquin Valley, the balance of transport, chemical, and deposition fluxes that gives rise to the observed concentrations, and the amount of O_3 that can be attributed to point sources, mobile sources, and biogenic sources.

A key indicator for the sensitivity of the oxidant system to VOC or NO_x is the ratio of HNO_3 and H_2O_2. Although HNO_3 was measured at many of the AUSPEX sites during the SJVAQS / AUSPEX, H_2O_2 measurements were only taken aboard one of the

aircraft used in the intensive studies. Measurements of H_2O_2 are highly recommended to characterize the sensitivity of O_3 to VOC or NO_x at urban, downwind, and rural locations.

Lu and Chang investigated the use of various photochemical indicators by simulating the August 5, 1990 conditions. They noted that most of the areas within the San Joaquin Valley were NO_x-sensitive. However, about 20% of the area were classified as "transition" and the sensitivity of O_3 to its precursors needs to be confirmed for these areas. Furthermore, August 6 represented a different set of meteorological conditions, with less stagnation over the valley and more transport from the Bay Area. As previously mentioned, there is some evidence for VOC-sensitivity in the Bay Area. Therefore, the northern part of the valley, influenced by pollutants originating Bay Area, may exhibit VOC sensitivity rather than NO_x sensitivity under these conditions. It is probably worthwhile to investigate the VOC / NO_x sensitivity issue further, especially for different meteorological conditions, to ensure that the conclusions are not misguided.

The NO_x and NO_2 measurements suffered from interference from oxidized nitrogen species such as PAN and HNO_3. Accurate measurements of NO_x and NO_2 are important both for the understanding of the characteristics of air masses of different chemical "age" and for model evaluation purposes.

Nitrate radical measurements were taken during the SJVAQS / AUSPEX. The concentrations of nitrate radicals in the San Joaquin Valley were sufficient to oxidize organic compounds at the same rate in the evening as they are oxidized by OH during the day (Smith et al., 1995). This unexpected conclusion (VOC oxidation at night by nitrate radical is typically expected to be two orders of magnitude slower than the day-time process initiated by OH (Atkinson, 1997)) shows that it is important to measure other radical species in addition to NO_3, especially OH, HO_2, and RO_2, which have never been measured in large-scale field programs in the San Joaquin Valley.

The new 8-hour average NAAQS may be exceeded at both urban and rural sites. A better understanding of the source-receptor relationships is needed to address O_3 at the rural receptor sites, and regional control strategies may be needed to meet the 8-hour NAAQS. In that regard, the new standard can be more difficult to attain. The temporal variations at polluted rural sites should be the subject of a modeling investigation. In particular, the aloft transport of O_3 from upwind locations, vertical exchange with the

valley surface layer or the free troposphere, local production from biogenic emissions, and O_3 scavenging by VOC may be key mass fluxes at these locations. The processes / fluxes that contribute to high 8-hour average concentrations need to be elucidated before effective attainment strategies may be identified. Model investigations to determine the O_3 sensitivity of the region to VOC and NO_x with respect to an 8-hour average should also be conducted to confirm the efficacy of control measures designed to reduce the maximum 1-hour average concentration.

Even with significant improvements in the emissions inventory for the San Joaquin Valley, the reconciliation with ambient data still indicates significant uncertainties in VOC emissions. Continuing efforts are needed to provide better emissions estimates for mobile, biogenic, oil production, and uninventoried sources. With accurate emissions information, models can be applied to understand the relative importance of these precursor sources to O_3 production in the San Joaquin Valley.

In addition to O_3 fluxes, deposition fluxes of precursors and products are needed to provide a better understanding of the pollutant removal processes within the valley. Measurements of deposition fluxes of NO, NO_2, HNO_3, PAN, PM, and VOC are needed over a range of surfaces and for a variety of meteorological conditions.

REFERENCES

Altshuler, S., 1998. Presentation at the workshop on draft emission inventory and draft attainment assessment, Bay Area Air Quality Management District, San Francisco, CA, October 8, 1998.

Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, *J. Phys. Chem. Ref. Data*, **26**, 215-290.

Blanchard, C.L., P.M. Roth, H.E. Jeffries, 1995. Continuing development of a methodology for assessing preferences for reductions in VOC versus NO_x emissions in non-attainment areas, transactions, regional photochemical measurement and modeling studies, An A&WMA International Specialty Conference, San Diego, CA, 7-12 November, 1993, ed. by J.G. Watson, J.C., Chow, and P.A. Solomon, Published by the Air & Waste Management Association, Pittsburgh, PA, pp. 335-350.

Blumenthal, D.L., 1993. Field program plan for the San Joaquin Valley Air Quality Study (SJVAQS) and the Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) Program, Version #3, Post-Field Revision, STI-98020-1241-FR, The Valley Air Pollution Study Agency, Sacramento, CA.

Blumenthal, D.L., F.W. Lurmann, P.T. Roberts, H.H. Main, C.P. MacDonold, W.R. Knuth and E.M. Niccum, 1997. Three-dimensional distribution and transport analyses for SJVAQS / AUSPEX, Final Report STI-91060-1705-FR, San Joaquin Valleywide Air Pollution Study Agency, c/o California Air Resources Board, Sacramento, CA.

CARB, 1998. ftp://themis.arb.ca.gov/pub/data/sarmapo3/datafiles.

Chow, J.C., J.G. Watson, D.H. Lowenthal, R.T. Egami, P.A. Solomon, R.H. Thuillier, K.

Magliano and A. Ranzieri, 1998. Spatial and temporal variations of particulate precursor gases and photochemical reaction products during SJVAQS/AUSPEX Ozone Episodes, *Atmos. Environ.*, **32**, 2835-2844.

DeMassa, J., S. Tanrikulu, K. Magliano, A.J. Ranzieri and L. Niccum, 1996. Performance evaluation of SAQM in Central California and attainment demonstration for the August 3-6, 1990 ozone episode, Modeling Support Section, Technical Support Division, California Air Resources Board, Sacramento, CA.

Desjardins, R.L., J.L. Macpherson, H. Neumann, G. Den Hartog and P.H. Schuepp, 1995. Flux estimates of latent and sensible heat, carbon dioxide, and ozone using an aircraft-tower combination, *Atmos. Environ.* **29**, 3147-3158.

Dickerson, R.R., Kondragunta, S., Stenchikov, G., Civerolo, K.L., Doddridge, B.G., Holben, B.N., 1997. The impact of aerosols on solar ultraviolet radiation and photochemical smog, *Science* **278**, 827-830.

Dreher, D.B. and Harley, R.A., 1998. A fuel-based inventory for heavy-duty diesel truck emissions. *J. Air & Waste Manage. Assoc.* **48**, 352-358.

Jacob, D.J., L.W. Horowitz, J.W. Munger, B.G. Heikes, R.R. Dikerson, R.S. Artz and W.C. Keene, 1995. Seasonal transition from NOx- to hydrocarbon-limited conditions for ozone production over the Eastern United States, *J. Geophys. Res.*, **100**, 9315-9324.

Jacobson, M.Z., 1998. Studying the effects of aerosols on vertical photolysis rate coefficient and temperature profiles over an urban airshed, *J. Geophys. Res.*, **103**: 10593-10604

Lehrman, D. E., T. B. Smith, W. R. Knuth and C. E. Dorman, 1994. Meteorological analysis of the San Joaquin Valley air quality study, atmospheric utilities

signatures, predictions and experiments (SJVAQS/AUSPEX), Final Report for Pacific Gas and Electric Company and California Air Resources Board. Technical & Business Systems, Inc., Santa Rosa, CA.

Lu, C.H. and Chang, J.S., 1998. On the indicator-based approach to assess ozone sensitivities and emissions features. *J. Geophys. Res.* **103**: 3453-3462.

Magliano, K.L., 1996. Descriptive analysis and reconciliation of emissions and ambient hydrocarbon data, SJVAQS / AUSPEX technical topic team #5 report, California Air Resources Board, Sacramento, CA.

Martien, P. and T. Umeda, 1993. Photochemical model sensitivity tests on the effects of utility boiler NO_x controls on ambient ozone concentrations. Technical Memorandum, BAAQMD, TM 93001, San Francisco, CA.

Martien, P. and T. Umeda, 1995. Cloud cover and mesoscale surface properties derived from AVHRR satellite data to supplement SARMAP field observations, Proceedings, Regional Photochemical Measurement and Modeling Studies, Volume 1, Results and Interpretation of Field Measurements, An A&WMA International Specialty Conference, San Diego, CA, 7-12 November 1993, ed. by A. J. Ranzieri and P. A. Solomon, Published by the Air & Waste Management Association, Pittsburgh, PA, pp. 265-284.

Niccum, E. M., D. E. Lehrman and W. R. Knuth, 1995. The influence of meteorology on the air quality in the San Luis Obispo County - Southwestern San Joaquin Valley region for 3-6 August 1990, *J. Appl. Meteor.*, **34**, 1834-1847.

Pederson, J.R., W.J. Massman, L. Mahrt, A. Delany, S. Oncley, G. Den Hartog, H.H. Neumann, R.E. Mickle, R.H. Shaw, K.R. Paw U, D.A. Grantz, J.I. Macpherson, R. Desjardins, P.H. Schuepp, R. Pearson, Jr., T.E. Arcado, 1995. California ozone deposition experiment: Methods, results, and opportunities, *Atmos. Environ.*, **29**,

3115-3132.

Pun, B.K. and C. Seigneur, 1998. Conceptual model for atmospheric particulate matter in the California San Joaquin Valley, Document CP045-1-98, Pacific Gas and Electric Company, San Ramon, CA.

Ranzieri, A. and R. Thuillier, 1994. SJVAQS and AUSPEX: A collaborative air quality field measurement and modeling program, Planning and Managing Regional Air Quality Modeling and Measurement Studies: A Perspective Through the San Joaquin Valley Air Quality Study and AUSPEX, ed. by P. A. Solomon. Published by Lewis Publishers, Chelsea, MI in conjunction with Pacific Gas and Electric Company, San Ramon, CA, pp. 1-28.

Rappolt, T. J. and L.H. Teuscher, 1995. Identification of regional air mass transport using tracer studies, Proceedings, Regional Photochemical Measurement and Modeling Studies, Volume 1, Results and Interpretation of Field Measurements, An A&WMA International Specialty Conference, San Diego, CA, 7-12 November 1993, ed. by A. J. Ranzieri and P. A. Solomon, Published by the Air & Waste Management Association, Pittsburgh, PA, pp. 166-180.

Rasmussen, R.A., 1992. SJV-AUXPEX 1990 Air Quality Study. Task 3: GC-MS full scan analysis of canister air samples (TIC-chromatograms), Vol. 1: Ground samples and Vol. 2: Aircraft samples, Data Report, California Air Resources Board, Sacramento, CA.

San Joaquin Valley Air Quality Study Policy Committee, 1996. San Joaquin Valley Air Quality Study Policy-Relevant Findings, California Air Resources Board, Sacramento, CA.

Seaman, N. L., D.R. Stauffer and A.M. Lario-Gibbs, 1995. A multiscale four-dimensional data assimilation system applied in the San Joaquin Valley during

SARMAP. Part 1: modeling design and basic performance characteristics, *J. Appl. Meteor.*, **34**, 1739-1761.

Sillman, S., 1995. The use of NO_y, H_2O_2, and HNO_3 as indicators for ozone-NO_x-hydrocarbon sensitivity in urban locations, *J. Geophys. Res.*, **100**, 14,175-14,188.

Smith, N., J.M.C. Plane, C.-F. Nien and P.A. Solomon, 1995. Nighttime radical chemistry in the San Joaquin Valley, *Atmos. Environ.*, **29**, 2887-2897.

Smith, T. B. and D.E. Lehrman, 1995. Long-range tracer studies in the San Joaquin Valley, Proceedings, Regional Photochemical Measurement and Modeling Studies, Volume 1, Results and Interpretation of Field Measurements, An A&WMA International Specialty Conference, San Diego, CA, 7-12 November 1993, ed. by A. J. Ranzieri and P. A. Solomon, Published by the Air & Waste Management Association, Pittsburgh, PA, pp. 151-165.

Thuillier, R.H., 1997. Summary description of meteorological conditions during SJVAQS/AUSPEX, R&D Final Report 005-97.7, Pacific Gas & Electric Company.

Ziman, S., 1998. Presentation at the workshop on draft emission inventory and draft attainment assessment, Bay Area Air Quality Management District, San Francisco, CA, October 8, 1998.

APPENDIX III

PHASE II REPORT

INTEGRATED MODELING STUDY 95: ASSESSMENT OF MATHEMATICAL MODELS AND ASSOCIATED DATA NEEDS

Phase II Report

Integrated Modeling Study 95:

Assessment of Mathematical Models and Associated Data Needs

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Executive Summary

A conceptual model was formulated (Pun and Seigneur, 1998) for the formation of particulate matter (PM) in California's San Joaquin Valley based on the observations and analyses of data from the 1995 Integrated Monitoring Study (IMS 95). Based on this conceptual model, we evaluate current PM air quality models, focusing on SAQM-AERO. Key objectives of this report include the identification of knowledge gaps, needs for model improvement, and recommendations regarding the field data needed for the execution and evaluation of mathematical models.

An approach that combines receptor modeling and source modeling is required for understanding the formation of primary and secondary PM in the San Joaquin Valley. Geological material accounted for over 50% of PM-10 observed in the fall. The winter PM episodes were dominated by fine particles, which include secondary components (e.g., ammonium nitrate) and primary components (from vegetative burning and mobile sources). Receptor models, such as Chemical Mass Balance (CMB), can be used to address the primary sources of PM, while source models, such as SAQM-AERO, are best used to simulate the formation of secondary PM. Due to the possibility of long-range aloft transport, we recommend for the source model a mesoscale domain that includes upwind metropolitan areas such as the San Francisco Bay Area, Monterey, and San Luis Obispo.

When used with MM5, a non-hydrostatic prognostic meteorology model, SAQM-AERO provides adequate treatment for the complex meteorology within the San Joaquin Valley, except possibly for calm periods. Major uncertainties in the emissions input must be resolved by measurements. Concentration measurements at the boundaries, lateral and top, are also recommended. A 12 km x 12 km grid size can capture the major features of PM build-up within the San Joaquin Valley. During stagnation, however, a finer grid size may be necessary to decipher the diffusion processes. The vertical range of SAQM-AERO extends to 15 km, which is adequate for modeling aloft transport in the free troposphere. Near the surface, a surface layer submodel increases the resolution to improve model predictions when the mixing layer is

shallow. Since reduced mixing heights are typically associated with PM accumulation, such a feature should prove useful in the application of SAQM-AERO to the San Joaquin Valley.

The representation of chemistry within SAQM-AERO may not be adequate for wintertime PM formation. Most gas-phase chemical mechanisms for oxidant productions have not been thoroughly tested in cool, foggy conditions. CBM-IV, the only mechanism currently implemented in SAQM-AERO, does not explicitly treat organic peroxides, which may be important radical termination products if the oxidant chemistry is NO_x-sensitive. Secondary organic aerosols (SOA) are simulated in CBM-IV; however, the current partition scheme amounts to a rudimentary fixed aerosol yield approach. The thermodynamic module, SEQUILIB, was found to perform well under the high nitrate, high ammonia conditions prevalent with the San Joaquin Valley (Zhang et al., 1998). However, aqueous-phase reactions are not represented. The aqueous oxidation of SO_2 to sulfate and the hydrolysis of N_2O_5 in the presence of droplets should be modeled if SAQM-AERO were to be applied to the San Joaquin Valley, where fog is typically associated with the winter PM episodes.

Gaps in current knowledge include the VOC or NO_x sensitivity of the oxidant system in the San Joaquin Valley, the rates of photolysis reactions in fog, the details of SOA formation, the source of fog buffering in some urban areas, and the transport processes responsible for the regional distribution of pollutants under calm conditions. We divided the key areas for model development and testing needs into two categories as follows.

(1) Areas where development is absolutely needed for the San Joaquin Valley application:

- Incorporate a detailed aqueous-phase chemical mechanism
- Reduce numerical diffusion during stagnation
- Implement plume-in-grid treatment for point and area sources
- Improve treatment of secondary organic aerosols

(2) Areas where testing is needed to ensure the accuracy of the model and, if testing is not satisfactory, development is needed:

- Implement SAPRC as an audit for the CBM-IV mechanism in SAQM-AERO

- Resolve mass adjustment issue by modifying MM5 post-processing procedures
- Test photolysis rates by comparing calculated radiative fluxes with measurements of UV and broad radiation
- Resolve vertical transport inconsistencies (K-theory vs. ACM)
- Test surface layer submodel (SLS) and modify as needed
- Resolve difference in dry deposition prediction of SAQM-AERO and other air quality models

A host of information is required for the execution and evaluation of the source model. Meteorological data, emissions data, and initial and boundary conditions (i.e., ambient concentrations) are required as inputs for the PM air quality model. Ambient concentrations and fluxes (e.g., deposition) of PM and precursors are needed to evaluate model performance. These data needs for model input and evaluation are summarized in Table E-1.

Table E-1. List of Recommended Measurements for Model Input and Evaluation.

Data	Spatial Resolution	Temporal Resolution
Meteorology		
Wind Speed and Direction	Surface and Aloft	< 1 hour *
Temperature	Surface and Aloft	< 1 hour
Mixing Height	Surface or Aircraft	< 1 hour
Relative Humidity	Surface and Aloft	< 1 hour #
Solar Radiation	Surface and Aloft	< 1 hour
Fog / Clouds	Surface and Satellite	< 1 hour
Emissions (PM-2.5, PM-10, Precursor Gases)	Representative Sources	N/A
Profiles (Anthropogenic, Biogenic)	Major Sources	1 to 4 hours
Emission Factors		
PM-2.5 / PM-10		
Total Mass	Surface and Aloft	1 to 4 hours
Sulfate	Surface and Aloft	1 to 4 hours
Ammonium	Surface and Aloft	1 to 4 hours
Nitrate	Surface and Aloft	1 to 4 hours
Elemental carbon	Surface and Aloft	1 to 24 hours
Organic carbon (speciated)	Surface and Aloft	1 to 24 hours
Chloride	Surface and Aloft	1 to 4 hours
Gases		
O_3	Surface and Aloft	1 hour
NO	Surface and Aloft	1 hour
NO_2	Surface and Aloft	1 hour
VOC (Speciated)	Surface and Aloft	1 to 4 hours
HNO_3	Surface and Aloft	1 hour
NH_3	Surface and Aloft	1 hour
H_2O_2	Surface and Aloft	1 hour
Organic Peroxides	Surface and Aloft	1 hour
PAN	Surface and Aloft	1 hour
OH	Surface	1 hour
HO_2	Surface	1 hour
NO_3	Surface	1 hour

Table E-1. List of Recommended Measurements for Model Input and Evaluation (continued).

Data	Spatial Resolution	Temporal Resolution
CO	Surface and Aloft	1 hour
SO_2	Surface and Aloft	1 hour
Droplet Chemistry		During Fog Event Only:
Liquid Water Content	Surface and Aloft	1 hour
Sulfate	Surface and Aloft	1 hour
Nitrate	Surface and Aloft	1 hour
Ammonium	Surface and Aloft	1 hour
Chloride	Surface and Aloft	1 hour
H_2O_2	Surface and Aloft	1 hour
Sulfite	Surface and Aloft	1 hour
H^+(pH)	Surface and Aloft	1 hour
Dissolved Fe^{3+} and Mn^{2+}	Surface and Aloft	1 hour
Wet Deposition	Representative Locations	During Fog Event Only
Sulfate		1 hour
Nitrate		1 hour
Ammonium		1 hour
Dry Deposition	Different Surface Types (aircraft measurements or tower measurements)	Representative Meteorology
PM-2.5		
PM-10		
HNO_3		
NH_3		
SO_2		
O_3		

* 5-minute temporal resolution is desired during stagnation

5-minute temporal resolution is desired during fog

1. Introduction

1.1 Background

Elevated levels of Particulate Matter (PM) were observed during the fall and winter seasons in the California San Joaquin Valley. Both PM-10 and PM-2.5 exceeded the respective 24-hour average National Ambient Air Quality Standards (NAAQS) during the Integrated Monitoring Study of 1995 (IMS 95). In addition, existing data suggest a non-attainment status of the annual average of PM-2.5 in several populated areas of the San Joaquin Valley.

In Phase I of this work, we assimilated information from the data analysis reports of IMS 95 into a coherent conceptual model. The formulation of the conceptual model was based on our understanding of the chemical transformations and physical transport processes that contributed to elevated levels of PM in the San Joaquin Valley during the fall and winter seasons. The conceptual model is discussed in the Phase I report titled "Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley" (Pun and Seigneur, 1998). Table 1-1 summarizes the key meteorological and air quality attributes of the conceptual model.

1.2 Objective

The conceptual model of PM formation in the San Joaquin Valley developed in Phase I can be used to guide the development of mathematical models. The objectives of Phase II are:

- assess the ability of existing mathematical models to represent PM formation,
- identify gaps in current knowledge and needs for model improvement,
- recommend specific tasks for field measurements, data analyses, and model performance evaluation.

Table 1-1. Key Attributes of the Conceptual Model for PM Formation in the San Joaquin Valley in the Fall and Winter Seasons

Meteorology
Cool Temperatures
Stagnant Conditions (Calm Winds)
Fog (Primarily in Winter)
Complex Terrain
Valley Geography
Air Quality
Sulfate Poor Environment with Respect to Ammonia
Nitric Acid-Sensitive Conditions for PM Nitrate
Local Sources
Transport (Various Ranges)
Oxidant Production

1.3 Outline

In Section 2, we discuss general modeling requirements based on the conceptual model and the selection of mathematical models for the San Joaquin Valley episodes. In Section 3, we assess the adequacy of current mathematical representations of the key processes responsible for PM formation in the San Joaquin Valley, focusing our discussion on one model, SAQM-AERO. The discussion in Section 3 also identifies tasks for further model development. Section 3 is further divided into subsections that address the input data requirements, resolution (spatial, temporal, and size), chemical transformation routines, and physical transport and removal processes of the model. Data requirements for model execution and performance evaluation are highlighted in Section 4. Conclusions are presented in Section 5.

2. Modeling Requirements and PM Source Models

2.1 Source Models vs. Receptor Models

The receptor modeling work of Magliano (1997) and Schauer and Cass (1998) indicates the presence of both primary and secondary components in PM-10 and PM-2.5. In the fall, over 50% of the observed PM-10 mass was attributed to geological material (dust). Urban PM-2.5 in the winter contained significant contributions from automobile emissions and vegetative burning. In addition to natural and anthropogenic primary emissions, PM also contained secondary components, including ammonium nitrate, which were dominant components in the winter at rural sites. Seigneur et al. (1998a) reviewed source models and receptor models for PM and recommended that receptor models be used to address the source of primary PM (e.g., fugitive dust) and that source models be used for secondary PM. Their recommendations are based on the fact that the large uncertainties associated with emissions of some primary PM sources (e.g., fugitive dust) limit the expected performances of source models for primary PM, whereas receptor models are limited in their ability to apportion secondary PM to specific sources. Therefore, receptor models, such as Chemical Mass Balance (CMB), should continue to be applied in future studies to characterize primary PM in the winter and fall seasons. These models must, however, be complemented by source models, which are currently the best available tools for characterizing the formation of secondary PM components.

2.2 Episodic Model vs. Annual Model

Although both the annual average and 24-hour average PM are expected to exceed the respective NAAQS, we focus on the assessment of episodic models. Long-term models have significant uncertainties in the formulation of their chemistry routines, and were not recommended for use in state implementation plans (SIP) (Seigneur et al., 1998a). An episodic model has been applied for a full year to simulate ozone concentrations in southern California (Glen Cass, private communication, 1998). However, the additional computational requirements associated with the simulation of PM formation and the fact that the annual PM-2.5 standard is an arithmetic average

of three consecutive annual average values (i.e., a three-year average) still limit the application of an episodic model to simulate annual PM-2.5. The alternative approach involves the use of episodic source models to predict the annual-average PM by combining episodic model results based on the frequencies of several types of meteorology. In this regard, episodic models are essential tools for compliance modeling of both the 24-hour average and annual average PM NAAQS.

2.3 Recommended Domain

A regional model is recommended for modeling PM-10 and PM-2.5 in the San Joaquin Valley. Regional models are typically designed to represent domains of scale greater than 1000 km, but can be adapted to smaller domains for mesoscale modeling by reducing the grid size. Urban scale models, such as UAM and CIT, may not be suitable for the San Joaquin Valley domain because of their limited treatment of upper air (free troposphere) meteorology (Seigneur et al., 1998a).

The winter distribution patterns of PM-2.5 suggest that the southern San Joaquin Valley must be treated as one system. Collins (1998) determined that clean air / non-anthropogenic background concentrations were not observed within the southern part of the San Joaquin Valley during IMS 95, and that no well-defined transport boundaries were observed. (Background concentrations were observed at elevated sites, which are probably not representative of valley locations.) Although there was no direct evidence to support long-range transport above the surface layer, this was postulated to be a mechanism for the dispersion of PM precursors within the valley. Therefore, it seems appropriate to extend the modeling domain beyond the valley to include as many potential upwind sources as possible. We recommend a domain that covers the metropolitan San Francisco Bay Area on the northeast, Monterey and San Luis Obispo along the coast, and the Tehachapi pass on the south (where polluted air exits the valley). The Sierra Nevada mountain range should be included in the domain to the east, because drainage flows and other relief-driven wind patterns may affect the dispersion of PM and PM precursors within the valley.

Combined regional- and urban-scale influences were consistent with the observations for PM-2.5 and PM-10. Consequently, it is advisable to model urban areas within the San Joaquin Valley (such as Fresno and Bakersfield) with better spatial resolution than afforded by typical regional / mesoscale resolution. Therefore, a model with nested grid capabilities is recommended for the domain.

2.4 Particulate Matter Air Quality Models

Seigneur et al. (1998a) reviewed seven episodic PM air quality models, including:

- The California Institute of Technology model (CIT)
- The Denver Air Quality Model (DAQM)
- The Gas, Aerosol, Transport and Radiation model (GATOR)
- The Regional Particulate Model (RPM)
- The SARMAP Air Quality Model with Aerosols (SAQM-AERO)
- The Urban Airshed Model Version IV with Aerosols (UAM-AERO)
- The Urban Airshed Model Version IV with Aerosol Inorganic Model (UAM-AIM)

The Regional Particulate Model provides the scientific formulation for the aerosol modules of two forthcoming PM air quality models: the Community Multiscale Air Quality Model (CMAQ) of Models-3 and the Multiscale Air Quality Simulation Platform (MAQSIP) of the Environmental Decision Support System (EDSS). DAQM has since the review been updated to DAQM-2, which is basically equivalent in its formulation to CMAQ and MAQSIP. Of these source models, three are based on urban-scale air quality models (CIT and UAM) that may be inappropriate for modeling PM within the San Joaquin Valley, because of the possible importance of long-range transport in an atmospheric layer decoupled from the surface layer (see Pun and Seigneur, 1998). Table 2-1 summarizes the major attributes of the other four regional PM air quality models. SAQM-AERO is a mesoscale model, which treats both the planetary boundary layer and the free troposphere. It has been applied to the San Joaquin Valley (Dabdub et al., 1998) and is currently being applied to Los Angeles, California (Pai et al., 1998). SAQM-AERO is available from the California Air Resources Board (whereas MAQSIP and Models-3

are not as readily available). SAQM-AERO also has an operational advantage over a research grade model such as GATOR, which has to be run on a Cray computer. For these reasons, SAQM-AERO was selected for a detailed assessment based on the modeling requirements inferred from the conceptual model.

Table 2-1. Attributes of Regional Scale PM Air Quality Models (Adapted from Seigneur et al., 1998a)

PM Air Quality Model	Host Air Quality Model	Meteorological Model	Gas-Phase Chemistry	Aerosol Thermodynamics	Inorganic PM	Organic PM	Size Distribution
SAQM-AERO	SAQM	MM5	CBM-IV	SEQUILIB	Sulfate, nitrate, ammonium, chloride, sodium, other PM material	Saturation vapor pressure defined for one condensable product of VOC oxidation	One section (PM-10) in latest applications
DAQM(1)	RADM	MM4	RADM2	MARS	Sulfate, nitrate, ammonium, EC, geological material, water	Fixed fractional yields of VOC oxidation by OH	Fine and coarse modes
GATOR	GATOR	MMTD	GATOR	EQUISOLV	Sulfate, nitrate, ammonium, chloride, sodium potassium calcium magnesium, EC, 7 metal oxides, other PM material	10 soluble and condensable organic compounds	Sectional distribution (16 sections up to 74 μm in latest application)
CMAQ(2) /Models-3 MAQSIP (3) /EDSS	CMAQ and MAQSIP	MM5	RADM2, CBM-IV	MARS-A	Sulfate, nitrate, ammonium, other PM material	Saturation vapor pressure defined for one condensable product of VOC oxidation	Lognormal distributions representing three modes up to 10 μm

(1) DAQM is being replaced by DAQM2, which is equivalent to MAQSIP with PM and cloud processes.
(2) CMAQ: Community Multiscale Air Quality Model is the air quality model in Models-3
(3) EDSS: Environmental Decision Support System; MAQSIP: Multi-scale Air Quality Simulation Platform; MAQSIP is the air quality model in EDSS

3. Mathematical Model Assessment and Recommendations for Model Development

SAQM-AERO has previously been applied to simulate a summer PM episode in the San Joaquin Valley (Dabdub et al., 1998). The modeling domain was very similar to the recommended domain and stretched from north of Sacramento to south of Arvin and San Luis Obispo. This domain covered the key upwind metropolitan areas such as the San Francisco Bay Area and the Monterey and San Luis Obispo regions. Air entering the valley from the San Francisco Bay Area may travel south to the San Joaquin Valley or north into the Sacramento valley. The inclusion of Sacramento completed the meteorological picture of the valley.

3.1 Input Data

3.1.1 Meteorology

The three-dimensional meteorological input fields of wind flow, temperature, pressure, and water vapor concentration may be calculated using a diagnostic or a prognostic meteorological model. Diagnostic models interpolate between observations, generally with some algorithm to preserve mass balance. Prognostic models solve the primitive equations of mass, momentum, and heat conservation to simulate the evolution of wind, temperature, pressure, and water vapor concentration as a function of time and space. When the prognostic model is run in the four-dimensional data assimilation (FDDA) mode, available observations are used to nudge the calculated meteorological fields. In areas with complex terrain such as the California San Joaquin Valley, a non-hydrostatic prognostic model is recommended to provide accurate predictions of mountain-valley wind patterns. Localized flows such as drainage flows and the Fresno eddy are examples of topographical effects that need to be simulated. As fog and low clouds were observed in the winter IMS 95, either a meteorological model that includes a cloud / fog module or a separate radiation fog model is needed to complete the meteorological description. Since the recommended modeling domain extends to the metropolitan areas along the coast, the meteorological model also needs to simulate land-sea breezes.

The meteorological fields for SAQM-AERO are provided by MM5, a prognostic, non-hydrostatic mesoscale meteorological model with FDDA capabilities. MM5 performs well in cases of complex topography and is suitable for modeling the vertical air motions in the mountainous areas of the San Joaquin Valley. In previous applications of MM5 to the San Joaquin Valley, details of topography-dominated flows such as the Fresno eddy have been resolved with a grid resolution of 4 km by 4 km. MM5 is currently being augmented in its capabilities of simulating fog and clouds under a CARB contract to use MM5 to simulate winter PM episodes within the San Joaquin Valley (Saffet Tanrikulu, personal communication, 1998). It should be noted that none of the available meteorological models, MM5 included, has been shown to perform well for calm conditions, which are quite prevalent in the San Joaquin Valley during winter.

When used as an input to an air quality model, the fields calculated by the meteorological model are processed so that the spatial and temporal resolutions match the requirements of the air quality model. A mismatch between the model resolution and the input data may cause uncertainties in the model predictions. MM5 uses a 4-km (or finer) grid to simulate the meteorology within the San Joaquin Valley. However, in the past, air quality applications employed grid cells of 12 km. MM5 also has finer vertical resolution than SAQM-AERO (see Figure 3-1). Therefore, the output of MM5 must be spatially averaged when used as input to SAQM-AERO. Furthermore, temporal interpolation is also needed because MM5 outputs the meteorological variables at the end of each hour while SAQM requires finer temporal resolution. Errors are thus introduced into the meteorological fields in the processing procedures. These errors are propagated in the air quality model simulation, resulting in uncertainties in the calculations of air quality variables. In addition, differences in the advective schemes of MM5 and SAQM-AERO may cause the pollutants (modeled in SAQM-AERO) to advect at a different rate or in a different direction than the parcel of air (advected in MM5) in which they are originally located. There are, therefore, several difficulties in using a meteorological model to provide meteorology inputs for an air quality model.

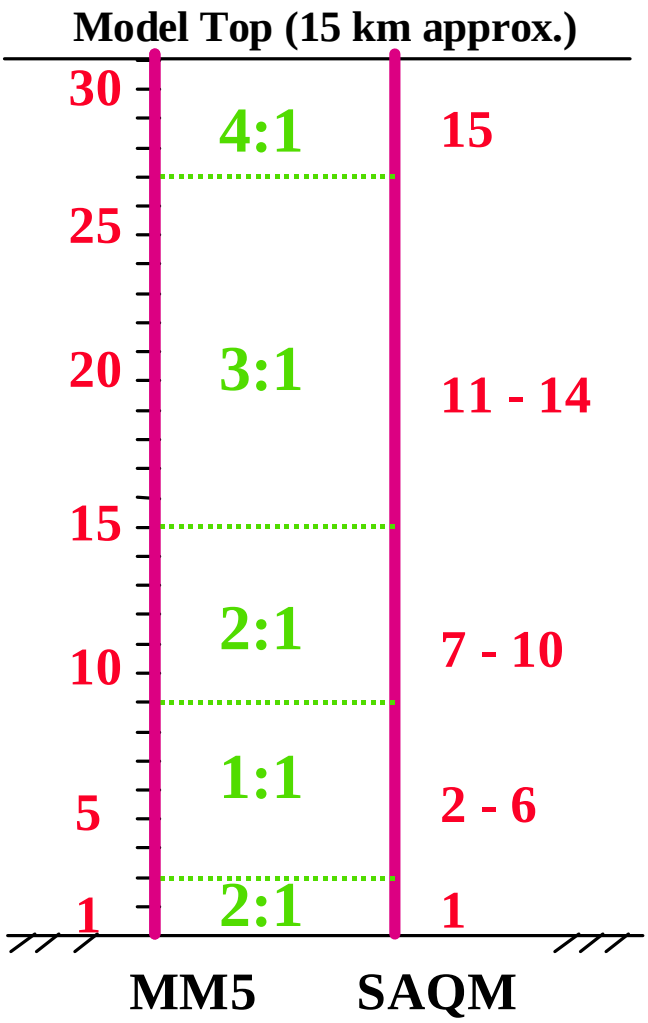

Figure 3-1. Vertical Grid of MM5 and SAQM

3.1.2 Emissions

The emissions that are important in the predictions of PM in the San Joaquin Valley include both primary sources of PM and precursors to secondary PM components. Emissions models relate the emissions of a source to a concentration profile for that type of source and the source strength, derived from the activity level (which may vary with time). There are major uncertainties associated with the concentration profiles and the source strength estimates; these uncertainties are discussed in Section 4.

3.1.3 Initial Conditions and Boundary Conditions

Initial and boundary conditions are needed to solve the partial differential equations in the PM air quality model. Initial conditions for the gas-phase concentrations of NO_x ($NO + NO_2$), sulfur dioxide (SO_2), ammonia (NH_3), speciated volatile organic compounds (VOC), and other key chemical (e.g., HNO_3, H_2O_2, O_3) are needed in each grid cell. Furthermore, PM concentrations (PM-2.5 and PM-10) and particle composition are also required. If the particle size distribution is simulated, its initial distribution must be precribed. A spin-up period of 12-36 hours is used in the SAQM-AERO modeling protocol to minimize the effects of initial conditions on the predictions of the model. Boundary conditions are required at the lateral boundaries, at the surface (emissions – deposition), and at the top of the domain for the variables mentioned above for the initial conditions. The data requirements are discussed in detail in Section 4.

3.2 Resolution

3.2.1 Particle Size Distribution and Fog Drop Size Resolution

The conceptual models indicate that the PM-10 problem in the fall of IMS 95 was different in several aspects from the PM-2.5 issue in the winter episodes. The fall PM episodes were dominated by geological material. Being mechanically generated, geological material was likely to populate the coarse fraction (> PM-2.5) of the size distribution. In the winter, however, secondary fine particles account for 70-80% of the observed PM. Therefore, we recommend that separate size fractions be used to treat the fine and coarse particles. At least two fractions should

be used to represent PM-2.5 and PM-10. Several current models use 8 or more size fractions to represent the particle size distribution. Overlapping lognormal distributions may also be used to represent particle size distributions with multiple modes (e.g., in Models-3). It is debatable whether those size distributions, using either sectional or modal representations, are necessary to address the PM NAAQS. Processes such as dry and wet deposition, cloud processes, light scattering, and in some cases, gas/particle partition strongly depend on particle size. However, uncertainties in the parameterization of these processes are likely to exceed the uncertainty that is introduced by using a default particle distribution (e.g., deduced from relevant ambient measurements) instead of calculating the evolution of modeled size distribution.

The size distribution of fog droplets also needs to be considered in PM modeling. The composition of droplets is a function of size. Due to the difference in pH among droplets of different diameters, the production rate of sulfate is a function of the droplet size. Gurciullo and Pandis (1997) showed that bulk aqueous-phase models always underpredict sulfate formation compared to a size-resolved one (they used seven sections in their modeling analysis). In addition to the production of PM sulfate and nitrate, fog droplets also remove PM when they settle to the ground. Since the settling velocity of droplets is a function of its size, accurate prediction of the wet deposition efficiency of PM requires information of the droplet size distribution. The optimal number of fog droplet sections is a compromise between the accuracy of the predictions and the computation requirements. We recommend a small study to weigh the computational cost against the accuracy gained by increasing the size resolution of droplets and determine the optimal number of fog sections to use in the model.

A sectional approach is included in the aerosol module of SAQM-AERO to represent particles and droplets. The modeling design allows the user to specify the section sizes used in each distribution. The original authors recommended using at least 8 size fractions for particles between 0.01 to 10 μm, and one section above 10 μm if fogs occur in the simulation period. However, the model has so far been applied in the San Joaquin Valley and the Los Angeles Basin with a single PM-10 size fraction (Dabdub et al., 1998; Pai et al., 1998). Neither application includes the modeling of droplets (> 10 μm). As we discussed above, it would be preferable to simulate the PM size distribution with two sections (PM-2.5 and coarse PM-10) and

the fog droplet size distribution with 2-3 sections, for example. If the model were to be applied with a fine size resolution of PM and a single size of fog droplets, the PM size distribution would be lost as fog is formed and could not be recovered as fog evaporates.

3.2.2 Spatial Resolution

Despite similarities in the build-up pattern of PM, the four core sites showed different PM concentrations during the winter episodes of IMS 95. Ground level winds were typically light (< 2 ms^{-1}); above ground wind speeds could be significantly higher (up to 15 ms^{-1} on some days). The typical spatial resolution of 10-12 km used in the mesoscale air quality simulation (e.g., by SAQM-AERO) of the San Joaquin Valley (Seaman et al., 1998) should capture the major features of the PM accumulation pattern and the associating processes. (The meteorology model MM5 was run at a 4-km spatial resolution.) During a stagnant period (3 to 5 hours), the median transport length scale was about 4 km, with turbulent diffusion dominating over ground-level advection on some occasions. In the modeling context, dispersion of pollutants between grid cells would be limited under these conditions during each time step. It is essential to limit the extent of numerical diffusion in the solution of the advection equation in order to obtain an accurate solution of the pollutant transport equations. Smaller grid cells may be necessary to decipher the transport processes.

As discussed in Section 2.3, increased resolution is recommended in the urban areas (e.g., Fresno, Bakersfield, San Francisco Bay Area) where many emissions sources are confined in a relatively small area. Nested grids with a resolution of 3 to 4 km (i.e., grid size of urban-scale models) are recommended for these areas. Strong local sources with neighborhood zone of influence (< 1 km) were consistent with the observations of IMS 95, especially during the fall season for PM-10. These sources cannot be modeled under the Eulerian grid-based framework of PM air quality models and should be analyzed by another technique such as receptor modeling.

There are typically three layers observed during the winter of 1995, schematically shown in Figure 3-2. The altitudes of the various layers varied with time and location. The depth of the

surface layer ranged from a few hundred meters to about 1000 m. At night, the surface layer was further divided into an inversion layer of 50 – 100 m and a decoupled surface layer. The upper mixed layer was typically between about 1 km and 2 km. The decoupled layer was roughly 2 km above ground level, and was free from terrain effects (free troposphere). The observed afternoon mixing layer height ranged from 125 m to 1100 m during the winter PM episodes of IMS 95. Therefore, a vertical resolution of less than 1 km near the ground is required to observe the pollutant build up in the surface layer, especially the inversion layer and the decoupled surface layer in the evening, and the upper mixed layer. Above 2 km, a vertical resolution of 1 km appears sufficient to simulate the air movement and concentration profiles in the decoupled layer.

In the previous applications of air quality models, the San Joaquin Valley domain was divided into a 12 km x 12 km regular grid in the horizontal direction. This spatial resolution should be adequate in capturing the major features of the PM buildup within the San Joaquin Valley. It is also possible to reduce the grid size of a regional model further by increasing the number of grid cells within the domain so as to provide a more detailed treatment of diffusion during stagnation. A nested grid version of SAQM exists and has been applied to the California San Joaquin Valley with three imbedded resolution of 36, 12, and 4 km horizontal grid size (Seigneur et al., 1998a, and references therein). The nested grid feature of SAQM has not been incorporated into SAQM-AERO.

SAQM-AERO is currently used with a 15-level vertical resolution from the ground to about 15 km (see Figure 3-1). Since the afternoon mixing height ranged from 125 m to 1100 m during the winter IMS 95 PM episodes, higher resolution is desirable close to the surface. A surface layer submodel (SLS) has been included in SAQM-AERO. This submodel increases the vertical resolution (60 m) at the surface and should improve the simulation of atmospheric chemistry, dry deposition, and emissions at night or when the mixing layer is shallow. Therefore, SAQM-AERO should provide adequate vertical resolution for simulating the San Joaquin Valley atmosphere.

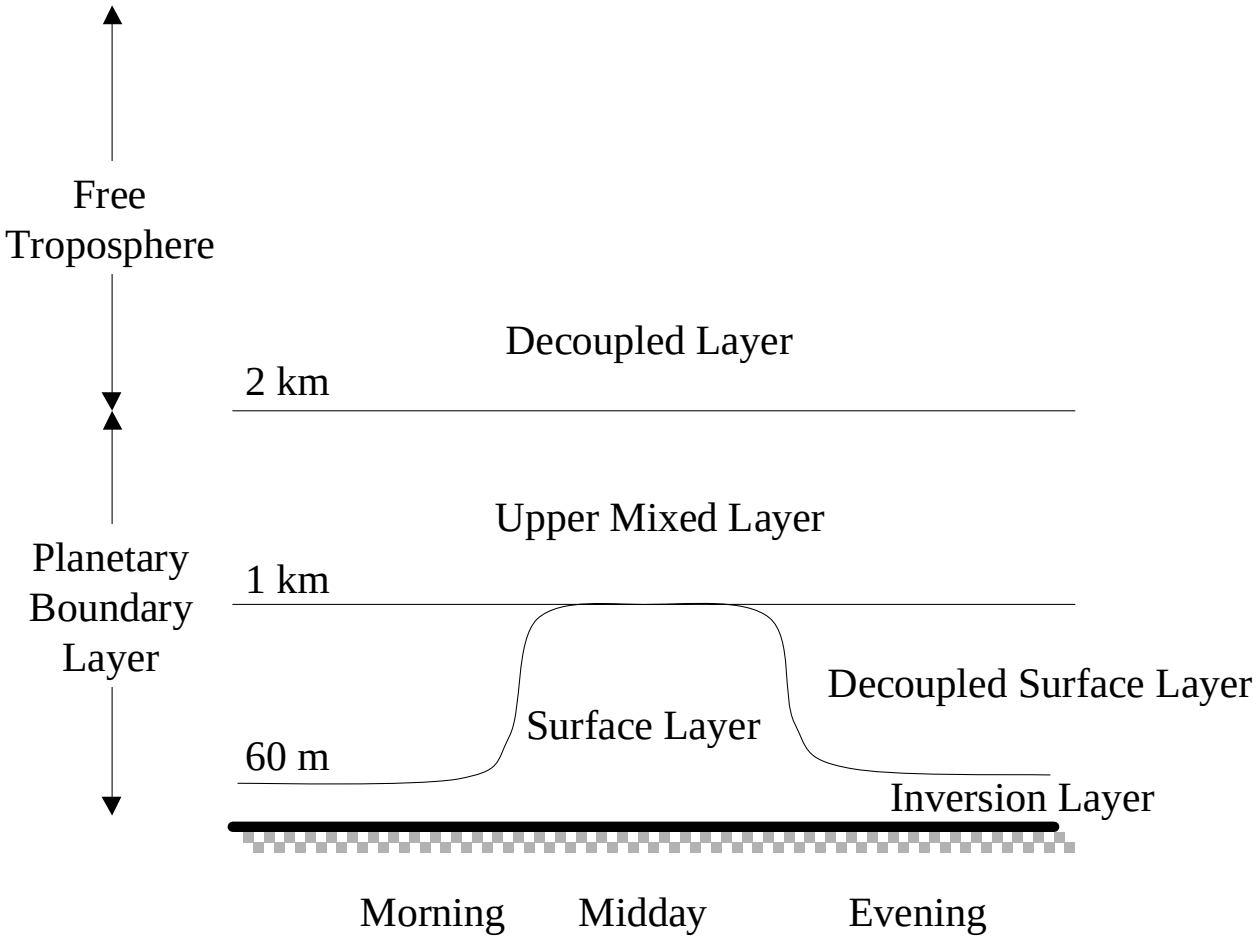

Figure 3-2. Schematic Representation of Atmospheric Layers in the San Joaquin Valley.

(Representations of heights and times are approximate.)

3.3 Chemical Transformations

3.3.1 Gas-Phase Chemistry

Oxidant Chemistry (OH, O_3, NO_3)

VOC / NO_x / oxidant chemistry affects the formation of all secondary PM components. The formation of ammonium nitrate is probably limited by the availability of HNO_3. The reactions responsible for the formation of HNO_3 are the oxidation of NO_2 by OH and the hydrolysis of N_2O_5, which can occur in both the gas phase and the aqueous phase. N_2O_5 is a combination product of NO_2 and NO_3, and NO_3 is in turn produced in the oxidation reaction of NO_2 by O_3. H_2SO_4 is formed in the gas phase and in the aqueous phase. The main gas-phase production route is the oxidation of SO_2 by OH. (The aqueous-phase oxidation of dissolved SO_2 by atmospheric oxidants is discussed in the next section.) Organic aerosols are produced in the atmospheric reactions of organic compounds with OH, O_3, and NO_3. Therefore, the abundance of oxidants such as OH and O_3 is an important factor in the production of nitrate, sulfate, and secondary organic aerosols (SOA). In addition, H_2O_2, a potent oxidant for SO_2 in the aqueous phase, is a termination product of the gas-phase radical reactions. Organic peroxides may also contribute to the aqueous oxidation of SO_2. A prerequisite of accurate predictions of secondary inorganic and organic aerosols from a PM air quality model is an up-to-date gas-phase chemistry module that provides accurate predictions of key oxidants such as O_3, OH, NO_3, and H_2O_2. In particular, it is important to understand whether the oxidant system is in a VOC- or NO_x-sensitive regime when evaluating control strategies for secondary compounds.

Two gas-phase mechanisms were implemented in SAQM, SAPRC and CBM-IV. However, only CBM-IV is incorporated in the current version of SAQM-AERO. CBM-IV uses a unique lumped structure approach to represent organic compounds. It has been extensively tested against environmental chamber data, and gives O_3 predictions that are similar to other commonly used mechanisms such as SAPRC and RADM. H_2O_2, OH, and NO_3 are modeled in CBM-IV. However, the applicability of CBM-IV to NO_x-sensitive chemistry may be complicated by the fact that CBM-IV provides no explicit treatment of organic peroxides in its current form. The condensed representation of the alkane and alkene reactions were developed based on the reactions of peroxyl radicals (RO_2) with NO_x only (typical of many urban areas), and NO_x-

sensitive oxidant chemistry (i.e., radical-radical reactions such as RO_2 + HO_2) was not considered in the original mechanism design (Gery et al., 1988). There was some evidence to support NO_x-sensitivity of oxidant chemistry within the San Joaquin Valley during the summer season (Lu and Chang, 1998). Any comprehensive effort to address O_3 and PM controls would require models that are capable of addressing both VOC- and NO_x-sensitive chemistry regimes.

The treatment of fog is limited in SAQM-AERO. In addition to serving as reactors for aqueous-phase chemistry, fog also alters the rates of gas-phase reactions. Photolysis rates are reduced within the fog layer and increased above due to back scattering of sunlight above the fog layer. In light of the effects of the photolysis reactions on the accumulation of NO_3 (and NO_2) and the formation of N_2O_5, it is possible that a more refined treatment of actinic fluxes is needed in SAQM-AERO (e.g., a detailed radiative transfer simulation such as that done in GATOR).

Secondary Organic Aerosol (SOA) Formation

Organic aerosols are formed in the atmospheric oxidation of alkanes, alkenes, and aromatic compounds. These organic compounds may be anthropogenic and biogenic in origin. In the smog chamber, the reactions of anthropogenic alkenes with O_3, and aromatic compounds with OH are known to produce particulate products. Aerosol formation is also observed when biogenic compounds, especially monoterpenes and more complex biogenic hydrocarbons, react with OH, O_3, and NO_3 in the ambient atmosphere. In addition, many oxygenated biogenic compounds may produce multifunctional products that are soluble in water.

Two types of information are needed for the detailed modeling of SOA: (1) speciated anthropogenic and biogenic organic emissions inventory, and (2) mechanistic information regarding the formation of condensable products. Although many of the condensable organic compounds are not identified, parametric approaches based on empirical results have been used to model the formation of condensable products and secondary organic aerosol. Implementing the SOA calculations involves modifications of the chemical mechanism to include condensable compounds. In addition, the partition of the condensable compounds between the gas and particle (aqueous and non-aqueous) phase must be treated. Organic compounds that partition into the aqueous phase may enhance or reduce water uptake by the inorganic components

(Saxena et al., 1995). The physical explanation of this phenomenon has not been well elucidated, although it is known that some organic compounds are hygroscopic while others may act as surfactants.

The treatment of SOA in SAQM-AERO involves the formation of a condensable product. A saturation vapor pressure is specified, below which the compound partitions into the gas phase, and above which the compound condenses until the gas-phase concentration reaches the saturation vapor pressure. In the current implementation of SAQM-AERO, a zero saturation vapor pressure has been specified. This formulation amounts to fixed fractional yields of PM directly from the gas-phase reactions. In the CBM-IV mechanism, SOA is produced in the OH-reactions of the paraffin bond (PAR) and aromatic structures (TOL, CRES, and XYL). The olefin bond (OLE) reacts with OH, O_3, NO_3, and O to produce SOA. (The O atom reaction is expected to be unimportant in the ambient atmosphere.) In addition, a separate olefin species (OLE2), which has identical gas-phase reaction rates and products but a higher SOA yield, was added to the CBM-IV mechanism to represent reactive biogenic alkenes. The fractional yields were obtained from Pandis et al. (1992). The fixed yield approach has been used extensively for modeling SOA. However, different organic precursors are likely to produce condensable compounds with different partition characteristics or vapor pressures. Modeling a single condensable compound that is completely non-volatile is unrealistic. An alternative modeling approach is based on the partition of condensable compounds through equilibrium absorption into an organic phase (e.g., Pankow, 1994; Odum et al., 1997). However, some organic compounds are known to be hydrophilic (Saxena and Hildemann, 1996) and absorption into an aqueous phase is also a plausible pathway for SOA formation.

3.3.2 Aqueous-Phase Chemistry

Aqueous-phase chemistry, especially in fog droplets, plays an important role in the formation of secondary particles, especially sulfate and nitrate compounds. Sulfates are produced in the aqueous phase by the oxidation reaction of dissolved SO_2. H_2O_2, O_3, and O_2 (reaction catalyzed by Fe^{3+} or Mn^{2+}) are the key oxidizing agents found in the San Joaquin Valley fog. The relative rates of these reactions are functions of oxidant concentrations and the pH of the droplet. Since the oxidation rates of SO_2 by O_3 and O_2 decrease with decreasing pH, these reactions are self-

limiting because their rates decrease as the product (H_2SO_4) accumulates in the fog droplet. On the other hand, the rate of the SO_2-H_2O_2 reaction is insensitive to pH, and this reaction can remain competitive at low pH. An understanding of the dominant reaction(s) responsible for the formation of sulfates at different stages of a fog episode is important for developing control options for this PM component. HNO_3 is produced in the aqueous phase as well. The hydrolysis of N_2O_5 to form HNO_3 is much faster in the aqueous phase than in the gas phase. Reactions that produce secondary H_2SO_4 and HNO_3 need to be represented in detail in the aqueous-phase chemistry module. Seigneur (1994) recommended a model that includes 40-70 reactions of radicals, metals, and organic compounds. Pandis et al. (1998) used an aqueous-phase mechanism with 109 reactions in their fog model studies.

Fog droplets in the urban areas of the San Joaquin Valley (Bakersfield and Fresno) were found to be highly buffered between pH 4 to pH 7 (Collett et al., 1998), although the nature of the buffering agent was not identified. Additional species and reactions are probably required, even in the most comprehensive aqueous-phase mechanisms, to represent the buffering process. Alternatively, a parametric approach may be used with a simpler mechanism in the interest of computational resources needed to model fog droplets.

In addition to the chemical reactions of sulfate and nitrate, current aerosol modules also treat the equilibrium relationships between gas-phase and aqueous-phase compounds and those between aqueous species. Furthermore, particulate water is associated with inorganic compounds, especially when the relative humidity is above the deliquescence point of the solute mixture. The amount of water plays a direct role in the size distribution of particles and droplets.

The formation of sulfate and nitrate in fog is not treated in the current version of SAQM-AERO. The original SAQM model contains the RADM cloud process module; however, it has not been activated in the SAQM-AERO implementation. The RADM aqueous-phase chemistry, used in Models-3 (CMAQ) and MAQSIP, contains explicit, pH-dependent SO_2 oxidation reactions. GATOR provides a more detailed description of the aqueous-phase reactions using a 64-reaction mechanism.

SAQM-AERO's aerosol module SEQUILIB treats the dissociation and equilibrium reactions involving inorganic molecules and ions, and calculates the gas-phase concentrations of NH_3, HCl, HNO_3, and the particulate-phase concentrations of H_2O, Na^+, NH_4^+, H^+, SO_4^{2-}, HSO_4^-, Cl^-, NO_3^-, H_2SO_4, Na_2SO_4, $NaHSO_4$, NaCl, $NaNO_3$, NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4, and $(NH_4)_3H(SO_4)_2$. A recent study (Zhang et al., 1998) showed that SEQUILIB compares well with the predictions of the more comprehensive SCAPE2 model under the high nitrate, high ammonia conditions found in the San Joaquin Valley. However, the predictions deviate from those obtained with more comprehensive modules (e.g., SCAPE2) by up to 40% in test cases with high sulfate and high chloride (Zhang et al., 1998).

3.4 Transport and Physical Removal Processes

3.4.1 Ground Level Transport

Advection and diffusion are standard transport processes simulated in most PM air quality models. When the mean wind speed is high, advection by the mean air movement is the dominant transport process. During IMS 95, diffusion in the ambient atmosphere, caused mainly by the turbulent fluctuations of the wind, was the dominant process during many stagnation periods when the mean wind velocity fell below 2 ms^{-1}.

Some regional models (e.g., RADM used in DAQM) do not simulate diffusion. During stagnation, the median length scale of transport, defined as the total transport distance during a stagnation event (stagnation events typically last 3 to 5 hours), is 4 km. The model's performance is expected to be impeded by numerical diffusion. This limited transport scale is commensurate with a grid size of 4 km that was previously used for urban areas in SAQM air quality simulations.

The chemistry of SO_2 and NO_x oxidation to H_2SO_4 and HNO_3 (precursors of PM) differs significantly in plumes and in the background (i.e., outside the plume). Recent work (Karamchandani et al., 1998; Karamchandani and Seigneur, 1998) shows that near the stack, acid formation in the plume is negligible; further downwind, it may approach and in some cases exceed background rates. SAQM includes a sub-grid scale treatment of plumes from large point

sources, but this algorithm has not been incorporated into SAQM-AERO. In any case, existing sub-grid scale treatment of plumes is unsatisfactory in several aspects: (1) empirical or first order closure algorithms are not always realistic (Gabruk et al., 1998; Seigneur et al., 1998b), (2) the effects of turbulent fluctuations on chemistry are not accounted for, and (3) plumes are idealized as a series of segments without the possibility to properly simulate windshear, inter- (multiple plumes) and intra-plume interactions (e.g., due to stagnation or wind flow reversal). Current plume-in-grid development (Sykes et al., 1997) includes adapting more advanced puff models in three-dimensional grid models to treat windshear, inter- and intra-plume interactions, as well as the effects of turbulence on chemical kinetics.

3.4.2 Vertical Mixing and Above-Ground Transport

Despite the lack of upper air concentration data taken during IMS 95 to evaluate the extent of above-ground pollutant transport, upper air transport and subsequent mixing into the surface layer was a postulated mechanism for the distribution of precursors. If vertical mixing is modeled adequately, then PM air quality models can be used to understand the effects of above ground transport, provided that the predictions of the aloft concentrations are accurate.

Vertical mixing involves either turbulent diffusion or convective mixing. Relief-driven vertical wind components, including upslope and downslope flows at the edge of the valley, may also be responsible for combining air that originates from different altitudes. Accurate meteorological predictions, including wind speeds, temperature profiles, mixing heights, surface heat fluxes etc., are necessary for the prediction of vertical transport at locations with complex terrain.

With the domain extending vertically to 15 km, SAQM-AERO provides sufficient treatment of atmospheric dynamics in the free troposphere to represent above ground transport of pollutants at the regional scale. Vertical convective transport (w-component of the wind vector) and diffusion are modeled. One known problem with SAQM-AERO is the significant adjustment for mass conservation when the magnitude of vertical transport is high. The mass adjustment term nearly cancels vertical transport by convection at some mountainous locations (Zion Wang, personal communication, 1998). Another potential issue is that vertical mixing schemes used under stable

and unstable conditions tend to result in different predictions. The semi-implicit K theory typically results in slower mixing than the asymmetric convective mixing (ACM) scheme. Therefore, at locations with high NO_x emissions, the semi-implicit K theory leads to lower O_3 predictions due to titration of NO_x. The difference in the O_3 predictions may be up to 15 ppb (Zion Wang, personal communication, 1998). These transport issues must be resolved before the model can be used reliably in regulatory applications.

3.4.3 Wet Deposition

Rain was not observed during the IMS 95 episodes. Rain events typically cleanse the atmosphere of PM; therefore, rain is not associated with PM episodes. The wet deposition of concern is the settling of fog droplets and the resulting removal of aqueous-phase PM such as sulfate, nitrate, and ammonium. The settling velocity is a function of droplet size, which in turn depends on the composition of PM and the associated water content. Resuspension and revolatilization of PM (or PM components or precursors) at the conclusion of the fog event may also be a possible PM source.

SAQM-AERO includes an algorithm to simulate wet deposition of droplets by gravitational settling. The gravitational settling velocity varies as the square of the particle diameter. The accuracy of the simulated wet deposition flux will depend on the resolution of the fog droplet size distribution. Resuspension and revolatilization of PM are not treated.

3.4.4 Dry Deposition

In addition to wet deposition, dry deposition is another process that needs to be investigated in detail. No dry deposition measurements were conducted during IMS 95. Due to the lack of advective transport out of the San Joaquin Valley during a PM episode, dry deposition may be an important removal process of the accumulated pollutants. The PM air quality model needs to treat the dry deposition of precursor gases (e.g., NO_x, NH_3, HNO_3, O_3, etc.) and particles (PM-2.5 and PM-10) over a variety of surfaces.

Dry deposition of particles and precursor gases is simulated in SAQM-AERO using the resistance (in-series and in-parallel) approach. The dry deposition of particles to surfaces may occur via diffusion, impaction and/or gravitational settling. The deposition layer resistance characterizes the transfer of particles through the thin, quasi-laminar layer just above the surface by Brownian diffusion and inertial impaction. Brownian diffusion is an efficient removal scheme for small particles, while inertial impaction is dominant for larger particles. The aerodynamic resistance is a function of the atmospheric stability. Gravitational settling depends on the size and mass of the particles; it only affects coarse particles significantly. Each gaseous precursor is assigned an individual deposition velocity, which is defined as the inverse of the sum of three resistance terms: (1) diffusion through the atmospheric surface layer, (2) diffusion across the boundary sublayer, and (3) absorption onto the surface, which defines the gas-surface interaction. A process analysis was conducted to compare several modules of dry deposition (Zion Wang, personal communication, 1998) and it was found that SAQM-AERO predicted higher dry deposition fluxes than other implementations, such as RADM.

3.5 Recommendations for Model Development

3.5.1 Receptor Modeling / Source Profiles

The dominance of fugitive sources such as geological material in the fall PM-10 and the contribution of area sources of vegetative burning and mobile sources to PM-2.5 in the winter lead to large uncertainties in the primary PM emissions rates. Consequently, it is recommended that receptor models be used in conjunction with source models to improve our understanding of the PM problem in the San Joaquin Valley (Seigneur et al., 1998a). Several receptor modeling techniques, e.g., CMB, can be used to perform source apportionment. Others, e.g., Principal Components Analysis (PCA), can be applied without specific source profiles. However, further developments of receptor modeling are needed for detecting the location of sources and for the apportionment of secondary PM components. Since receptor models are driven by the observed PM composition and known source profiles (in most applications), more detailed source profiles (e.g., tracer compounds) will improve their resolution. For example, generic profiles used by Magliano (1997) allowed only the apportionment of one vegetative burning category. Using fingerprint compounds such as levoglucosan (wood smoke tracer), propionylsyringol and

butyrylsyringel (hard wood), and resin acids (pine wood), Schauer and Cass (1998) were able to apportion ambient aerosol to specific categories of hardwood and softwood burning. Further work should focus on providing detailed chemical profiles for the source types prevalent in the San Joaquin Valley. Some of the data needed for better receptor modeling are also beneficial to the execution and evaluation of a source model.

3.5.2 Spatial Resolution

Low mixing layer height correlated with PM build-up during the fall and winter episodes. This phenomenon can be better represented with increased vertical resolution close to the surface by using the surface layer submodel (SLS) in SAQM-AERO. However, there are some concerns about its performance (Prasad Pai, personal communication, 1998). While predictions of ozone and other pollutants at night are more accurate near the surface, the performance of the model during the day is unsatisfactory with the introduction of the surface sublayer. A performance evaluation should be conducted for the application of the SLS in the San Joaquin Valley. A possible approach is to use SLS to represent only the nighttime inversion layer (50-100 m), i.e., to implement the SLS with an activation mechanism which engages it when the mixing layer height falls below the resolution of the bottom layer.

3.5.3 Chemistry

Due to the predominance of secondary PM in the San Joaquin Valley (~60% of PM-2.5 in the winter, 20-30% of PM-10 in the fall on average), there is a critical need to improve our ability to model the chemical processes leading to the formation of ammonium nitrate, ammonium sulfate, and secondary organic aerosol. Since ammonia sources are abundant within the San Joaquin Valley (except possibly in the western part of the valley), the production of nitric acid and the oxidation of SO_2 to sulfate are key inorganic processes of concern.

Oxidant chemistry is critical to the formation of secondary PM. The current mechanisms have not been thoroughly tested under the wintertime conditions that are conducive to PM formation in the San Joaquin Valley. SAQM-AERO currently uses CBM-IV to simulate oxidant chemistry. As a first step in testing this component of the model, another mechanism, such as

SAPRC, should be incorporated into SAQM-AERO to provide an audit of the gas-phase predictions of oxidants.

The gas-phase and aqueous-phase production processes of nitric acid (see Section 3.2) need to be represented accurately in source models that predict secondary PM. The chemistry of $NO_3/N_2O_5/HNO_3$ is sharply dependent on photolysis since NO_3 photolyzes rapidly under clear sky conditions. Currently, the parameters used for photolysis rates in the fog are highly uncertain, due to uncertainties in the actinic fluxes in a fog. Measurements of the solar flux (UV and broad radiation) are recommended to test the model's ability to treat photochemical processes under cloudy / foggy conditions and, if warranted, to improve the current empirical treatment in SAQM-AERO by adding a radiative transfer component.

Available laboratory results of the aqueous N_2O_5 hydrolysis rate (Robinson et al., 1997) should be incorporated into the aqueous-phase mechanisms. The aqueous-phase oxidation of SO_2 was a significant source of sulfate during the winter IMS 95 episodes with fog. As discussed in the previous section, SAQM-AERO does not account for aqueous-phase SO_2 reactions in its present form. Cloud and fog processes from SAQM need to be coupled to the code. Despite the observed buffering capacity of fogs, especially in the urban areas, the pH of fog droplets is not constant during a fog episode. A detailed aqueous-phase reaction mechanism is desirable in a state-of-the-art PM air quality model, which can be used to understand the relative importance of the SO_2 oxidation reactions during a PM episode with fog. In addition, some treatment of the observed fog buffering in the San Joaquin Valley should also be incorporated in the modeling system. An empirical approach is recommend for the near-term for operational purposes; for the longer term, however, additional research is needed to provide the details required for modeling the fog buffering capacity.

Secondary organic aerosols (SOA) are another area requiring further model development work. The current treatment of SOA in SAQM-AERO is equivalent to the fixed yield approach (see Section 3.2) and is fairly rudimentary. Improvements in the modeling approach may include modeling multiple condensable products with different partition characteristics or vapor pressure. Even the current state-of-the-science approaches are necessarily empirical, because

information is lacking regarding the identity of the condensable compounds for many precursor compounds. There is a dire need for mechanistic information to support a more detailed approach for modeling SOA. In particular, multifunctional products that have affinity towards the aqueous phase should be a research focus because they may alter the hygroscopic behavior of inorganic particles and droplets. Until more information is available regarding the identity and partition characteristics of condensable products, the absorption approach proposed in Odum et al. (1997) may be implemented to provide an improved estimate of SOA formation, and account for the formation of SOA at vapor pressures below saturation.

3.5.4 Transport

The limited extent of horizontal advection during many of the PM episodes makes it important to limit the numerical error in the solution of the advection equation. Many current air quality models use finite difference techniques, for which numerical diffusion can be significant, particularly under low wind conditions. Bott's numerical scheme, used in SAQM-AERO, is expected to be less susceptible to numerical diffusion. However, more accurate numerical integration techniques may need to be developed and incorporated into PM air quality models to reduce the errors in the solutions of the transport equations during stagnation. An alternative modeling technique to reduce errors due to numerical diffusion would be to implement a variable grid size system, activated to reduce the grid size during stagnant conditions to mediate the effects of numerical diffusion. Methods to treat sub-grid scale diffusion processes should also be considered for simulating stagnant conditions using a regional-scale model, if the grid cell size is greater than the transport length scale when diffusive processes are the dominant mode of transport. Major SO_2 and NO_x plumes from refineries near Bakersfield and NO_x plumes from fossil-fuel fired power plants should be modeled with an up-to-date plume-in-grid treatment until they reach a size commensurate with that of the grid cells.

Several issues are related to the treatment of vertical transport within SAQM-AERO. The mass adjustment issue (discussed in Section 3.4) may be a result of the incompatibility of the resolution of the meteorological model and that of the air quality model. Steps should be taken to ensure the consistency of the flow fields in the processing of the meteorological fields for air

quality model inputs. The differences between the semi-implicit K theory and the asymmetric convective mixing schemes for the treatment of diffusive mixing in the vertical direction also need to be addressed. A comparative study is recommended to select the more appropriate scheme for the meteorological conditions encountered in the San Joaquin Valley.

Fog and clouds are not treated in the current SAQM-AERO framework. Due to the prevalence of fog in the winter, fog processes must be simulated if SAQM-AERO is to be applied to simulate the IMS 95 episodes. This involves activating the modules in SAQM for aqueous processes. Neither the prevalence of clouds nor the effect of cloud processes was studied in detail during IMS 95. It may be important to incorporate the simulation of clouds in the PM air quality model.

Wet deposition of fog droplets is a strong function of droplet size and the chemical composition of the droplets varies with size. Therefore, several droplet sizes must be simulated in order to represent the fluxes of wet deposition of PM components.

The dry deposition velocities of particles are functions of particle size and density. However, many parameters used in the dry deposition model are highly uncertain. Therefore, simulating the evolution of particle size distribution seems superfluous since the increased accuracy would be overwhelmed by the other uncertainties of the dry deposition process (e.g., the characterization of downward fluxes through the surface layer and the laminar sublayer). Two size fractions should be adequate for the representation of PM-2.5 and PM-10. The differences identified by Wang (Zion Wang, personal communication, 1998) between the dry deposition module of SAQM-AERO and RADM should be resolved because dry deposition is potentially an important removal process for precursors and PM.

We grouped the key areas of model development and testing needs into two categories as follows.

(1) Areas where development is absolutely needed for the San Joaquin Valley application:

- Incorporate a detailed aqueous-phase chemical mechanism

- Reduce numerical diffusion during stagnation
- Implement plume-in-grid treatment for point and area sources
- Improve treatment of secondary organic aerosols

(2) Areas where testing is needed to ensure the accuracy of the model and, if testing is not satisfactory, development is needed:

- Resolve mass adjustment issue by modifying MM5 post-processing procedures
- Implement SAPRC as an audit for the CBM-IV mechanism in SAQM-AERO
- Test photolysis rates by comparing calculated radiative fluxes with measurements of UV and broad radiation
- Resolve vertical transport inconsistencies (K-theory vs. ACM)
- Test surface layer submodel (SLS) and modify as needed
- Resolve difference in dry deposition prediction of SAQM-AERO and other air quality models

4. Data Requirements for Model Input and Evaluation

Field data are required in the modeling exercise as inputs to the mathematical model and as a basis for model evaluation. Meteorological data, emissions data, and initial and boundary conditions (i.e., ambient concentrations) are required as inputs for the PM air quality model. Ambient concentrations and fluxes (e.g., deposition) of PM and precursors are needed to evaluate model performance. These data needs for model input and evaluation are listed in Table 4-1 and are discussed below. (A detailed discussion of available measurement methods is available in Seigneur et al., 1998c.)

4.1 Model Inputs

Ground level and upper air measurements of winds, temperature, pressure (to relate data to altitude), solar radiation, mixing height, and humidity can be used through FDDA to improve the performance of prognostic meteorological models. The denser the network of meteorological measurements, the more accurate the predictions of the prognostic meteorological model. Therefore, the use of remote sensing instruments (e.g., sodars, radar profilers, RASS, Lidar Raman spectroscopy) that provide continuous measurement of meteorology aloft are preferable to rawinsondes that provide a limited number of soundings per day. For surface measurements, sonic anemometers with low wind speed threshold are recommended to better characterize calm conditions. Observations of fog and cloud are necessary to determine its spatial coverage and duration. Automatic surface observations systems (ASOS), being installed at airports, should provide a reliable network for surface observations of fog (Richards et al., 1998). Satellite data may be used to supplement automatic ground level fog and cloud observations.

There are significant uncertainties in the emissions inventories of PM and precursors in the San Joaquin Valley. Detailed PM profiles are needed for receptor modeling and will improve the accuracy of the emissions input of the source models. The key primary sources of PM include geological material (PM-10), mobile sources, and vegetative burning (PM-2.5). Of particular interest are area sources such as fugitive dust and controlled and uncontrolled burning. Gaseous

Table 4-1. List of Recommended Measurements for Model Input and Evaluation.

Data	Spatial Resolution	Temporal Resolution
Meteorology		
Wind Speed and Direction	Surface and Aloft	< 1 hour *
Temperature	Surface and Aloft	< 1 hour
Mixing Height	Surface or Aircraft	< 1 hour
Relative Humidity	Surface and Aloft	< 1 hour #
Solar Radiation	Surface and Aloft	< 1 hour
Fog / Clouds	Surface and Satellite	< 1 hour
Emissions (PM, Precursor Gases)		
Profiles (Anthropogenic, Biogenic)	Representative Sources	N/A
Emission Factors	Major Sources	1 to 4 hours
PM-2.5 / PM-10		
Total Mass	Surface and Aloft	1 to 4 hours
Sulfate	Surface and Aloft	1 to 4 hours
Ammonium	Surface and Aloft	1 to 4 hours
Nitrate	Surface and Aloft	1 to 4 hours
Elemental carbon	Surface and Aloft	1 to 24 hours
Organic carbon (speciated)	Surface and Aloft	1 to 24 hours
Chloride	Surface and Aloft	1 to 4 hours
Gases		
O_3	Surface and Aloft	1 hour
NO	Surface and Aloft	1 hour
NO_2	Surface and Aloft	1 hour
VOC (Speciated)	Surface and Aloft	1 to 4 hours
HNO_3	Surface and Aloft	1 hour
NH_3	Surface and Aloft	1 hour
H_2O_2	Surface and Aloft	1 hour
Organic Peroxides	Surface and Aloft	1 hour
PAN	Surface and Aloft	1 hour
HNO_2	Surface and Aloft	1 hour

Table 4-1. List of Recommended Measurements for Model Input and Evaluation (continued).

Data	Spatial Resolution	Temporal Resolution
OH	Surface	1 hour
HO_2	Surface	1 hour
NO_3	Surface	1 hour
CO	Surface and Aloft	1 hour
SO_2	Surface and Aloft	1 hour
HCl	Surface and Aloft	1 hour
Droplet Chemistry		During Fog Event Only:
Liquid Water Content	Surface and Aloft	1 hour
Sulfate	Surface and Aloft	1 hour
Nitrate	Surface and Aloft	1 hour
Ammonium	Surface and Aloft	1 hour
Chloride	Surface and Aloft	1 hour
H_2O_2	Surface and Aloft	1 hour
Sulfite	Surface and Aloft	1 hour
H^+(pH)	Surface and Aloft	1 hour
Dissolved Fe^{3+} and Mn^{2+}	Surface and Aloft	1 hour
Wet Deposition	Representative Locations	During Fog Event Only
Sulfate		1 hour
Nitrate		1 hour
Ammonium		1 hour
Dry Deposition	Different Surface Types (aircraft measurements or tower measurements)	Representative Meteorology
PM-2.5		
PM-10		
HNO_3		
NH_3		
SO_2		
O_3		

* 5-minute temporal resolution is desired during stagnation

5-minute temporal resolution is desired during fog

precursors of PM include NO_x, SO_2, NH_3, and VOC. Haste et al. (1998) compared the ambient ratios of CO/NO_x, SO_2/NO_x, NH_3/NO_x, PM/NO_x, and $NMHC/NO_x$ to the values in the inventories. They concluded that the current inventories underestimated VOC emissions (by factors of 2-4) and overestimated SO_x (by factors of 2-4) and PM sources (by factors of 2-3). Ammonia concentrations compared favorably to inventory values only over a 25-km radius area. Better spatial and temporal emissions profiles are required for PM precursors from both anthropogenic and biogenic sources, including the size fraction of PM (PM-2.5 and PM-10), chemical composition of PM (EC, OC, sulfate, trace metals), and VOC speciation (especially long chain compounds that may be SOA precursors). Uncertainties in emissions inventories need to be reduced before modeling results may be relied upon for decisions regarding control options.

More accurate boundary conditions at the lateral boundaries and at the top of the domain are needed to provide accurate estimates of the PM within the domain. During IMS 95, conditions representative of non-anthropogenic / clean air background levels were not observed within the San Joaquin Valley (Collins, 1998). In previous applications of SAQM to O_3 in the San Joaquin Valley, the effects of boundary conditions were quite pronounced for species such as NO_x, because a large fraction of the NO_x within the San Joaquin Valley originated from the boundary at the NW corner of the region and was advected into the valley. Due to relatively low mean wind speeds in the winter, the winter PM simulation results are expected to be less sensitive to errors in the boundary condition in the winter than in the summer. However, detailed measurements for precursor concentrations and particle size and composition, especially at the surface, should be taken at the lateral boundaries of the modeling domain to define boundary conditions and to evaluate the effects of long-range transport.

Upper air measurements are also needed to define the pollutant concentrations and particle characteristics at the top of the modeling domain. In the past, insufficient upper air measurements have resulted in the reliance on expert judgment to define the aloft concentrations. New developments in remote sensing technology allow the quantification of air pollutants in situ. For example, LIDAR / DIAL measurements can be used to measure O_3 and aerosols (using UV-DIAL); H_2O, aerosol / clouds, SO_2, CH_4, CO, NH_3, NO_2, NO (using IR-DIAL); and SO_2, NO_2,

HNO_3 (using Chemical Ionization Mass Spectroscopy or CIMS). Airborne or remote sensing measurements will reduce the uncertainties in air quality modeling due to subjective judgment of the top boundary condition.

4.2 Performance Evaluation

The upcoming CRPAQS field campaign provides a unique opportunity to compile a database for the execution and comprehensive evaluation of PM air quality model. Seigneur et al. (1998c) defined four levels of model evaluation:

- Operational evaluation
- Diagnostic evaluation
- Mechanistic evaluation
- Probabilistic evaluation

Operational evaluation pertains to the ability of the model to predict accurately the variable of concern, i.e., daily average PM-10 and PM-2.5 for an episodic model. These PM measurements are obtained from routine ambient monitoring. Note that operational evaluation alone is not sufficient to assess the accuracy of the model. Diagnostic evaluation compares the model's predictions of various components of PM to the experimental values. Seigneur et al. (1998c) recommended that several tests be conducted, including:

- Analysis of PM chemical composition
- Analysis of the precursors of secondary PM and associated oxidants
- Analysis of PM size distribution
- Analysis of shorter time average concentrations
- Analysis of mass fluxes (emission, deposition, transport)

Mechanistic evaluation tests the model's ability to predict the response of the output variables to changes in the model's inputs. Simulating several time periods (e.g., multi-day episodes of different meteorologies) tests the model's response to changes in meteorology. Changes in

emissions and initial and boundary conditions can be achieved by applying the model in different geographical locations (preferably outside of California), or in the same location over different time periods (i.e., with different emissions levels). A probabilistic evaluation allows the quantification of uncertainties associated with the model design and inputs, as well as those associated with measurements. However, this exercise is resource intensive and should probably be reserved until the model has satisfactorily met the performance criteria for operational, diagnostic, and mechanistic evaluations. Our focus is, therefore, on a diagnostic and mechanistic (with respect to meteorology) evaluation of the PM air quality model. The following paragraphs discuss the field data that are needed for testing various components of the PM air quality model.

PM composition data from IMS 95 were instrumental in the development of a conceptual model for PM formation. The inorganic and organic composition of PM-10 and PM-2.5 was analyzed. Individual species measured included ammonium, nitrate, sulfate, chloride, EC, various OC, and a variety of elemental species. These measurements should be taken at sufficient spatial resolution to observe the range of concentrations prevalent within the San Joaquin Valley. Blanchard et al. (1998) analyzed the spatial representativeness of monitoring sites and the zone of influence of sources. Their results may be used to guide the spatial resolution of the monitoring network.

A prerequisite for good PM predictions is the ability of the model to predict gaseous PM precursors accurately. This pertains to the performance of the gas-phase reaction mechanism to simulate the concentration evolution of condensable species (HNO_3, NH_3, condensable organic products), their precursors (SO_2, NO, NO_2, and VOC), and oxidants, O_3, OH, NO_3, and H_2O_2 (and organic peroxides). Measurements of these compounds will provide the opportunity to evaluate the gas-phase under a set of meteorological conditions for which it has typically not been evaluated (e.g., winter foggy cool conditions instead of summer sunny warm conditions).

Since we do not recommend using a size-resolved PM model (except for two fractions 0 - 2.5 μm and 2.5 to 10 μm), the measured size distribution of PM is not directly needed for model performance evaluation. Nonetheless, size-resolved PM mass measurements may provide useful information regarding the chemical pathways of sulfate and nitrate formation. The oxidation of

SO_2 and NO_x in the aqueous phase is typically associated with larger particles (e.g., 0.5 μm mass median diameter) than the gas-phase oxidation of SO_2 and NO_x (0.2 to 0.3 μm mass median diameter) (McDade et al., 1997; Hering and Friedlander, 1982). We recommend, therefore, particle size-resolved measurements for sulfate and nitrate. During IMS 95, size-resolved samples were taken using a multi-stage impactor. Chemical speciation was performed on 10 size fractions below 15 μm.

Another test for the PM model is the prediction of the diurnal variation of PM concentration. Instead of 24-hour average samples, this requires the collection of 1-2 hour average PM samples when PM concentrations and compositions change rapidly, and 4-6 hour samples when the changes are slower. Accurate predictions of the diurnal profile of PM may be used to confirm the temporal emission profiles, chemical production pattern, or other time-specific processes, such as the production or removal of PM in fog.

Individual components of the mass fluxes should be verified to the extent possible as part of the diagnostic evaluation. It is important that the model predict correctly not only PM, but also its mass balance for applications in regulatory modeling. The components of a comprehensive mass balance include emission, transport, chemical transformation, dry deposition, and wet deposition. Although ideally one would want to characterize the various fluxes in a virtual atmospheric "box", such an exercise is likely infeasible. Nonetheless, it is beneficial to test various fluxes individually (even if a complete mass balance cannot be constructed) to ascertain that the model does not underestimate any mass flux (e.g., dry deposition) while overestimating another (e.g., wet deposition).

Independent verifications of emissions may be conducted by comparing predicted precursor or ratios of precursors with the ambient values (e.g., Haste et al., 1998). Transport fluxes may be estimated at any well-defined point of advective transport, such as a mountain pass, using either artificial or endemic tracers.

Wet and dry deposition can be directly measured and compared against model predictions. Fog settling is the primary mode of wet deposition of interest during PM episodes, and may be

measured by passive collection of fog samples on a surface during an episode. Dry deposition of particles and precursor gases and oxidants (HNO_3, NH_3, SO_2, and O_3) should be measured over a variety of surface types using the eddy correlation technique on an aircraft platform. Tower measurements with different crops provide a relatively economical alternative. Since the surface boundary condition is defined by the ground-level emission and deposition fluxes, flux measurements will aid the definition of the surface boundary condition.

5. Conclusions

5.1 Identification of Data Gaps

The phenomena responsible for the formation of PM in the fall and winter seasons in the San Joaquin Valley are complex. Many of the processes involved in the formation of PM are unknown or uncertain: ranging from undetermined fog buffering capacity and unidentified organic PM composition to an uncertain NH_3 emission inventory and poorly characterized surface deposition fluxes of PM and key precursor gases. It may be some time before a comprehensive PM air quality model can be developed that represents detailed understanding of all aspects of meteorology, chemistry, and PM thermodynamics.

Fundamental understanding is incomplete in some areas that may be important for describing PM within the San Joaquin Valley. In addition to uncertainties in the biogenic organic compounds emissions inventory, little information is available regarding the formation of secondary organic aerosol and their role in the ambient atmosphere. The identities of the condensable products resulting from the oxidation of biogenic and anthropogenic compounds are frequently unknown. Another area that needs to be addressed is the interactions between inorganic aerosols and hydrophobic / hydrophilic organic compounds. Saxena et al. (1995) pointed out that SOA might increase or decrease the water uptake of PM predicted by the inorganic composition. Organic compounds may also be responsible for the unexplained fog buffering capacity observed by Collett et al. (1998) at Fresno and Bakersfield.

The status of current models has been discussed from three perspectives: (1) field data / analyses are required to further the understanding of several processes, (2) several processes need to be represented in models in greater detail, and (3) field data are required for the execution and evaluation of PM models.

The VOC- and NO_x-sensitivity of the oxidant system can be elucidated by analyzing field concentration data (e.g., studying the ambient ratio of H_2O_2 / HNO_3). This basic characterization of the atmospheric system is important for the qualitative understanding of the gas-phase

formation of all secondary PM components, including nitrate, sulfate, and SOA. However, this approach has not been tested for nighttime, fog chemistry and there is a need to develop such an indicator for the VOC- or NO_x-sensitivity of the nocturnal / foggy atmospheric system.

Several aspects of nitrate and sulfate chemistry are still unclear. The formation of N_2O_5 during a fog episode is enhanced because of reduced photolysis dissociation of NO_3 and NO_2. Information is scarce regarding the extent of photolysis in foggy weather. In order to evaluate the contribution of the N_2O_5 hydrolysis pathways for producing HNO_3 relative to the gas-phase reaction of NO_2 + OH, measurements may be needed for NO_x, NO_3, HNO_3, and particulate nitrate in fog. The formation of sulfate in aqueous particles is expected to be slower than in fog droplets (Saxena and Seigneur, 1987; Meng and Seinfeld, 1994). Further analyses are needed to generate the photolysis rates in fog and available kinetic data for particle / droplet chemistry shoud be incorporated into SAQM-AERO.

Ammonia, a primary compound, was found to be abundant in most of the San Joaquin Valley. However, this may not be the case in the western part of the valley (Phil Roth, private communication, 1998). Since the ammonia inventory is relatively uncertain, it is desirable to assess the spatial and temporal emission patterns of NH_3 and to affirm its abundance relative to nitric acid and sulfuric acid.

The transport condition that predominated during the PM episodes of IMS 95 was stagnation. Under stagnant conditions, the transport scale of advection is similar to that of diffusion. The processes responsible for the uniform dispersion (regional background) of some precursors and secondary pollutants during stagnant conditions need to be investigated. Aloft transport of pollutants is emerging as a candidate mechanism for transport. A tracer study may be conducted to evaluate the magnitude of aloft transport as a dispersion mechanism. Provided sufficient data to evaluate the performance of source models, a modeling study may also provide insights into the transport fluxes.

5.2 Assessment of Mathematical Models

Based on current understanding, it is recommended that several processes be incorporated into models. The aqueous-phase chemistry representation in SAQM-AERO was found to be deficient. Due to the prevalence of nitrate and sulfate compounds in PM, aqueous reactions responsible for the formation of HNO_3 and H_2SO_4 should be represented in detail, especially the pH dependence of various reaction rates. Some empirical treatment of the droplet pH buffering may also be necessary for the prediction of aqueous-phase processes.

The representation of organic condensables by the fractional aerosol yield approach is now believed to be unsatisfactory in light of recent smog chamber experiments (e.g., Odum et al., 1997; Hoffmann et al., 1997). At the minimum, several species should be used to represent condensable compounds of different saturation vapor pressures. We recommend that an absorption model be included to simulate parametrically the formation of SOA when the vapor pressure is below saturation (e.g., Odum et al., 1997).

Horizontal diffusion is an important dispersion process during stagnant conditions. This process is not well simulated in regional scale PM models (and not simulated at all in some models). When the horizontal resolution of the model exceeds the diffusive transport scales and the advective transport is negligible, it may be desirable to improve the simulation of this process, e.g., by using nested grids for periods and regions of calm conditions. The surface layer submodel (SLS) was designed to increase the vertical resolution of the model near the surface so that the evening inversion layer can be accurately represented. However, the current implementation seems to provide mixed results. A detailed evaluation is needed for the formulation and implementation of the SLS within SAQM-AERO.

Subgrid scale treatment of plumes should be implemented in the SAQM-AERO to model emissions from large point and line sources. Due to frequent stagnation events observed in the San Joaquin Valley, advanced plume-in-grid modules are needed to treat windshear, inter- and intra-plume interactions, and the effects of turbulence on chemical kinetics.

Even though fogs are the prevalent form of condensed water during the IMS 95 winter episodes, the significance of cloud processes should be understood. Higher level clouds may be present during the fall, or they can theoretically coexist with fog during the winter episodes. In addition to aqueous production of sulfate and nitrate, cloud processes also include convective vertical transport and scavenging removal of PM should rain develop. Moreover, clouds affect photolysis rates of gas-phase reactions, thereby influencing oxidant levels and subsequently secondary PM formation.

5.3 Data Needs

Field data are required for the execution and evaluation of a PM air quality model. Recommendations are made to measure the following:

- Diurnal profiles of PM and PM components
- Oxidant concentrations, especially for O_3 at the ppb levels, OH, H_2O_2, NO_3 (within fog or at night)
- Precursor concentrations (e.g., NO_x, SO_2, NH_3, speciated VOC)
- San Joaquin Valley emissions profiles of geological material, mobile sources, vegetative burning
- Emissions inventories, particularly PM profiles for geological material, mobile sources, and vegetative burning, and PM precursors such as VOC, SO_2, and NH_3
- Dry deposition of PM and gaseous precursors
- Wet deposition of PM
- Meteorology at the surface and aloft

Oxidant and precursor measurements are needed to evaluate the gas-phase reaction mechanism, especially when the reactivity of the system is relatively low. The measured oxidant levels are also important in evaluating the processes that are responsible for the formation of sulfate and nitrate in the aqueous phase. Precursor concentrations can be used to evaluate the model and/or verify the overall emissions inventory. Accurate emissions profiles are necessary for both receptor modeling and source modeling. Measurements of deposition rates (both wet and dry) are important for assessing the mass fluxes of PM since under the calm conditions observed in

the valley, deposition may play an important role in the overall PM atmospheric budget. Meteorological data are used in the prognostic meteorological models to improve the calculated fields using FDDA. Such data, collected with sufficient temporal and spatial resolution, are essential to a proper characterization of meteorology in the San Joaquin Valley.

In the forthcoming Phase III report, we will compare the list of data needs proposed here with the list of measurements currently planned for the CRPAQS.

References

Blanchard, C.L., Michaels, H.M., Tanenbaum, S.J., and Fine, J., 1998. Spatial Representativeness of Monitoring Sites and Zone of Influence of Emission Sources. Draft Final Report for Tasks 4.2.1 and 4.5.6. Contract Number 97-1PM. California Air Resources Board, Sacramento, CA.

Collett Jr., J.L., Hoag, K.J., Pandis, S.N., 1998. Final Report: IMS 95 Data Analysis Work Element 4.6.8. How does Acidification of Drops Due to Aqueous Phase Acid Production Limit Aerosol Formation in Fog Drops? California Air Resources Board, Sacramento, CA.

Collins, J.F., 1998. Characterization of Boundaries and Backgrounds in the San Joaquin Valley Integrated Monitoring Study 1995. Draft Final Report. California Air Resources Board, Sacramento, CA.

Dabdub D., Dehaan, L.L., Kumar, N., Lurmann, F., Seinfeld, J.H., 1998. Computationally Efficient Acid Deposition Model for California. Draft Report, ARB Contract # 92-304, California Air Resources Board, Sacramento, CA.

Gabruk R.S., Sykes, R.I., Seigneur, C., Pai, P, Gillespie, P., Bergstrom, R.W., Saxena, P., 1998. Evaluation of the Reactive and Optics Model of Emissions (ROME) *Atmos. Environ.*, in press.

Gery, M.W., Whitten, G.Z., Killus, J.P., 1988. Development and Testing of the CMB-IV for Urban and Regional Modeling. EPA/600/3-88/012. Contract No. 68-02-4136. Office of Research and Development, U.S. E.P.A., Research Triangle Park, NC.

Gurciullo, C.S. and Pandis, S.N., 1997. Effect of Composition Variations in Cloud Droplet Populations on Aqueous-Phase Chemistry. *J. Geophys. Res.*, **102**: 9375-9385.

Haste T.L., Chinkin, L.R., Kumar, N., Lurmann, F.W., Hurwitt, S,B., 1998. Use of Ambient Data Collected During IMS 95 to Evaluate a Regional Emission Inventory for the San Joaquin Valley. Draft Final Report STI-997211-1800-DFR. California Air Resources Board, Sacramento, CA.

Hering, S.V. and Friedlander, S.K., 1982. Origins of Sulfur Size Distributions in the Los Angeles Basin. *Atmos. Environ.,* **16**: 2647-2656.

Hoffmann, T., Odum, J.R., Bowman, F., Collins, D., Klockow, D., Flagan, R.C., Seinfeld, J.H., 1997. Formation of Organic Aerosols from the Oxidation of Biogenic Hydrocarbons, *J. Atmos. Chem.*, **26**:189-222.

Karamchandani, P., Koo, A., Seigneur, C., 1998. Reduced Gas-Phase Kinetic Mechanism for Atmospheric Plume Chemistry. *Environ. Sci. Tech.* **32**: 1709-1720.

Karamchandani, P. and Seigneur, C., 1998. Simulation of Sulfate and Nitrate Chemistry in Power Plant Plumes. *J. Air Waste Manage. Asso.,* in press.

Lu, C.-H. and Chang, J.S., 1998. On the Indicator-Based Approach to Assess Ozone Sensitivities and Emissions Features. *J. Geophys. Res.* **103**: 3453-3462.

McDade C., Tombach, I., Hering, S., Kreisberg, N., 1997. Optical Properties of the Urban Aerosol in Dallas-Fort Worth. Visual Air Quality, Aerosols, and Global Radiation Balance. Proceedings of a Specialty Conference Sponsored by the Air & Waste Management Association and the American Geophysical Union. September 9-12, 1997 Bartlett, NH, Volume I, pp.400-406.

Meng, Z. and Seinfeld, J.H., 1994. On the Source of the Submicron Droplet Mode of Urban and Regional Aerosols. *Aerosol Sci. Tech*. **20**: 253-265.

Odum, J.R., Jungkamp, T.P.W., Griffin, R.J., Flagan, R.C., Seinfeld, J.H., 1997. The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor, *Science*, **276**:96-99.

Pai, P., Vijayaraghavan, K., Seigneur, C., 1998. Particulate Matter modeling in the Los Angeles Basin Using MM5 and SAQM-AERO – Preliminary Results. $PM_{2.5}$ A Fine Particle Standard, January 28-30, 1998, Proceedings of Specialty Conference Sponsored by AWMA, US EPA, and US. DOE, Ed. J. Chow and P. Koutrakis, pp.748-758.

Pandis, S.N., Harley, R.A., Cass, G.R., Seinfeld, S.H., 1992. Secondary Organic Aerosol Formation and Transport. *Atmos. Environ.* **26A**: 2269-2282.

Pandis, S., Lillis, D., Collett, Jr., J. Richards., L.W., 1998. Fog Effects on PM Concentration and Composition in the San Joaquin Valley. Final Report, IMS 95 Data Analysis Report, California Air Resources Board, Sacramento, CA.

Pankow, J.F., 1994. An Absorption Model of the Gas/Aerosol Partitioning Involved in the Formation of Secondary Organic Aerosol, *Atmos. Environ*., **28**:189-193.

Pun, B.K. and Seigneur, C., 1998. Conceptual Model for Particulate Matter Pollution in the California San Joaquin Valley. Draft Report CP045-1-98, Pacific Gas and Electric Company, San Ramon, CA.

Richards, L.W., Hurwitt, S.B., Main. H.H., Chinkin, L.R., 1998. Characterization of the Validity of Light Scattering Measurements During the 1995 Integrated Monitoring Study. Draft Final Report. STI-997216-1796-DFR, California Air Resources Board, Sacramento, CA.

Robinson, G.N., Worsnop, D.R., Jayne, J.T., Kolb, C.E., Davidovits, P., 1997. Heterogeneous uptake of $ClONO_2$ and N_2O_5 by Sulfuric Acid Solutions. *J. Geophys. Res.* **102**: 3583-3601.

Saxena, P., Hildemann, L.M., McMurry, P.H., Seinfeld, J.H., 1995. Organics Alter Hygroscopic Behavior of Atmospheric Particles, *J. Geophys. Res.*, **100**: 18755-18770.

Saxena, P. and Seigneur, C., 1987. On the oxidation of SO_2 to Sulfate in Atmospheric Aerosols. *Atmos. Environ.* **21**: 807-812.

Seaman, N.L., Stauffer, D.R., Hunter, G.K., Lario-Gibbs, A.M., 1998. The Use of the San Joaquin Valley Meteorological Model in Preparation of a Field Program in the South Coast Air Basin and Surrounding Regions of Southern California. Volume II. Numerical Modeling Studies to Support the Design of the 1997 Southern California Ozone Study (SCOS-97) Field Program. Contract number 94-730. Final Report, California Air Resources Board, Sacramento, CA.

Schauer, J.J. and Cass, G.R., 1998. Source Contributions to Airborne Particles in the San Joaquin Valley During the IMS 95 Study. Draft Final Report. Contract 97-6PM. California Air Resources Board, Sacramento, CA.

Seigneur, C., 1994. The Status of Air Quality Models. Chapter 3.2 of Planning and Managing Regional Air Quality. Ed. P.A. Solomon. Lewis Publishers, Boca Raton, FL, pp. 403-433.

Seigneur, C., Pai, P., Louis, J.-F., Hopke, P., Grosjean, D., 1998a. Review of Air Quality Models for Particulate Matter. Document No. 4669 (http://www.api.org). American Petroleum Institute, Washington, D.C.

Seigneur, C., Pai, P., Tombach, I., McDade, C., Saxena, P., Mueller, P., 1998b. Modeling of Potential Power Plant Plume Impacts on Dallas-Fort Worth Visibility. Visual Air Quality, Aerosols, and Global Radiation Balance. Proceedings of a Specialty Conference Sponsored by

the Air & Waste Management Association and the American Geophysical Union. September 9-12, 1997 Bartlett, NH, Volume I, pp.722-732.

Seigneur, C., Pun, B., Pai, P., Louis, J.-F., Solomon, P. Emery, C., Morris, Zahniser, M., Worsnop, D., R., Koutrakis, P., White, W., Tombach, I., 1998c. Guidance for the Performance Evaluation of Three-Dimensional Air Quality Modeling Systems for Particulate Matter and Visibility. Draft Report CP033-98-1a. American Petroleum Institute, Washington, D.C.

Sykes, R.I., Santos, L.P., Seigneur, C., Karamchandani, P., 1997. A New Model for Simulating Stack Plume Dispersion and Chemistry. 90th Air and Waste Management Association Annual Meeting, June 8-13, 1997, Toronto, Ontario, Canada.

Zhang, Y., Seigneur, C., Seinfeld, J.H., Jacobson, M.Z., Binkowski, F., 1998. A Comprehensive Evaluation of Aerosol Modules used in 3-Dimensional Air Quality Models. 1998 Annual Meeting of the American Association of Aerosol Research, June 22-26, 1998, Cincinnati, Ohio.

APPENDIX IV

ASSESSMENT OF MM5/SAQM FOR MODELING OZONE FORMATION IN THE SAN JOAQUIN VALLEY

ASSESSMENT OF MM5/SAQM FOR MODELING OZONE FORMATION IN THE SAN JOAQUIN VALLEY

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1.0 INTRODUCTION

1.1 Background

The 1990 San Joaquin Valley Air Quality Study (SJVAQS) and Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) were designed to study the summer ozone (O_3) air pollution problem in the California Central Valley. During the O_3 episodes of SJVAQS/AUSPEX, the 8-hour average O_3 National Ambient Air Quality Standard (NAAQS), promulgated in 1997, was exceeded on 12 days at Academy (downwind of Fresno) and on 9 days at Caliente (downwind of Bakersfield) (Chow et al., 1998). In Phase 1 (Pun et al., 1998), a conceptual model was synthesized based on available information from the field study by addressing the chemical transformations and the physical processes that were responsible for O_3 formation and accumulation within the California Central Valley.

1.2 Objectives

The SJVAQS/AUSPEX Regional Model Adaptation Project (SARMAP) was a collaborative effort by SJVAQS, AUSPEX, and EPRI for modeling and data analysis following the field study. The SARMAP modeling system consists of the SARMAP Meteorological Model (a version of MM5, hereafter referred to as MM5) (Seaman and Stauffer, 1996), the SARMAP Air Quality Model (SAQM) (Chang et al., 1997) and the data processing software for generating SAQM inputs. This modeling system simulates atmospheric dynamics and the chemistry, transport, and deposition of O_3 and precursors. In this work (Phase 2), we compare MM5 / SAQM to the conceptual model developed in Phase 1. Specific objectives of this work include:

- Assess the ability of MM5 / SAQM to represent O_3 formation processes
- Document the processes that are not well represented in the mathematical modeling system and recommend tasks for mathematical model improvement
- Identify gaps in current knowledge and recommend specific measurements and data analysis tasks

1.3 Outline

An assessment of the MM5 is provided in Section 2, followed in Section 3 by a discussion of SAQM and the associated input processing software. In Section 4, we give our recommendations regarding (1) field measurements and data analyses for improving the conceptual model, and (2) tasks needed for mathematical model improvements and performance evaluation. Conclusions are presented in Section 5.

2.0 ASSESSMENT OF MM5

In this section, we evaluate the extent to which the simulations of the SARMAP episode using the MM5 mesoscale model agree with the available data and we examine whether there are weaknesses or deficiencies in MM5 that preclude it from agreeing with the conceptual model developed under Phase 1 of this work. This evaluation is based primarily on the work of Seaman et al. (1995) and Seaman and Stauffer (1996). We also use our experience with MM5 simulations performed at AER for other purposes, mainly over the Los Angeles basin and the Tennessee valley.

MM5 is a non-hydrostatic mesoscale model developed at the Pennsylvania State University and the National Center for Atmospheric Research (NCAR). Basic references for MM5 are Dudhia (1993) and Grell et al. (1993). The model can be run in nested mode, with one or more fine mesh inner grids communicating with a coarser mesh outer grid. This approach makes it possible to perform very fine resolution simulations on a small area without it being overly influenced by the lateral boundary conditions, which need to be imposed only on the outermost grid. Typically, an inner grid has a mesh size three times smaller than the outer grid in which it is imbedded.

MM5 includes a complete set of physical parameterizations. In fact, since MM5 is widely used in the weather research community, several types of parameterizations have been developed for each physical process. Even the standard code supported by NCAR comes with several different choices.

A data assimilation system is also available for MM5. It is a newtonian relaxation or “nudging” system, in which an extra term is added to the tendency equations. This extra term is proportional to the difference between the model solution and the observations or a large-scale analysis.

Seaman et al. (1995) performed simulations with a triply nested grid, as shown in Figure 2-1, with the inner grid covering the entire San Joaquin Valley basin with a horizontal mesh size of 4 km and a vertical resolution of 30 layers from ground level to the tropopause. They used several configurations but, for our purpose, the most important results come from three experiments: (1) a control run without data assimilation (called CNTRL), (2) a run with nudging towards a larger scale analysis for

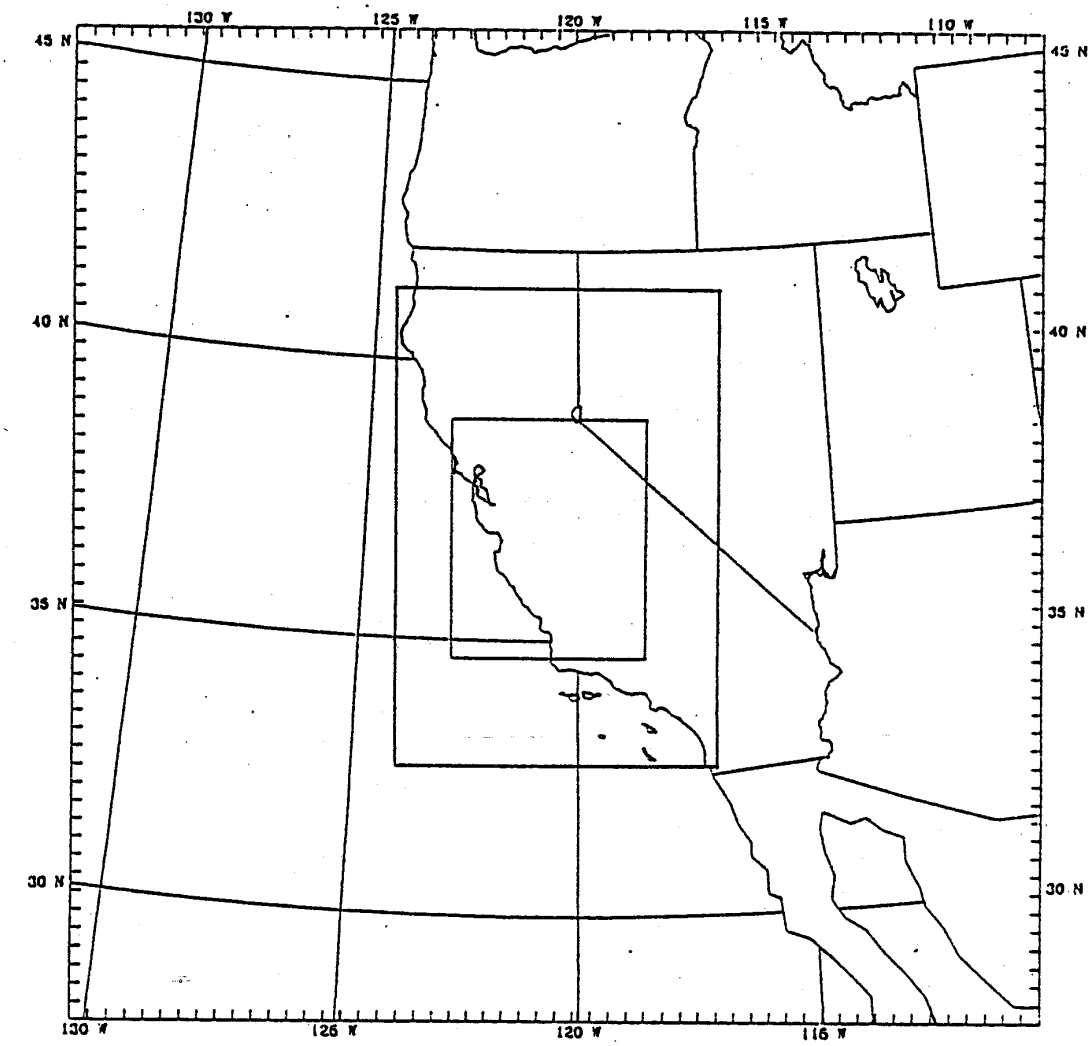

Figure 2-1. SARMAP Meteorological Model Domains (Source: DaMassa et al., 1996)

the outer grid and nudging towards the special SARMAP observations in the inner grids (CFDA), and (3) a nudging run in which only a reduced set of special observations is used (RFDA), with the rest being used for model evaluation.

Overall, the MM5 simulations of the SARMAP episodes are quite good, especially the runs that assimilate the special observation data through nudging. All the important meteorological aspects of transport in the San Joaquin Valley are qualitatively well simulated by the model, when run with a 4 km resolution for the inner grid that covers the whole valley. This includes the sea breezes, the funneling of the flow through the Carquinez Straight and the other openings of the Coastal Range, the upslope flow during the day along the Coastal Range and the Sierra Nevada, the nocturnal jet along the valley axis, and the Fresno Eddy. Although these simulations are generally successful, there are several aspects that are not quite correct and which could be improved, including:

- Inability, even with a 4 km mesh size, to simulate the largest wind velocities due to funneling in the passes
- Inner domain somewhat too small in the northern part of the domain
- Inability to assimilate low level data because of the planetary boundary layer (PBL) scheme used
- Possible problem with ground temperature initialization
- Radiation scheme not state-of-the-art
- Vertical diffusion somewhat too strong
- Horizontal diffusion not based on physical understanding
- Difficulty in simulating calm conditions

These issues are discussed further below.

2.1 Domain and Resolution

One of the main deficiencies of the simulations was the inability of the model to split the flow, west of the Carquinez Straight, in the highest resolution domain. Normally, the low level flow should split into two branches, one going southeast up the San Joaquin Valley and the other one turning north up the Sacramento Valley. The northern part of the flow is generally absent in the high resolution domain, though there are indications of it in the lower resolution domains. There is evidence that this problem is related to the position of the northern boundary of the domain. In most experiments, the innermost domain covered the entire San Joaquin Valley with a 4 km resolution. Its northern boundary was near Sacramento and excluded the northern Sacramento Valley. In one experiment, the inner domain was enlarged to the north, and the split of the flow was much better simulated.

The strength of the wind through the Carquinez Straight and Altamont Pass, east of the San Francisco Bay, is also generally too weak in the MM5 simulations. This is due to the resolution of the model: even the 4 km resolution of the inner grid is not sufficient to describe the very small scale topography that funnels the wind through the pass and accelerates it. This limitation could be overcome by increasing the resolution of the model, but this quickly becomes prohibitively expensive in terms of computational resources. It must be remembered that, as horizontal resolution is increased, the time step must be proportionally reduced. If the number of vertical levels is also increased to preserve the aspect ratio of the grid, doubling the resolution means increasing the computational cost by a factor of 16. This increase is not limited to the high-resolution domains, as all domains are required to have the same number and vertical distribution of levels in the current version of MM5.

While the inability to simulate the peak wind may result in an inaccurate transport time between the San Francisco area and the San Joaquin Valley, it should be noted that these observed high velocities are characteristic of very small areas. The total flux of material through the straights and passes is probably more accurately simulated than the maximum wind. The main effect of these high winds, which is not well simulated by the

model, is an increased stretching of the air parcels resulting in increased mixing of the pollutants.

2.2 Data Assimilation

The data assimilation procedure used in these simulations is nudging towards a combination of large-scale analysis and special observations. The analysis used in this case is that of Cressman, a successive correction type scheme, which is fairly primitive and cannot easily take into account the specific error characteristics of different observing systems. Seaman and Stauffer (1996) argue against using the more sophisticated optimal interpolation method because of the lack of appropriate error covariance matrices. These error covariance matrices are now available (Nehrkorn and Hoffman, 1996; Nehrkorn et al., 1996), making it possible to use various types of data, such as radiosondes, profilers, or satellite retrievals, with the proper weights, using optimal interpolation. Nudging towards this kind of analysis would be preferable to the method used by Seaman and Stauffer.

It was found that, using the Blackadar PBL scheme (see below), it was not possible to assimilate surface observations of temperature. The reason for this problem is that the diagnosed PBL height, which is a critical input to the scheme, is very sensitive to the surface temperature. Nudging towards a higher or lower temperature can easily result in an unrealistic deepening or collapse of the PBL. This problem could be reduced by using a scheme (such as the Gayno-Seaman (G-S) scheme discussed below) in which the PBL structure depends more on the predicted turbulent kinetic energy than on the surface temperature. None of the simulations reported by Seaman and Stauffer used surface observations. Being able to assimilate the large number of surface observations will likely improve the simulations.

The high density of observations in the study area made it possible to obtain remarkably good simulated fields. There is evidence, however, that errors in the PBL height in the San Francisco area are due to the lack of data to the north and east of the region. Adequate data coverage extending beyond the limits of the region of interest should be considered in future studies.

2.3 Parameterizations

The two most important parameterization schemes used for these simulations are the PBL scheme and the radiation scheme. There was no large scale precipitation and little moist convection during the period; therefore, the cloud and precipitation parameterizations could not be tested.

The radiation scheme used by Seaman et al. (1995) was fairly simple. It was essentially a computation of the surface energy balance and a uniform cooling rate throughout the atmosphere. The transfer of radiation between atmospheric layers was not computed. This sort of scheme is sufficient to simulate the first-order effects of radiative transfer, but it cannot reproduce accurately the details of atmospheric heating and cooling. In particular, the cooling of the PBL at night tends to be underestimated. The radiative cooling of the marine boundary layer as it moves beyond the San Francisco Bay Area towards Sacramento and Davis is also poorly simulated by the model. Surface layer temperatures are approximately 4 to 6 ºC too high in this area. A more complete radiation scheme (Dudhia, 1989) is available for MM5, but it makes the computation somewhat more expensive.

Two different PBL formulations were used in Seaman's simulations. The first one is Blackadar's first-order scheme (Zhang and Anthes, 1989). The other is the Gayno-Seaman (G-S) higher-order scheme (Gayno, 1994), which has a prediction equation for the turbulent kinetic energy, from which diffusion coefficients are deduced. The latter scheme can also handle fog, including its radiative effects, but this is not important for this study (although it would be relevant to wintertime simulations). When running with the G-S scheme, a slightly higher vertical resolution was used, with two additional levels in the PBL (12 levels below 1500 m instead of 10). Overall, the G-S scheme performed marginally better than the Blackadar scheme, except that the time of maximum wind speed in the lowest model layer was one to two hours later than observed.

It should be noted that these two schemes are not as different as one might think. They both rely on a diffusion equation to exchange heat and momentum between model layers. In one case (Blackadar), the diffusion coefficients are directly related to the

thermodynamic structure of the atmosphere, through the Richardson number. In the other case (G-S), the diffusion coefficients are related to the turbulent kinetic energy (TKE), which is a prognostic variable. The TKE evolution, however, is closely tied to the thermodynamic structure of the model. Therefore, the solutions should not be expected to be greatly different.

There is evidence that the MM5 simulations have a problem with the initialization of the ground temperature and moisture. Due to the lack of ground temperature and moisture data, this problem is not peculiar to MM5, but is quite general to all weather forecast models. In order for the surface temperature to respond correctly to flux forcing of various time scales, the soil needs to be represented by several layers (2 in these simulations, up to 5 in more recent versions of MM5). There are, however, no systematic observations of temperature or moisture in these different ground layers. It is therefore not possible to initialize them properly. Since the soil has a large heat capacity and moisture retention capacity, errors in the initial specification of deeper layers can affect the simulation over several days. Seaman and Stauffer (1996) suggest that the deep soil temperature may be too high in the model, resulting in overestimated heat fluxes that may contribute to the overestimation of surface temperatures at night in some areas. It would be helpful to make special measurements of these quantities during intensive observation periods, but the large variability of soil types makes it difficult to develop a proper measurement strategy.

The vertical and horizontal diffusion schemes of the model are important for winds, heat, and water vapor. Besides the PBL parameterization, MM5 also treats vertical diffusion in the free atmosphere. The diffusion coefficient depends on the Richardson number and is generally small, but has a minimum value to ensure numerical stability of the integration. This minimum diffusion coefficient was set at 1 m^2/s in these runs and that is an unrealistically high value, especially for stable conditions. It tends to make the vertical profiles too smooth. For example, the sharp discontinuity in the nocturnal inversion is too weak in the model. Leidner (personal communication, AER, 1998) has successfully decreased this minimum vertical diffusion coefficient to 0.01 m^2/s without encountering excessive numerical noise.

The horizontal diffusion scheme has little physical basis, besides being of the fourth order and therefore fairly strongly scale dependent. It is used mainly for numerical stability. We are not aware of any detailed studies of the effects of horizontal diffusion in MM5.

All meteorological models, including MM5, have more difficulty forecasting calm conditions than situations with a strong dynamical forcing. When the dynamics is very strong, the dominant terms of the equations of motion are the advection terms, which can be computed very accurately. Under calm conditions, the diabatic terms (radiation, turbulence, convection, etc.) are dominant. Since these terms are simulated with parameterizations that are far from perfect, meteorological models tend not to perform well under calm conditions.

3.0 ASSESSMENT OF SAQM

SAQM is a three-dimensional regional scale air quality model. It is based on the modeling framework of the Regional Acid Deposition Model (RADM), with the most fundamental change being the reformulation of the model to use non-hydrostatic meteorological data. SAQM takes as inputs emissions data, meteorological data (output from MM5), and initial / boundary conditions, and simulates the chemical and physical processes that are relevant to O_3 formation. Cloud processes are ignored in SAQM (the RADM submodule was bypassed), because of the general lack of clouds (or fogs) during O_3 episodes. SAQM, as developed under SARMAP, does not treat aerosol formation, since aerosols were not prevalent in the San Joaquin Valley during the summer O_3 season. (SAQM-AERO, the version of SAQM that includes aerosol formation, was discussed in the perspective of wintertime particulate matter (PM) formation by Pun and Seigneur, 1998.)

The ability of SAQM to simulate O_3 patterns on a regional scale (hundreds of km) requires attention to features that are less important on the urban scales (tens of km). The time scale for transport over regional scales is of the order of days, during which complex regional wind flow patterns play a crucial role in the transport and mixing of O_3 and its precursors. These flow patterns are simulated by MM5, as discussed in the previous section. SAQM simulates the following processes: emissions, mean wind transport, turbulent dispersion, chemistry, and dry deposition. The technical formulations of the modules that treat these processes are summarized in Table 3-1. Additional details on the individual process modules are provided in the following sections.

3.1 Domain and Resolution

Though surrounded by mountain ranges, the California Central Valley is by no means an isolated system. Transport of O_3 and precursors from the San Francisco Bay Area was identified in our conceptual model (Pun et al., 1998) as an important contributing factor to high O_3 in the northern part of the San Joaquin Valley under certain meteorological conditions. In addition, air exchange between the southern San Joaquin

Table 3-1. The Simulation of Key Processes by SAQM.

Process Modeled in SAQM	Technical Formulation	Role in Conceptual Model
Emissions	Emissions from area, mobile, and biogenic sources are treated in the surface layer. Point sources are identified by location. Plume rise is calculated based on Briggs (1975).	Influence of mobile emissions at urban locations and biogenic emissions at rural locations.
Transport by mean wind	Bott's fourth-order scheme for horizontal advection and second order scheme for vertical advection.	Transport of O_3 and precursors from upwind locations to SJV Aloft transport by nocturnal jet
Turbulent Dispersion	Simulated by a first-order turbulence closure eddy diffusion model for non-convective conditions. A non-local closure asymmetrical mixing scheme is used for convective conditions.	Preservation of O_3 aloft from surface titration by NO emissions Entrainment of aloft O_3 into mixed layer
Chemistry	Gas-phase chemistry with SAPRC-90 or CBM-IV. Aqueous-phase chemistry is ignored.	Local production of O_3 in and downwind of urban areas, and possibly in rural areas with significant biogenic sources
Deposition	Dry deposition is calculated using dry deposition velocities, which in turn are parameterized using the inverse resistance approach. Wet deposition is ignored.	Significant removal mechanism for O_3 (up to 3000 tons per day); extent unknown for precursors

Valley and the San Luis Obispo area contributed to high O_3 levels in the southwestern San Joaquin Valley and in San Luis Obispo County under different synoptic scale meteorology (Niccum et al., 1995). Polluted air exits the San Joaquin Valley primarily through the Tehachapi pass. Transport was also observed from the Sacramento area into the San Joaquin Valley (Blumenthal et al., 1997). The modeling domain used in the ARB simulations (DaMassa et al., 1996) extended from just north of the Sacramento metropolitan area to the Tehachapi Mountains in the southeast corner, and included the upwind coastal cities on the west. We recommend including the entire Sacramento Valley (up to Redding in the North) and extending the eastern boundary farther away from the Tehachapi Pass.

Aloft transport was an important dispersion process for O_3 and precursors during SJVAQS / AUSPEX (See Section 2). Due to the mesoscale nature of these aloft wind flows, a domain covering the surface layer and the free troposphere was used in the simulation of the San Joaquin Valley.

Seaman et al. (1995) applied MM5 to the San Joaquin Valley domain with a horizontal resolution of 4 km and found the resolution adequate for simulating most of the meteorological features of the valley (See Section 2). In previous studies, air quality models were applied with coarser resolution (e.g., 12 km) than meteorological models. As a result, meteorological model outputs had to be spatially averaged when used as inputs to air quality models. The processing of meteorological fields may introduce inconsistencies in the flow fields, which necessitate mass adjustment in the air quality model in areas with significant vertical transport (Zion Wang, personal communication, 1998). Therefore, it is important to ensure the consistencies of flow fields when using a meteorological model to provide inputs for air quality simulations.

For a regional domain such as the Central Valley, decreasing the grid size to be commensurate with the meteorological models may be infeasible for an air quality simulation because of the associated computational cost. However, SAQM was developed with nested grid capabilities. In the San Joaquin Valley simulations, 4-km nested grids were used for urban areas, such as Fresno, Bakersfield, San Francisco Bay Area, and Sacramento, to simulate in detail the formation of oxidants in and downwind of urban centers (DaMassa et al., 1996).

Despite high surface temperatures in the summer afternoon, the mixing layer within the San Joaquin Valley tended to be fairly low (400 – 1200 m) due to large-scale subsidence and mountain effects. At night, a strong surface inversion developed in the bottom 100 m near the surface. NO surface emissions scavenge O_3 near the ground but are isolated from the O_3 aloft. A high model resolution (tens of meters) near the surface is necessary to properly simulate the processes within this surface layer. Above 2 km, a resolution of greater than 1 km (1.5, 1.6, 2.0, 3.3, and 4.9 km used in previous SAQM simulation) is sufficient to simulate the synoptic scale flows.

A surface layer submodel (SLS) is included in SAQM to provide finer resolution close to the surface (to match the resolution of the lowest level of MM5, with three layers in the first 60 m). Unfortunately, the SLS has not been fully evaluated, and there are some concerns about its performance based on our experience with the model in simulating the 1987 South Coast Air Quality Study (SCAQS) August episode. While predictions of O_3 at night are improved by the use of SLS, the performance of the model during the day and for other pollutants is unsatisfactory. A comprehensive evaluation is needed to ensure that the representation of the processes in SLS is accurate.

3.2 Treatment of Processes

Emissions

Emission sources handled by SAQM include area and point sources. Area sources consist of a variety of emissions that cannot be resolved as point sources within the model formulation. In SAQM, these are grouped into three categories: mobile sources, biogenic emissions, and other area sources (e.g., industrial emissions except major stack emissions, residential emissions). Emissions from the area sources are injected into the lowest model layer, and point sources are emitted at an effective height, based on the plume rise for each point source. The emissions processor calculates the plume rise for an individual point source using meteorological parameters provided by MM5. Estimates of wind speed and temperature at the stack top are interpolated from the MM5 estimates and then used in the plume rise calculation. The linkage between the emission processor and SAQM is described in the next section.

The chemistry of sulfur dioxide (SO_2) and NO_x differs significantly in plumes and in the background (Karamchandani et al., 1998; Karamchandani and Seigneur, 1999). SAQM contains a sub-grid scale treatment of plumes from large point sources (Myers et al., 1996). Plume-in-grid treatments have been applied to sources in the Bay Area, and their effects on O_3 predictions were found to be small. However, the algorithm is unsatisfactory in several respects: (1) it uses empirical diffusion coefficients that not always realistic (Gabruk et al., 1998; Seigneur et al., 1999b), (2) the effects of turbulent fluctuations on chemistry are not accounted for, and (3) idealized treatments of plumes as a series of segments do not allow the proper simulation of wind shear, inter- (multiple plumes) or intra-plume (due to stagnation or wind flow reversion) interactions. Newer plume-in-grid models (Sykes et al., 1997; Karamchandani et al., 1999) that overcome these limitations should be incorporated into SAQM to simulate major SO_2 and NO_x plumes from refineries near Bakersfield and NO_x plumes from fossil-fuel fired power plants until they reach a size commensurate with that of the grid cells.

Transport by the Mean Wind

The numerical treatment of transport is particularly important for regional-scale applications due to the presence of low concentrations of chemical species in rural areas. During several episodes of SJVAQS/AUSPEX, weak ground level winds seemed to be a contributing factor for O_3 build-up. At surface wind speeds of < 2 m/s, it is important to minimize numerical errors in the advection scheme. Bott's scheme, used in SAQM, has undergone rigorous testing and was shown to treat low concentrations with great accuracy (Bott, 1989). It is expected to be less susceptible to numerical diffusion than the Smolarkiewicz's scheme it replaced. However, significant upstream numerical diffusion has been observed in some applications of Bott's scheme (Zhang et al., 1998). New advection schemes may help reduce numerical diffusion problems (Chock, private communication, 1998; Dabdub, private communication, 1998). In addition, further testing and development work may be needed for low wind speeds. Reducing the grid size may be one way to reduce numerical diffusion during stagnation.

Turbulent Dispersion

Over regional scales, turbulent dispersion plays an important role in determining the mixing of the precursors of O_3. For example, during the night, turbulence levels are very low and hence precursors emitted at different heights are likely to mix very slowly. Over the course of the night, the wind shear in the nocturnal boundary layer will result in the transport of these unmixed O_3 precursors to widely separated areas of the regional domain. Thus, in rural areas, where precursor emissions are low, O_3 formed during the day is likely to be the product of reactions among pollutants that originate from distant source regions. These considerations suggest that an accurate treatment of turbulent dispersion is important for simulating regional scale O_3. Turbulent dispersion in SAQM is calculated using a vertical eddy diffusion coefficient, K_z, which is calculated internally in the model. The numerical values of K_z depend on the representative velocity and length scales (e.g., friction velocity, PBL height) of the atmospheric boundary layer.

Aloft transport, especially at night, was identified in the conceptual model as an important dispersion process for O_3 and VOC (Pun et al., 1998). To properly simulate the effects of aloft transport on ground level O_3, vertical mixing needs to be accurately represented. Vertical mixing involves either turbulent diffusion or convective mixing. Relief-driven vertical wind components, including upslope and downslope flows at the edge of the valley, may also be responsible for combining air parcels that originate from different altitudes. Accurate meteorological predictions from MM5, including wind speeds, temperature profiles, mixing heights, and surface heat fluxes, are necessary for the accurate prediction of vertical transport, particularly in locations with complex terrain where convective vertical transport can be significant. However, in most SAQM applications, several MM5 layers are combined to form SAQM layers. This can result in the smoothing of some meteorological fields, e.g., vertical wind velocity. In addition, mass consistency should be examined in processing the meteorological model output to eliminate the need for mass conservation adjustment within SAQM in areas of high vertical transport.

Another potential issue is that vertical mixing schemes used under stable and unstable conditions result in different predictions. The semi-implicit K theory (used under stable conditions) typically results in slower mixing than the asymmetric

convective mixing (ACM) scheme (used under unstable conditions). Therefore, at locations with high NO_x emissions, the semi-implicit K theory leads to lower O_3 predictions due to titration of O_3 by NO. The difference in the O_3 predictions may be up to 15 ppb (Zion Wang, personal communication, 1998). These vertical transport issues must be resolved before the model can give reliable estimations of the zones of influence of emission sources under conditions of long-range aloft transport.

Gas-Phase Chemistry

Only gas-phase chemistry is treated by the model; aqueous-phase chemistry is ignored. SAQM was designed to be used with either the Statewide Air Pollution Research Center (SAPRC-90) mechanism (Carter, 1990) or the Carbon Bond Mechanism, version 4 (CBM-IV) (Gery et al., 1989). A key difference between these two mechanisms is the procedure used for lumping organic compounds. SAPRC uses the lumped molecule approach by classifying each molecule into a model class based on its homologous series and its size. The lumped structure approach in CBM-IV assigns each molecule to model classes that represent functional groups. Both mechanisms have been extensively tested against environmental chamber data, which were typically obtained at pollutant concentrations higher than observed in the ambient atmosphere. The implementation of the mechanisms in SAQM only included rudimentary treatments of isoprene chemistry. Both SAPRC-97 (Carter et al., 1997) and the current version of CBM-IV have been updated with revised isoprene chemistry. In light of the abundance of biogenic emissions in the inventory (Magliano, 1996) and the high reactivity of these compounds, more detailed isoprene reactions should be implemented in the mechanisms.

Several authors (e.g., Blanchard et al., 1995; Lu and Chang, 1998) alluded to the possible NO_x-sensitivity of the O_3 system in the San Joaquin Valley, and VOC-sensitivity in upwind areas such as the San Francisco Bay Area (Altshuler, 1998; Lu and Chang, 1998; Ziman, 1998). Therefore, it is important that the chemical mechanisms properly simulate both NO_x-sensitive and VOC-sensitive regimes. When NO_x is abundant (VOC sensitive regime), the primary termination product for radicals is nitric acid (HNO_3). However, when the NO_x concentration is low, HO_2 and RO_2 radicals recombine to form H_2O_2 or organic peroxides (ROOH). The results of the SAQM/SAPRC and

SAQM/CBM-IV models should be compared for consistency for both NO_x-sensitive chemistry and VOC-sensitive chemistry before the predictions of SAQM are used in regulatory decision making.

Deposition

Only dry deposition is treated by the model; wet deposition is ignored because O_3 episodes occur primarily during dry conditions. The time scales involved in regional-scale transport suggest that dry deposition can be a very important process that determines concentrations of O_3 precursors in rural areas. Dry deposition is simulated in SAQM using the resistance-in-series approach. The aerodynamic resistance characterizes the transport through the surface layer, and is a function of the atmospheric stability. The diffusion across the quasi-laminar boundary sublayer is characterized by the deposition layer resistance. The final resistance term describes the surface absorption of a gas. The dry deposition velocities are calculated by the meteorology preprocessor. The dry deposition module in SAQM was reportedly updated (DaMassa et al., 1996) based on findings from the California Ozone Deposition Experiment (Massman et al., 1994). Massman et al. (1994) found that RADM, the precursor of SAQM, overpredicted the deposition velocity of O_3 for two types of plant cover and incorrectly partitioned O_3 fluxes between transpiring and non-transpiring components of the third site. A recent process analysis comparison (Zion Wang, personal communication, 1998) found that SAQM predicted higher deposition fluxes than other models, which seems inconsistent with the modifications reported in DeMassa et al. Since dry deposition is potentially an important mass flux in the San Joaquin Valley, any inaccuracy of the model representation needs to be understood and rectified.

3.3 Model Input Linkages

In addition to SAQM, the SARMAP modeling system comprises two other models, MM5 and EMS (Emission Modeling System). These models provide key inputs to the process modules of SAQM discussed in the previous section. For example, EMS provides gridded and speciated emission estimates to SAQM. A compatible linkage

between MM5, EMS, and SAQM ensures that a minimal amount of processing takes place between the output from these models and the input to SAQM. Intermediate processors, as shown in Figure 3-1, establish the linkages between the three models. The processors consist of various submodels with individual functions identified in Figure 3-1.

MM5 has been designed to be fully compatible with SAQM. Therefore, meteorological fields generated by MM5 can be directly used by SAQM with minimal processing. The only processing that is needed is due to differences in the horizontal domain and the vertical grid system of SAQM and MM5. SAQM is typically run on a smaller domain and with fewer vertical layers than MM5. These differences require the meteorological preprocessor to manipulate MM5 output files to match the SAQM horizontal and vertical grid system. The manipulation is purely numerical and, in some cases, involves interpolation and averaging. It is important to ensure that the manipulation of the MM5 fields does not violate the inherent physics of the fields, e.g., mass conservation properties.

The meteorological preprocessor also calculates parameters not provided by MM5 but required by SAQM, such as dry deposition velocities and photolysis rates. It is unclear why these variables are not estimated internally in SAQM using the processed MM5 input fields and procedures similar to those in the preprocessor. Another important variable that is used by both MM5 and SAQM but is calculated independently in the two models is the turbulent diffusion coefficient, K_z. It seems intuitive that MM5 and SAQM use the same K_z fields to simulate subgrid scale turbulent dispersion. This is because the turbulent eddies responsible for dispersion of heat, momentum, and water vapor in MM5 are also responsible for dispersion of pollutants in SAQM. However, as currently formulated, SAQM estimates the K_z fields internally and these fields could be different from those estimated by MM5.

EMS was designed to provide input emission rates for precursors of O_3 at the temporal and spatial resolutions required by SAQM. The linkage between EMS and SAQM appears to be quite good since very little processing is required on the EMS output files before they can be used as input to SAQM. The processing consists primarily in merging the emission rates from the following four source types: area, point, mobile, and biogenics, into one single SAQM input file. Emission rates from three of the four

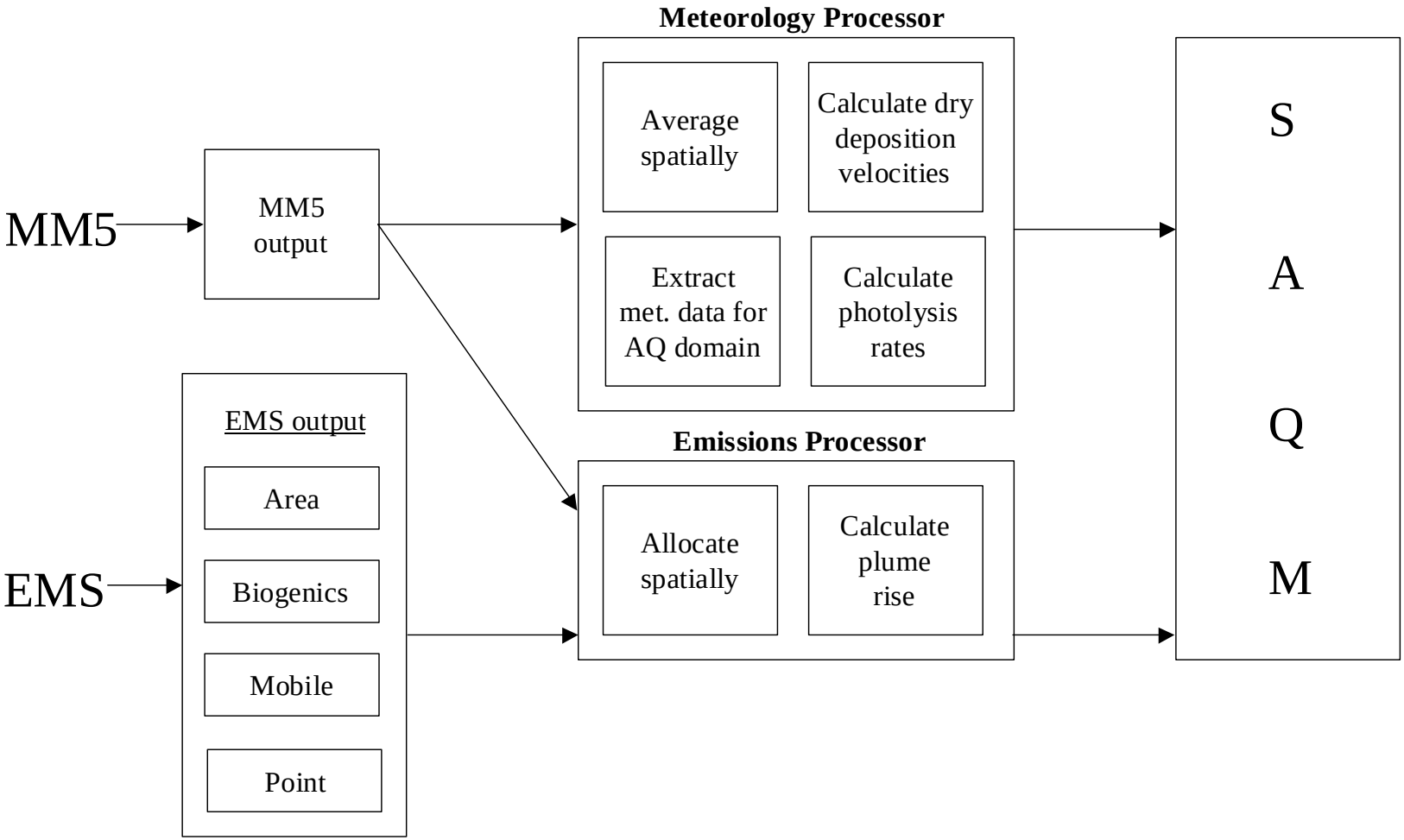

Figure 3-1. SAQM Input Linkages

source types, i.e., area, mobile, and biogenics, are added for each horizontal grid cell since they are treated in the lowest vertical layer of SAQM. The point sources, representing major stationary sources, are treated differently because they are released in SAQM at an elevation that is typically above the first vertical grid layer. The vertical location of the emission input is determined by the effective stack height of the source. This height is estimated by the plume rise module of the emission preprocessor. The meteorological fields required for the plume rise calculation are provided by the MM5 output. It is unclear why the plume rise calculation is not done internally in SAQM. As currently formulated, there could be uncertainties associated with the fact that meteorological fields (e.g., wind speed at stack height) used in the plume rise calculation are not consistent with those used in simulating other processes (e.g., advection transport in the vertical layer corresponding to the stack height).

4.0 RECOMMENDATIONS

4.1 Field Measurements and Data Analysis

Table 4-1 summarizes the field data needed to improve the conceptual understanding of the system and to support model application and evaluation. Field measurements needed to apply air quality models include initial and boundary conditions. Initial conditions are not critical because the model can be run for a period of time to flush these initial conditions out of the domain (spinup period). Boundary conditions, on the other hand, are very important. They are needed at the edges and top of the modeling domain. Clean air concentrations should not be assumed at the edge of the domain because aircraft measurements have shown that the polluted air mass can extend for several kilometers offshore. Therefore, measurements are needed at the boundaries of the modeling domain for O_3 and its precursors. The lack of information at the top boundary of the modeling domain has traditionally been a major source of uncertainty in model predictions. Since the SAQM model domain extends to the free troposphere, aloft measurements of O_3, VOC, and NO_x at a few locations will be needed for model performance evaluation purposes.

It is recommended that in future experimental campaigns, meteorological data be obtained in an area extending somewhat beyond the area of interest, especially in the regions where strong advection may be expected. Such data would be used with FDDA in MM5 to better characterize mesoscale wind flow patterns that extend to the edges of the modeling domain (e.g., flow up the Sacramento Valley from the flow divergence that occurs east of the Carquinez Straight). It would also be useful to obtain measurements of ground temperature and moisture or surface fluxes at various points throughout the domain. This information would be used in evaluating the causes of surface temperature overprediction by the model.

Even though significant improvements were made for the San Joaquin Valley emissions inventory in the 1990 field study, reconciliation with ambient data still indicates significant uncertainties in VOC emissions. Continuing efforts are needed to provide better emissions estimates for biogenic, mobile, oil production, and

Table 4-1. Field Measurements to Improve the Conceptual Model and to Support Air Quality Modeling.

Data	Use
Emissions Inventories (mobile sources, biogenic sources, oil production, uninventoried sources)	Emissions input
Meteorological data (winds, temperature, RH) especially aloft, mixing layer height (including areas beyond the immediate area of interest); ground temperature and moisture or surface heat and moisture fluxes	Meteorology model input (FDDA), evaluation of meteorological model predictions (e.g., the boundary layer parameterization).
O_3 and precursors at boundaries of modeling domain and within domain (surface and aloft)	Boundary conditions / Initial conditions Operational (surface O_3) and diagnostic model evaluation (surface precursors, aloft O_3 and precursors)
Photochemical products (e.g., HNO_3, PAN, H_2O_2, organic peroxides)	Diagnostic model evaluation; assessment of the sensitivity of oxidants to precursors
NO_2, PAN, and other nitrogen species	Diagnostic model evaluation
NO_3 and other radicals (OH, HO_2 / RO_2)	Diagnostic model evaluation
Dry deposition fluxes of NO, NO_2, HNO_3, PAN, VOC, and O_3 over a range of surfaces and atmospheric conditions	Assessment of key mass fluxes, diagnostic model evaluation

uninventoried sources. Based on reconciliation with ambient data, there are some concerns that the biogenic inventory may be overestimated. Biogenic compounds are highly reactive, and are, therefore, not prone to accumulation in the ambient atmosphere. Since exceedances of the new 8-hour O_3 standard are likely at rural locations with high biogenic VOC emissions, the formulation of effective strategies for these areas will require accurate biogenic emission inventories and proper representation of biogenic reactions in the chemical mechanisms. Major differences in the anthropogenic emissions inventories are observed between the week and the weekend. The effects of changes in NO_x and VOC emissions on O_3 concentrations should be studied using both data analysis and modeling approaches.

A key feature of the conceptual model is that high O_3 concentrations are preserved aloft at night because the thermal inversion insulates the aloft layer from the effects of surface NO_x emissions. The contributions of sources in different upwind areas to the aloft O_3 need to be analyzed. In addition, the effects of aloft point sources need to be studied to determine the zones of influence and dispersion characteristics of such sources. The nocturnal jet at 200 – 400 m may provide the vehicle for long range transport of these pollutants. To understand the impact of aloft transport, aloft winds and pollutant concentrations need to be accurately predicted by the meteorology / air quality modeling system. Aloft measurements of wind and concentrations must be taken at sufficient temporal and spatial resolution to provide for data assimilation (meteorological model) and model evaluation (meteorological and air quality models). While SJVAQS / AUSPEX seemed to have provided enough upper air meteorological data to support data assimilation (except in the northern part of Sacramento Valley), the concentration data were obtained much less frequently by aircraft. More aloft concentration data should be collected to allow for better characterization of the magnitude of aloft transport.

Measurements of H_2O_2 / ROOH and HNO_3 are useful for estimating the relative sensitivity of O_3 to VOC and NO_x at urban, suburban, and rural locations. Note that the sensitivities may be a function of location and meteorology. For example, some evidence indicates that the San Francisco Bay Area is in a VOC-sensitive regime during summertime, while most of the San Joaquin Valley appears to be more sensitive to NO_x. The sensitivities of O_3 to its precursors in the northern part of the San Joaquin Valley

may alter as a result of increased transport from the San Francisco Bay Area. In addition to measuring the relevant indicator species (e.g., HNO_3, H_2O_2, NO_y), a more comprehensive modeling study is recommended for evaluating the indicator approach (e.g., Sillman, 1995) under different meteorological scenarios.

The NO_x and NO_2 measurements suffered from interference from oxidized nitrogen species such as PAN and HNO_3. Accurate measurements of NO_x and NO_2 are important both for the understanding of the characteristics of air masses of different chemical "age" and for model evaluation purposes.

Nitrate radical measurements were taken during the SJVAQS / AUSPEX. The concentrations of nitrate radicals in the San Joaquin Valley were sufficient to oxidize organic compounds at the same rate in the evening as they are oxidized by OH during the day (Smith et al., 1995). This unexpected conclusion (VOC oxidation at night by nitrate radicals is typically expected to be two orders of magnitude slower than the day-time process initiated by OH (Atkinson, 1997)) shows that it is important to measure other radical species in addition to NO_3, especially OH, HO_2, and RO_2, which have never been measured in large-scale field programs in the San Joaquin Valley.

In addition to O_3 fluxes, dry deposition fluxes of precursors and products are needed to provide a better understanding of the pollutant removal processes within the valley. Measurements of deposition fluxes of NO, NO_2, HNO_3, PAN, and VOC are needed over a range of surfaces and atmospheric conditions.

4.2 Model Development

Specific areas of model development of MM5 are highlighted below:

- Use optimal interpolation to analyze the data in order to assimilate various types of data with different error characteristics
- Reduce as much as possible the numerical diffusion by using better algorithms
- Use a full radiation scheme and use a PBL scheme that is not overly sensitive to surface temperature in its definition of the PBL height

Specific areas of model development of SAQM are highlighted below:

- Implement advanced subgrid-scale treatment of plumes
- Evaluate the performance of the dry deposition module
- Resolve mass adjustment by modifying the processing procedures of MM5 outputs
- Resolve vertical transport inconsistencies
- Test surface layer submodel and modify as needed

5.0 CONCLUSIONS

We have reviewed the MM5 / SAQM modeling system and concluded that, in principle, it represents the key features of the conceptual model for O_3 formation in the San Joaquin Valley. Several aspects of the model related to vertical mixing and transport need to be tested and improved. Modeling studies are recommended to (1) elucidate the sensitivities of O_3 to its precursors at different locations where the 8-hour NAAQS is expected to be exceeded, and (2) investigate the zones of influence of emission sources due to long-range aloft transport.

Until now, O_3 and PM pollution issues have been considered independently. In the San Joaquin Valley, exceedances of the PM and O_3 NAAQS occur in different seasons. Recent studies (e.g., Meng et al., 1998) have shown that control strategies for O_3 may have adverse effects on PM in the same modeling scenario. Pun and Seigneur (1998) postulated that the formation of PM in the San Joaquin Valley is sensitive to the availability of oxidants. Since control strategies are seldom season-specific, measures for controlling summer O_3 will certainly affect the oxidant concentrations, hence PM formation, in the winter.

Also, particulate matter has been shown to affect O_3 in modeling studies through their light extinction properties (Dickerson et al., 1997; Jacobson, 1998), typically leading to higher photochemical activity and higher O_3 concentrations aloft and lower photochemical activity and lower O_3 concentrations at the surface. Dreher and Harley (1998) postulated that this effect may partly explain the increased O_3 concentrations observed on weekends at some locations affected by heavy truck traffic during the week. Although PM is not a significant problem in the San Joaquin Valley summer O_3 season, the extent of its influence, if any, on O_3 formation has never been quantified in the San Joaquin Valley.

Therefore, the effects of any control measures designed for the summer O_3 problem on PM need to be investigated. In this regard, a model that treats both PM and O_3 (see Seigneur et al., 1999a for a review of such models) is required for air quality studies in the San Joaquin Valley.

REFERENCES

Altshuler, S., 1998. Presentation at the workshop on draft emission inventory and draft attainment assessment, Bay Area Air Quality Management District, San Francisco, CA, October 8, 1998.

Blanchard, C.L., P.M. Roth, H.E. Jeffries, 1995. Continuing Development of a Methodology for Assessing Preferences for Reductions in VOC versus NO_x Emissions in Non-attainment Areas, Transactions, Regional Photochemical Measurement and Modeling Studies, An A&WMA International Specialty Conference, San Diego, CA, 7-12 November, 1993, ed. by J.G. Watson, J.C., Chow, and P.A. Solomon, Published by the Air & Waste Management Association, Pittsburgh, PA, pp. 335-350.

Blumenthal, D.L., F.W. Lurmann, P.T. Roberts, H.H. Main, C.P. MacDonold, W.R. Knuth and E.M. Niccum, 1997. Three-dimensional Distribution and Transport Analyses for SJVAQS / AUSPEX, Final Report STI-91060-1705-FR, San Joaquin Valleywide Air Pollution Study Agency, c/o California Air Resources Board, Sacramento, CA.

Bott, A., 1989. A Positive Definite Advection Scheme Obtained by Non-linear Renormalization of the Advection Fluxes, *Mon. Weather Rev.* **117**, 1006-1115.

Briggs, G.A. 1975. Plume Rise Predictions, pp. 59-111. In D.A. Haugen, ed. Lectures on Air Pollution and Environmental Impact Analyses. AMS Workshop on Meteorology and Environmental Assessment, September 29-October 3, 1975, Boston. AMS, Boston, MA.

Carter, W.P.L., 1990. A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds. *Atmos. Environ.* **24A**, 481-518.

Carter, W.P.L., D. Lu, I.L. Malkina, 1997. Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment. Report prepared for the California Air Resources Board, Sacramento, CA, Contract 92-345, Coordinating Research Council Atlanta, GA, Project M-9, and the National Renewable Energy Laboratory, Contract ZF-2-12252-07

Chang, J.S., S. Jin, Y. Li, M. Beauharnois, C.-H. Lu, H.-C., Huang, S. Tanrikulu, and J. DaMassa, 1997. The SARMAP Air Quality Model. Final Report, California Air Resources Board, Sacramento, CA.

Chow, J.C., J.G. Watson, D.H. Lowenthal, R.T. Egami, P.A. Solomon, R.H. Thuillier, K. Magliano and A. Ranzieri, 1998. Spatial and Temporal Variations of Particulate Precursor Gases and Photochemical Reaction Products during SJVAQS/AUSPEX Ozone Episodes, *Atmos. Environ.* **32**, 2835-2844.

DaMassa, J., S. Tanrikulu, K. Magliano, A.J., Ranzieri, L. Niccum, 1996. Performance Evaluation of SAQM in Central California and Attainment Demonstration for the August 3-6, 1990 Ozone Episode. Air Resources Board, Sacramento, CA.

Dickerson, R.R., Kondragunta, S., Stenchikov, G., Civerolo, K.L., Doddridge, B.G., Holben, B.N., 1997. The Impact of Aerosols on Solar Ultraviolet Radiation and Photochemical Smog, *Science* **278**, 827-830.

Dreher, D.B. and Harley, R.A., 1998. A Fuel-Based Inventory for Heavy-Duty Diesel Truck Emissions. *J. Air & Waste Manage. Assoc.* **48**, 352-358.

Dudhia, J., 1989. Numerical Study of Convection Observed during the Winter Monsoon Experiment Using a Mesoscale Two-Dimensional Model. *J. Atmos. Sci.* **46**, 3077-3107.

Dudhia, J., 1993. A Nonhydrostatic Version of the Penn State-NCAR Mesoscale Model: Validation Tests and Simulation of an Atlantic Cyclone and Cold Front. *Mon. Wea. Rev.* **121**, 1493-1513.

Gabruk R.S., Sykes, R.I., Seigneur, C., Pai, P, Gillespie, P., Bergstrom, R.W., Saxena, P., 1998. Evaluation of the Reactive and Optics Model of Emissions (ROME) *Atmos. Environ.*, in press.

Gayno, G. A., 1994. Development of a Higher-Order, Fog Producing Boundary Layer Model Suitable for use in Numerical Weather Prediction. M. S. Thesis, Pennsylvania State Univ., 104 pp.

Gery, M.W., Whitten, G.Z., Killus, J.P., Dodge, M.C., 1989. A Photochemical Kinetics Mechanism for Urban and Regional Scale Computer Modeling. *J. Geophys. Res.* **94**, 12925-12926.

Grell, G. A., J. Dudhia and D. R. Stauffer, 1993. A Description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5). NCAR Technical Note No. 398+1A. 107 pp., National Center for Atmospheric Research, Boulder, CO.

Jacobson, M.Z., 1998. Studying the Effects of Aerosols on Vertical Photolysis Rate Coefficient and Temperature Profiles over an Urban Airshed, *J. Geophys. Res.* **103**: 10593-10604.

Karamchandani, P., Koo, A., Seigneur, C., 1998. Reduced Gas-Phase Kinetic Mechanism for Atmospheric Plume Chemistry. *Environ. Sci. Tech.* **32**, 1709-1720.

Karamchandani, P., Seigneur, C., Pai, P., Lohman, K., Zhang, Y., Tonne, C., Vijayaraghavan, K., Santos., L., Sykes, I., Nehrkorn, T., Henderson, J., Louis, J.F., Hansen, A., Saxena, P., 1999. Development and Testing of a New Plume-in-Grid Model to Examine the Effect of Power Plant Plumes on Ozone Formation. Electric Utilities Environmental Conference, January 11-13, 1999, Tucson, AZ.

Karamchandani, P. and Seigneur, C., 1999. Simulation of Sulfate and Nitrate Chemistry in Power Plant Plumes. *J. Air Waste Manage. Asso.*, in press.

Lu, C.-H. and J.S. Chang, 1998. On the Indicator-Based Approach to Assess Ozone Sensitivities and Emissions Features. *J. Geophys. Res.* **103**, 3453-3462.

Magliano, K.L., 1996. Descriptive Analysis and Reconciliation of Emissions and Ambient Hydrocarbon Data, SJVAQS / AUSPEX Technical Topic Team #5 Report, California Air Resources Board, Sacramento, CA.

Massman, W.J., J. Pederson, A. Delany, D. Grantz, G. den Hartog, H.H. Neumann, S.P. Oncley, R. Pearson, Jr., R.H. Shaw, 1994. An Evaluation of the Regional Acid Deposition Model Surface Module for Ozone Uptake at Three Sites in the San Joaquin Valley of California. *J. Geophys. Res.* **99**, 8281-8294

Meng Z., Dabdub, D., Seinfeld, J.H.,1998. Chemical Coupling Between Atmospheric Ozone and Particulate Matter. *Science* **277**, 116-119.

Myers, T.C., Guthrie, P.D., Wu, S.-Y., 1996. The Implementation of a Plume-in-Grid Module in the SARMAP Air Quality Model (SAQM). Final Report. San Joaquin Valleywide Air Pollution Study Agency / California Air Resources Board, Sacramento, CA

Nehrkorn, T., R. N. Hoffman, J. Sparrow, and M. Yin, 1996. Development and Testing of Theater Analysis Procedures (TAP): Results from Year 2. PL-TR 96-2246, Phillips Laboratory, Hanscom Air Force Base, MA. [NTIS ADA319121]

Nehrkorn, T. and R. N. Hoffman, 1996. Development of a Small-Scale, Relocatable Optimum Interpolation Data Analysis System. In 11th Conference on Numerical Weather Prediction, pages 91--93, Norfolk, Virginia, 19-23 August, American Meteorological Society, Boston, MA.

Niccum, E. M., D. E. Lehrman and W. R. Knuth, 1995. The Influence of Meteorology on the Air Quality in the San Luis Obispo County - Southwestern San Joaquin Valley Region for 3-6 August 1990, *J. Appl. Meteor.* **34**, 1834-1847.

Pun, B.K., J.F. Louis, and C. Seigneur, 1998. A Conceptual Model for Ozone Formation in the San Joaquin Valley. Draft Report CP049-1-98. Pacific Gas & Electric Company, San Ramon, CA.

Pun, B.K. and Seigneur, C., 1998. Integrated Modeling Study 95: Assessment of Mathematical Models and Associated Data Needs. Report CP045-2-98. Pacific Gas & Electric Company, San Ramon, CA.

Seaman, N. L., D.R. Stauffer and A.M. Lario-Gibbs, 1995. A Multiscale Four-Dimensional Data Assimilation System Applied in the San Joaquin Valley during SARMAP. Part 1: Modeling Design and Basic Performance Characteristics, *J. Appl. Meteor.* **34**, 1739-1761.

Seaman, N. L. and D. R. Stauffer, 1996. SARMAP Meteorological Model Final Report. San Joaquin Valleywide Air Pollution Study Agency and California Air Resource Board, Sacramento, CA. 173 pp.

Seigneur, C., P. Pai, P. Hopke, D. Grosjean, 1999a. Modeling Atmospheric Particulate Matter. *Environ. Sci. Technol.*, in press.

Seigneur, C., Pai, P., Tombach, I., McDade, C., Saxena, P., Mueller, P., 1999b. Modeling of Potential Power Plant Plume Impacts on Dallas-Fort Worth Visibility. *J. Air Waste Manage. Assoc.*, in press.

Sillman, S., 1995. The Use of NO_y, H_2O_2, and HNO_3 as Indicators for Ozone-NO_x-Hydrocarbon Sensitivity in Urban Locations, *J. Geophys. Res.* **100**, 14,175-14,188.

Sykes, R.I., Santos, L.P., Seigneur, C., Karamchandani, P., 1997. A New Model for Simulating Stack Plume Dispersion and Chemistry. 90th Air and Waste Management Association Annual Meeting, June 8-13, 1997, Toronto, Ontario, Canada.

Zhang, D. L. and R. A. Anthes, 1982. A High-Resolution Model of the Planetary Boundary Layer - Sensitivity Tests and Comparisons with SESAME-79 Data. *J. Appl. Meteor.*, **21**, 1594-1609.

Zhang, Y., Seigneur, C., Seinfeld, J.H., Jacobson, M.Z., Binkowski, F.S., 1998. Simulation of Aerosol Dynamics: A Comparative Review of Algorithms Used in Air Quality Models. To be submitted to *Aerosol Sci. Technol.*

Ziman, S., 1998. Presentation at the Workshop on Draft Emission Inventory and Draft Attainment Assessment, Bay Area Air Quality Management District, San Francisco, CA, October 8, 1998.

APPENDIX V

COMMENTS ON

FIELD PROGRAM PLAN FOR THE CALIFORNIA

REGIONAL

$PM_{2.5}/PM_{10}$ AIR QUALITY STUDY

Comments on
Field Program Plan for the California Regional
$PM_{2.5}/PM_{10}$ Air Quality Study

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1.0 INTRODUCTION

The California Regional $PM_{2.5}/PM_{10}$ Air Quality Study (CRPAQS) of 1999 – 2000 contains three components: the annual study, the winter study, and the fall study. The monitoring domains are shown in Figure 1-1. The objectives of the CRPAQS are to: (1) obtain a quality data base, (2) evaluate the backbone network (used to determine compliance), (3) examine temporal and spatial distributions of PM concentrations, (4) examine boundary layer and regional circulation, (5) estimate source zones of influence and contributions, (6) determine sources of secondary aerosols, (7) refine conceptual models, and (8) improve simulation methods.

The long-term average study will take place from December 1, 1999 to January 31, 2001, with daily continuous aerosol sampling and meteorological measurements at several sites to supplement the ARB backbone network. Upper air measurements of wind speed and direction will be acquired continuously (15-minute averaging time) at 11 sites using radar profilers, and at one site using a sodar. Upper air measurements of the virtual air temperatures will be obtained at the radar profiler sites using radioacoustic sounding systems (RASS). In addition, radiosondes will be launched twice a day at 4 sites to obtain aloft measurements of wind speed and direction, temperature, and relative humidity (RH). A 100-m micrometeorological tower will be set up at Angiola to obtain high time resolution measurements of meteorology and particle size at several levels. Information from the tower will aid in the interpretation of boundary layer evolution. Special studies will also be carried out for measurement technique evaluation, winter PM forecast, assessment of background site elevation, and summer organic aerosols.

The winter study will be held towards the end of the annual study from December 1, 2000 to January 31, 2001. In addition to continuous measurements of PM mass, size distribution, light scattering, sulfate, nitrate, and elemental carbon / organic carbon (EC/OC), gaseous measurements of oxidized nitrogen (NO_y)/NO, ammonia (NH_3), sulfur dioxide (SO_2), nitric acid (HNO_3), and ozone (O_3) will be obtained. About 20 episode days will be selected for intensive monitoring. On those days, PM-2.5 elements, ions, some speciated organic compounds (both particulate and gas phases) will be obtained

Figure 1-1. CRPAQS Monitoring Domains for Annual, Winter, and Fall Studies. (Source: Watson et al., 1998)

at intervals of 5-6 hours to supplement the continuous measurements. Additional upper air meteorological sites will also be set up to measure daily profiles of wind and temperature using radar profilers, RASS, and sodars. On episode days, 2 to 6 soundings of radiosondes will be made to capture the diurnal changes in upper air meteorology, including RH.

Details regarding the fall study are not clear, as the description of measurements in Section 7 recapitulates that for the annual study. Two special studies will be conducted to investigate agricultural dust suspension and deposition, and ammonia or nitric acid limitation in the vicinity of ammonia sources.

The objectives of this work are to:

- Review the Field Program Plan for the CRPAQS (hereafter referred to as the Field Program Plan)
- Recommend any modifications to the Field Program Plan
- Provide feedback on modeling data needs, priorities, and potential tradeoffs

A general review of the Field Program Plan is provided in Section 2. Section 3 describes the knowledge gaps in the conceptual model of PM formation in the San Joaquin Valley (Pun and Seigneur, 1998a) and the measurements that are useful for understanding these processes. The data needed for model execution and evaluation are presented in Pun and Seigneur (1998b) and compared against the Field Program Plan in Section 4. In Section 5, we present our recommendations on the priorities and potential tradeoffs of field measurements, based on the CRPAQS objectives.

2.0 GENERAL REVIEW OF THE FIELD PROGRAM PLAN

The outlined plans in Sections 5.6, 6.5, and 7.3 of the Field Program Plan for using the data from the CRPAQS annual, winter, and fall studies to attain the field program objectives contain the same text. It is clear that the annual study is designed to understand the causes of PM-2.5 annual averages that might exceed the National Ambient Air Quality Standard (NAAQS), while the winter study focuses more on PM episodes and on generating the necessary data for the application and evaluation of episodic air quality source models. (The main goal for the fall program is not defined because the text in that section is duplicated from the winter / annual sections.) Without clear directions on how to apply the data from each study to fulfil the CRPAQS objectives, it is difficult to evaluate the effectiveness of the proposed measurement strategies.

In addition to unclear objectives, incomplete descriptions of the Angiola tower measurements (Section 6.3), the aircraft valley-wide layer depth study (Section 6.4.1), and the free radical study (Section 6.4.5) make it hard to determine how these measurements aid in furthering the understanding of PM formation and / or model evaluation. The Field Program Plan also provides few details for the development of emissions inventories, which should be an integral part of any field program. The only mention of measurements to support emissions modeling is found in Section 3 (Conceptual model, questions, and data needs) of the Field Program Plan:

> Separate studies will be carried out during CRPAQS field studies to 1) estimate traffic volumes, makeup, and the distribution of primary particle emission rates; 2) create chemical profiles for emissions from cooking, cold start exhaust, visible exhaust, diesel exhaust, residential burning, and suspended dust; and 3) determine day and site specific events that might affect concentrations.

No information is available regarding the measurement approach, the testing sites, and the time frame of these measurements. The details for the fall measurement program

are sketchy, as the fall program description in Section 7 appeared to be duplicated from the annual program of Section 5.

While nearby sources and high wind fugitive dusts were highlighted in the sections that describe the uses of annual / winter / fall study measurements to attain the objective of refining the conceptual model (Section 3.1), several aspects of the proposed conceptual models require verification. Measurements that are useful in verifying the conceptual models will be discussed in Section 3 in conjunction with those required to fill the knowledge gaps identified by Pun and Seigneur (1998a).

3.0 KNOWLEDGE GAPS

Several knowledge gaps were identified in the conceptual models for PM formation in the California San Joaquin Valley (Watson et al., 1998, Section 3; Pun and Seigneur, 1998a). To verify Watson et al.'s conceptual model, specific measurements are needed to assess the effects of mixing in the morning and early afternoon, the influence of stratus clouds on secondary aerosols, the extent of oxidant production (surface and aloft), the importance of aqueous sulfate production, and the magnitude of aloft transport in the winter. Pun and Seigneur (1998a) augmented the conceptual model of Watson et al. (1998) and emphasized the need to understand the formation of atmospheric oxidants during the winter season. Oxidants play an important role in the production of secondary compounds, including HNO_3 (precursor to particulate nitrate), sulfate, and secondary organic aerosols (SOA). In the fall, the areas that need to be studied include the sources of fugitive dust, the dispersion processes responsible for the subregional distribution of PM, and the limiting reagent (i.e., HNO_3 or NH_3) for the formation of ammonium nitrate. Table 3-1 summarizes the key areas of uncertainties and the measurements that may be taken to reduce those uncertainties. The field data needs are discussed further in the next paragraphs.

3.1 Gas-Phase Measurements

Gas-phase data are needed for both the precursors of secondary PM and for oxidants. These data are important not only for the evaluation of chemical pathways for the formation of sulfate, nitrate, and secondary organic aerosols, but also for the evaluation of the gas-phase chemical mechanism used in the host air quality model. Gas-phase data from routine monitoring stations will be supplemented with 5-minute NO_y/NO data and light hydrocarbons samples collected every sixth day in the annual study. For the winter study, continuous monitors are proposed for NO_y, NO, NH_3, SO_2, HNO_3, and O_3. Light and heavy hydrocarbons will be measured with 5 or 6 hour samples during PM episodes.

Table 3-1. Knowledge Gaps

Question	Information Needed	Proposed Measurements in the Field Program Plan
Re: Ammonium Nitrate		
Is NH_3 abundant for NH_4NO_3? Everywhere in the valley? During all seasons?	Ammonia inventory, spatial coverage, area sources, non-winter conditions. Measurements of NH_3, HNO_3, and NH_4NO_3.	Emission study (ES), special fall study in the vicinity of an ammonia source. 5 sites during winter episodes (HNO_3 and NO_2 separation if possible).
What chemical processes are responsible for the formation of HNO_3?	Diurnal profiles of NO, NO_2, NO_3, HNO_3, OH, O_3, including in fog. Spatial and Temporal distributions of fog and clouds. Measurements of solar radiation in fog.	NO, NO_y, NH_3, HNO_3, O_3 winter study continuous sites 5 minutes. Fog observed at airports and backbone sites. Solar radiation only measured at routine sites.
Is the formation of HNO_3 limited by oxidants or NO_x?	Same as above.	Same as above.
Is the formation of oxidants limited by VOC or NO_x?	Evaluation of the gas-phase chemical mechanisms and the indicator approach in the winter season (through modeling studies and field data, see below). H_2O_2, HNO_3/PM nitrate measurements.	No continuous H_2O_2 measurements.

Table 3-1. Knowledge Gaps (continued)

Question	Information Needed	Proposed Measurements in the Field Program Plan
Re: Secondary Organic Aerosols		
What is the abundance of SOA during non-winter seasons?	PM OC profiles for primary sources, especially tracer-based profiles in SJV. Ambient organic PM composition.	ES. Anchor sites.
What are the precursors of SOA?	Anthropogenic and biogenic VOC inventory. Understanding of gas-phase reactions forming condensable compounds (laboratory research and data analysis).	ES.
Re: Sulfate		
Is the sulfuric acid formed neutralized by NH_3?	Inventories of NH_3 and SO_2.	ES.
What are the key chemical processes (gas-phase and aqueous-phase) for the formation of sulfate?	Measurements of OH, SO_2, O_3, H_2O_2, Mn^{2+}, Fe^{3+}, RH, pH, particulate water, including low concentrations in fog. Understanding of pH evolution and buffering capacity within fog droplets (laboratory analysis of fog composition, including organic buffering agents). Spatial and temporal distribution of fog and clouds.	No continuous measurements for H_2O_2, OH; SO_2 at only one (Bakersfield) site. Only total Fe, Mn, ions during episodes. 9 RH sites with 5-minute data. No continuous monitor for particulate water (maybe fog study?) Any collection of fog droplets? Limited fog observations likely taken at airports, nephelometers at backbone sites.

Table 3-1. Knowledge Gaps (continued)

Question	Information Needed	Proposed Measurements in the Field Program Plan
Re: Primary Sources		
How to improve receptor modeling?	Better profiles for primary sources (dust, mobile, burning): SJV specific, fingerprint compounds.	ES.
Re: Horizontal Transport		
Where does aloft transport take place?	Measurements of wind speeds as a function of time and height.	7 sites during episodes, 2 – 6 /day.
What is the extent of upper air transport of precursors? PM?	Measurements of diurnal upper air meteorology and concentrations of O_3, NO_x, VOC, SO_2, HNO_3, PM	Wind speed, direction, temperature, RH daily or 2-7 times / day. Aloft concentrations not measured except PM measurements aloft during one episode (to be compared to elevated Sierra sites).
What is the range of surface level transport during the fall?	Surface meteorology measurements taken at PM monitoring sites. PM size measurements (used to estimate deposition life time of particles).	Sensitive, fast wind and RH monitors at core sites. Wind measurements at transport sites. Daily 5-minute particle size distribution at 3 core sites for annual study.
What are the influences of widespread area sources (fall)?	PM emission inventories for geological material sources, uninventoried sources.	ES.

Table 3-1. Knowledge Gaps (continued)

Question	Information Needed	Proposed Measurements in the Field Program Plan
Re: Vertical mixing		
Is upper air transport responsible for dispersion of pollutants?	Measurements of temporal and spatial variations of mixing height. Concentration profiles of PM and precursors in the vertical direction.	Aircraft study (winter special study, spatial variability), 2 to 6 soundings per day during winter episodes at 4 sites. Aloft concentration measurements not planned.
Re: Wet deposition		
What are the wet deposition fluxes?	Size fractionated fog samples. Collection of settled fog droplets. Measurements of sulfate, nitrate, OC, other elements/ions.	Fog study at Angiola tower may include some fog droplet sampling.
Is re-suspension of PM a concern after a fog episode?	Fog/PM/PM component fluxes during / after fog episodes.	Same as above.
Re: dry deposition		
What is the extent of dry deposition?	Direct eddy flux measurements of PM and precursors over a range of surfaces and under a range of meteorological conditions (tower or aircraft).	Dust deposition/suspension experiments planned. Gases and fine particles mentioned for deposition experiments at the tower, but no details available.

Missing in this list are NO_2, VOC other than hydrocarbons (such as oxygenates), and other radical and oxidants such as OH, H_2O_2, and NO_3. Although NO_2 may be separable from NO_y measurements, NO_2 should be measured independently because it is the immediate precursor to HNO_3, the probable limiting reagent for NH_4NO_3 according to the conceptual models. With accompanying measurements of other nitrogen species, the important processes responsible for the formation of nitric acid and the limiting reagent in the system may be inferred.

Oxygenated organic compounds, such as aldehydes and ketones, are primary VOC as well as intermediate products of the atmospheric oxidation if VOC. Aldehydes contribute significantly to oxidant formation through their photolysis and atmospheric reactions. In addition, both aldehydes and ketones can provide useful information on the extent of reactions of organic compounds. These measurements are needed to initialize the model and are also very useful for the evaluation of chemical mechanisms. Note that chemical mechanisms for oxidant formation have not been evaluated for cool and wet conditions.

OH is obviously a key gas-phase oxidant for both NO_2 and SO_2. H_2O_2 (possibly also organic peroxides, ROOH) is an important aqueous oxidant for SO_2. NO_3 is a precursor to HNO_3, both in the aqueous phase and gas phase when photolysis is reduced. Although ozone will be continuously monitored in the winter study of CRPAQS, an ozone monitor with sufficient sensitivity for measuring ozone in the fog has yet to be identified. Measuring these radicals and oxidants will yield information directly relevant for understanding nitrate and sulfate chemistry.

Gas-phase measurements of ammonia and nitric acid during the annual study will be useful in determining the relative abundance of the precursors to NH_4NO_3 in the spring, summer, and fall. Higher temporal resolution (e.g., hourly data) may be beneficial for understanding emissions and chemical reactions of primary organic compounds. Five-minute measurements may be unnecessary for some of the other compounds, especially secondary compounds such as NO_y. Intermittent sources of NH_3, NO_x, and SO_2 may be detected using high resolution data; however, inference regarding the location of the source and the duration of the emission activity may be difficult under calm conditions.

Watson et al. (1998) postulated that the production of secondary aerosol, including sulfate and nitrate, takes place aloft and in cloud droplets. Therefore, measurements of aloft concentrations of precursor gases (SO_2, NO_x, NH_3) and oxidants (O_3, H_2O_2) should be taken to verify those aspects of their conceptual model. In addition, this information is useful in assessing the extent of vertical mixing at various times of the day, the importance of aloft production of oxidants, the importance of aloft transport of PM precursors and oxidants from upwind areas such as the San Francisco Bay Area, and the efficiency of upper air transport as a mechanism for pollutant dispersion within the San Joaquin Valley (e.g., for NH_3).

3.2 Particle Measurements

There is a strong emphasis on particle measurements in the Field Program Plan: continuous measurements of PM-10, PM-2.5, size distribution, light scattering, and PM-2.5 components at resolution of 5 minutes (sulfate, nitrate, EC/OC) to 6 hours. PM size distributions in the fall are useful for estimating deposition rates of geological particles and the zones of influences of the emission sources. Indirect evidence may also be obtained from the size distribution regarding the dominant processes for the production of secondary compounds. For example, sulfate of gas-phase origin tends to deposit onto smaller particles than sulfate formed in the aqueous phase (Hering and Friedlander, 1982; Meng and Seinfeld, 1994; Hering et al., 1997).

The special study of fog intensity and composition should address some of the questions raised in IMS 95. Since details of the fog study to be conducted at Angiola tower are not yet available, we could not assess whether additional measurements should be recommended. Areas requiring additional research include (1) the agent(s) responsible for the unexplained fog buffering capacity observed in urban fog droplets, (2) accurate measurements of oxidants (O_3, H_2O_2), catalysts (Fe or Mn), and SO_2 at low levels to confirm the relative importance of the sulfate-forming reactions, and (3) wet deposition fluxes of fog water and fog components such as nitrate, sulfate, ammonium, and organic compounds.

3.3 Surface and Upper Air Meteorological Measurements

The temporal and spatial variations of the mixing layer height have a strong impact of the dispersion and transport of PM and PM precursors. A special study is scheduled during the winter of 2000 for an aircraft investigation of the spatial variations of the mixing layer depth. The frequency of flights is unknown at this time. During the winter episode, 17 stations will be operational with radar profilers and RASS, and 10 stations will be equipped with sodars for continuous (15 minute) measurements (versus 11 radar profilers/RASS and 1 sodar during the annual study). In additions, 2-6 soundings will be made at 6 upper air radiosonde stations to measure wind, temperature, and relative humidity (RH) as a function of height. On the other hand, the backbone network only contains 11 stations that make 1 to 2 soundings per day. Higher spatial and temporal resolutions are desired for both the annual study and the intensive studies in the fall and winter to characterize the mixing conditions in the SJV and to provide information from which the impacts (time, location) of aloft transport may be inferred.

Measurements of solar radiation are essential to assess the importance of NO_3 as a precursor for the production of HNO_3. Fog reduces the amount of radiation available at the surface, and reduces the photolysis rate of NO_3. Together with increased water content, the accumulation of NO_3 may increase the importance of N_2O_5 hydrolysis as a pathway for the formation of HNO_3. To properly analyze the production of nitrate, measurements of radiation, especially during a daytime fog episode, are recommended.

The spatial and temporal distribution of fog and clouds may be an important factor affecting the efficiency of the production of nitrate and sulfate. Fog observations are made at the airports by automatic surface observation systems and at the backbone sites, indirectly, by nephelometers. Information about the vertical extent of fog is, however, limited to the observations of the special study. The spatial and temporal extent of clouds may be observed by satellites, but the use of satellite data is not currently included in the Field Program Plan.

3.4 Vertical Mixing and Aloft Transport

The impacts of aloft transport and reaction processes are key areas of uncertainty in the conceptual models and are related to vertical mixing within the San Joaquin Valley. The mixing layer height during the day is variable in time and in space. Different estimation techniques tend to result in inconsistent answers. Since PM correlates well with aloft temperature, which can be related to atmospheric stability, a consistent understanding of the daytime mixing layer is needed to evaluate the dispersion processes of PM.

The evening inversion plays an important role in trapping emissions within a shallow layer next to the surface, resulting in increased concentrations of PM (and probably precursors as well) at the urban sites. The conceptual model in Section 3 of the Field Program Plan states that as the inversion layer breaks, the trapped material is mixed into the "valley wide" layer aloft. This is where chemical reactions take place to produce secondary compounds such as HNO_3 during the day. Stronger winds aloft are postulated to be a mechanism for the dispersion of pollutants. This conceptual model seems simpler than the conceptual model developed by Pun and Seigneur (1998a) based on the findings of Dye et al. (1998). Dye et al. found that the atmosphere within the San Joaquin Valley is typically divided into 3 layers, as shown in Figure 3-1. Wind speeds with the surface layer are typically low. The upper mixed layer is characterized by uniform wind flows at higher speeds (up to 10 m/s). According to Dye et al. (1998), this layer is between 1 and 2 km.

It is not clear in the Field Program Plan which layer is the so-called "valley wide" layer and where aloft transport, suggested by the conceptual model, takes place. Watson et al. (1998) described the mixing situation in Section 2 (pg. 2-10) as follows:

> During winter nights and mornings, a shallow (30 to 50 m agl) radiation inversion forms, which only begins to couple to the valleywide mixed layer between 1000 and 1200 PST, and reasserts itself after sunset at 1800 PST.

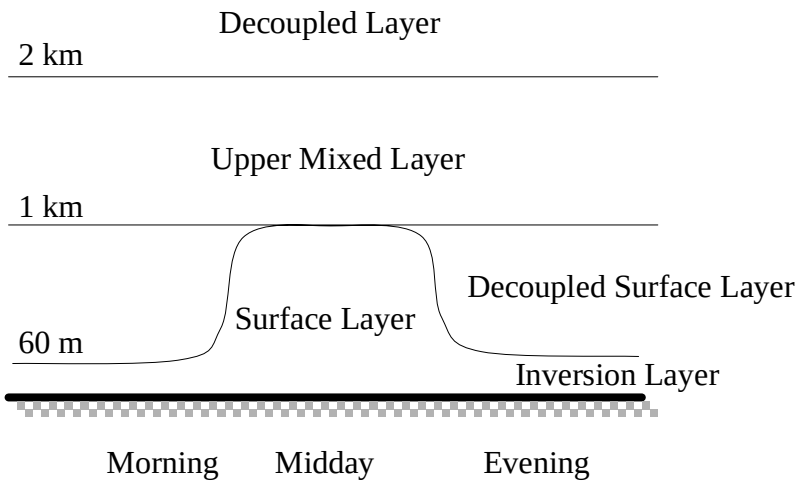

Figure 3-1. Vertical Layers in the San Joaquin Valley (Dye et al., 1998)

From this description, the valleywide mixed layer seems to be the equivalent of the decoupled surface layer depicted in Figure 3-1. (Figure 2.4-1, which might help clarify the definitions, is missing in the Field Program Plan). If this is the case, it should be confirmed that the wind speed in the decoupled surface layer (typically less than 5 m/s) can be responsible for the aloft transport that is inferred in the model. Another possibility is that transport takes place in the upper mixed layer. Upper air measurements to characterize the height of this layer, and concentration measurements aloft to understand the vertical extent of mixing in the afternoon could be useful. Currently, no upper air measurements of chemical / PM concentrations are planned. Ground level measurements at elevated sites are proposed; however, they will characterize the valley slopes and may not represent aloft conditions in the center of the valley. A winter special study is planned to compare PM measurements taken at 250 m above ground level in the valley and those taken at the Sierra Foothills sites. However, there is no back-up plan to study the aloft concentrations of PM and their gaseous precursors in case the foothill sites are found to be unrepresentative of concentrations aloft in the valley.

3.5 Data for Receptor Modeling

Receptor models are particularly useful tools for understanding the source contributions of primary sources. The requirements of running a receptor model such as Chemical Mass Balance (CMB) are accurate ambient measurements of PM composition and detailed source profiles specific to the area of interest. Key areas of uncertainties include fugitive dust profiles, motor vehicle emissions categories such as cold start, running losses, and exhaust, and various vegetative burning profiles. Accurate measurements of PM source profiles (specific for the San Joaquin Valley) and the measurement of compounds that provide source signatures will extend the resolution of CMB to a larger number of sources and allow more accurate determination of source contributions of all relevant sources.

4.0 Data Needs for PM Air Quality Model Evaluation

The data needed for executing and evaluating PM source models are discussed in Pun and Seigneur (1998b) and summarized in Table 4-1. The meteorology and chemistry measurements proposed in the Field Program Plan should form a reasonable database for model execution and evaluation. However, several areas require supplemental data.

In general, additional aloft measurements of meteorology are desirable. The planned measurements combine continuous measurements (11 radar profilers/RASS and 1 sodar during the annual study; 17 radar profilers/RASS and 10 sodars during the winter study) with radiosondes (twice per day during the annual study and up to six times per day during winter episodes). The continuous measurements provide 15-minute temporal resolution for wind speed, wind direction, and temperature data. However, the range of radar profilers (wind measurements) and RASS (virtual temperature measurements) are limited to 500 to 800 m, respectively, while sodars can measure wind speed and direction up to 2000 m. The ranges of the continuous measurements fall short of the decoupled layer. Radiosondes, which obtain data from 0.1 to 10 km above ground level, are only launched 2 to 6 times a day during CRPAQS.

Other improvements are also desired in the meteorology network. The spatial and temporal variations of mixing height and observations of fog and clouds are important inputs for data analysis and for the meteorological model. In addition, measurements of solar radiation during a fog episode will aid the testing of the current assumptions made in air quality models and provide useful information to refine chemical kinetic calculations within the fog module.

Emissions inventories are particularly important for the performance of PM air quality models and should be independently verified. Coupled with accurate source profiles, source strength (emission factors) information obtained in a separate emission study will allow the independent evaluation of the emissions programs within the air quality modeling system. Emissions measurements are a critical component of a field program designed to generate a database for model performance evaluation. A model performance evaluation is meaningless when poor model performance can be attributed to large uncertainties in the input data. Although details regarding the emissions study

Table 4-1. Data Needs for Episodic Modeling

Data	Spatial Resolution	Temporal Resolution	Proposed Measurements in the Field Program Plan
Meteorology			
Wind Speed and Direction	Surface and Aloft	< 1 hour *	Surface/tower: 1-5 min; aloft: 4-7 radiosondes twice per day to 2-6 times per day (w); 15-min average data from 11 to 17 radar profilers, 1 to 10 sodar
Temperature	Surface and Aloft	< 1 hour	Same as wind measurements for sondes; 15-min average data from 11 to 17 RASS
Mixing Height	Surface or Aircraft	< 1 hour	Winter aircraft measurements (f?), temperature profile soundings 2-6 times per day at 4 sites (w)
Relative Humidity	Surface and Aloft	< 1 hour #	Surface: 5 min, aloft 2-6 times per day at 4 sites (w)
Solar Radiation	Surface and Aloft	< 1 hour	Radiation at backbone sites only (f?)
Fog / Clouds	Surface and aloft (coverage and depth)	< 1 hour	Fog/cloud observations probably obtained at airports (f?)
Emissions (PM-2.5, PM-10, Precursor Gases)			Details of emission study unavailable
Profiles (Anthropogenic and Biogenic)	Representative Sources	N/A	
Emission Factors	Major Sources	1 to 4 hours	
PM-2.5 / PM-10			
Total Mass	Surface and Aloft	1 to 4 hours	10 min (annual, winter anchor sites)
Sulfate	Surface and Aloft	1 to 4 hours	5 min (PM-2.5 winter anchor sites)

Table 4-1. Data Needs for Episodic Modeling (continued)

Data	Spatial Resolution	Temporal Resolution	Proposed Measurements in the Field Program Plan
Ammonium	Surface and Aloft	1 to 4 hours	24 hour
Nitrate	Surface and Aloft	1 to 4 hours	10 min (PM-2.5 winter anchor sites)
Elemental carbon	Surface and Aloft	1 to 24 hours	30 min (PM-2.5 winter anchor sites)
Organic carbon (speciated)	Surface and Aloft	1 to 24 hours	OC 30 min, speciation 5-6 hours (PM-2.5 winter anchor sites, episodes)
Chloride	Surface and Aloft	1 to 4 hours	3-6 hours (PM-2.5 winter anchor sites, episodes)
Gases			No aloft gases measurements planned (except for a special winter study)
O_3	Surface and Aloft	1 hour	5 min (winter anchor sites)
NO	Surface and Aloft	1 hour	5 min (winter anchor sites)
NO_2	Surface and Aloft	1 hour	5 min (winter anchor sites; separated from NO_y if possible)
VOC (Speciated)	Surface and Aloft	1 to 4 hours	5-6 hours (hydrocarbons only; no oxygenates such as aldehydes)
HNO_3	Surface and Aloft	1 hour	5 min (winter anchor sites)
NH_3	Surface and Aloft	1 hour	5 min (winter anchor sites)
H_2O_2	Surface and Aloft	1 hour	None (fog study?)
Organic Peroxides	Surface and Aloft	1 hour	None (fog study?)
PAN	Surface and Aloft	1 hour	Lumped into NO_y
OH	Surface	1 hour	None
HO_2	Surface	1 hour	None
NO_3	Surface	1 hour	None
CO	Surface and Aloft	1 hour	Backbone sites (annual, f?)
SO_2	Surface and Aloft	1 hour	5 min (winter anchor sites)

Table 4-1. Data Needs for Episodic Modeling (continued)

Data	Spatial Resolution	Temporal Resolution	Proposed Measurements in the Field Program Plan
Droplet Chemistry		Fog Only	Details of fog study unavailable
Water Content	Surface and Aloft	1 hour	
Sulfate	Surface and Aloft	1 hour	
Nitrate	Surface and Aloft	1 hour	
Ammonium	Surface and Aloft	1 hour	
Chloride H_2O_2	Surface and Aloft	1 hour	
Sulfite	Surface and Aloft	1 hour	
H^+(pH)	Surface and Aloft	1 hour	
Dissolved Fe^{3+} and	Surface and Aloft	1 hour	
Mn^{2+}	Surface and Aloft	1 hour	
Wet Deposition	Representative Locations	Fog Only	Details of fog study unavailable
Sulfate		1 hour	
Nitrate		1 hour	
Ammonium		1 hour	
Dry Deposition	Different Surface Types (aircraft measurements or tower measurements)	Representative Meteorology	Dust (coarse PM) deposition study at Angiola tower (Tower measurements of gases and fine particles mentioned, but details unavailable)
PM-2.5			
PM-10			
HNO_3			
NH_3			
SO_2			
O_3			

* 5-minute temporal resolution is desired during stagnation

5-minute temporal resolution is desired during fog

f? frequency unknown

w winter study supplements annual study with additional sites and increased frequency of observations

are limited, we recommend the verification of the abundance of ammonia emissions relative to nitric acid production as a priority. The temporal and spatial profiles of NH_3 and SO_2 are also uncertain. Accurate source profiles of San Joaquin Valley sources will be beneficial to the application of receptor modeling from which the contributions of secondary organic aerosols (SOA) can be determined. In addition, a review of the anthropogenic and biogenic VOC emissions inventories is necessary for the accurate modeling of oxidant chemistry and SOA formation.

The particulate-phase data needed for source models of PM include both mass concentration and composition. Since the evaluation of PM source models is a strong emphasis of the CRPAQS field study, a fairly complete set of measurements is proposed. These data should form a good database for the operational evaluation of a PM air quality model, as well as the diagnostic evaluations addressing PM components and diurnal profiles. Some redundancy has been built into the mass measurements. Several PM measurements are also taken at high time resolutions compared to our recommendations. The redundancy and excess resolution provide opportunities for tradeoffs in other areas. We suggest increasing the time resolutions in the measurements of NH_3, HNO_3, and other precursors (i.e., shorter averaging time) to make them comparable to those of the PM chemical components.

Measurements of gases are important for the evaluation of the chemistry modules, which typically have only been evaluated against data taken in warm temperatures. The biggest challenge for CRPAQS may be to incorporate aloft measurements of PM precursors and oxidants. Even surface measurements are inadequate for several important oxidants and precursors, including radical species such as NO_3, OH, HO_2, and molecular species such as H_2O_2, NO_2, and PAN. Some of these species are likely to be important for the understanding of sulfate and nitrate chemistry and should be taken during some fog episodes. Higher frequencies of speciated VOC measurements (including oxygenated VOC, particularly aldehydes) are also desired, because of their importance as precursors to SOA and to oxidants.

To understand the effects of fog, droplet chemistry should be studied. This involves collecting size-resolved fog samples both at the surface and aloft and analyzing their composition in terms of water, sulfate, nitrate, ammonium, chloride, H_2O_2, sulfite,

pH, and dissolved metals. A resolution of one hour is recommended, because fog episodes typically last less than 10 hours.

A set of measurements is needed to evaluate the prediction of fluxes in the PM air quality model, and to ensure that there are no major compensating errors in the model. For example, if a model overpredicts wet deposition and underpredicts dry deposition, it may perform well with a test case with fog. However, if the model is then applied to an area without fog, the predictions will be erroneous. The main fluxes of concern are emissions, advection, vertical mixing, wet deposition, and dry deposition. Data needed for the independent evaluation of emissions and vertical mixing have been discussed previously.

The amount of pollutants entering the valley at the surface could be determined by the horizontal flux (concentration and wind measurements) at a well-defined point of transport, such as a mountain pass. During IMS 95, the wind flow was too poorly defined at flux plane monitoring sites to calculate the fluxes entering the monitoring area. This conclusion was not unexpected given the dominance of stagnation. Aloft fluxes of pollutants should also be evaluated due to their potential importance for the transport of precursors and oxidants from upwind source areas (such as the San Francisco Bay Area) or within the San Joaquin Valley. These fluxes may be estimated from aircraft measurements of concentrations at a flux plane with good characterization of upper air winds.

Wet deposition of sulfate, nitrate, ammonium, and organic compounds can be measured directly by collecting fog samples at the ground surface and analyzing the chemical composition (see above).

Some dry deposition measurements are planned at Angiola. In addition to dust, fine and coarse PM should also be studied. We recommend also dry deposition measurements of precursor gases, including HNO_3, NH_3, SO_2, and oxidants such as O_3. All deposition measurements need to be conducted under a variety of meteorological conditions, and for different surface types. Aircraft measurements are recommended for sampling a variety of surfaces during a sampling period of a particular type of meteorology. However, well-planned tower measurements are also a viable option.

5.0 RECOMMENDATIONS

5.1 Priorities

The priorities for the CRPAQS field study can be summarized as follows in terms of measurement categories (not in order of importance).

- PM mass: PM-2.5 and PM-10
- PM composition: sulfate, ammonium, nitrate, elemental carbon, speciated organic carbon, chloride
- Gas-phase species:
  - precursors of PM (surface, aloft): NO, NO_2, speciated VOC (including aldehydes), HNO_3, NH_3, SO_2
  - oxidants: O_3, H_2O_2, organic peroxides
  - radicals: OH, HO_2, NO_3 (highest priority to OH)
- Emissions: source profiles, inventories of NH_3, SO_2, VOC with good spatial and temporal resolution (hourly for weekday and weekend) and, for VOC, chemical speciation
- Mixing layer height: spatial and temporal resolution
- Meteorology (surface and upper air): wind speed and direction, temperature, RH, radiation flux
- Dry deposition measurements of PM and precursor gases
- Droplet chemistry for PM components and precursors
- Wet deposition measurements of PM components

Measurements that we consider as low priority include the following.

- Particle size distribution of PM-2.5. Some size distribution of PM-10 may be useful in the fall study to characterize settling velocities of coarse PM. Although particle size distribution of PM-2.5 can provide some useful information on the chemical

pathways that led to secondary PM formation, chemical measurements of PM, precursors, and oxidants are considered to be more important.

- Measurements of NH_3 and HNO_3 near an NH_3 emission source to study NH_3/HNO_3 limitation. Such an area should be characterized by high NH_3 concentrations compared to HNO_3 concentrations and, therefore, it is not clear what information will be gained from this study. Measurements of NH_3 and HNO_3 should be conducted in priority in the areas which experience high NH_4NO_3 levels, i.e., receptor areas. If the NH_3 source area corresponds to such a receptor area, then, such measurements may be justified.
- Duplicate measurements are very useful for evaluating the measurement techniques. The extent of such measurement duplication must, however, be weighed against other priorities (e.g., sufficient spatial coverage and temporal resolution; measurements of other variables)

5.2 Tradeoffs

Based on the measurements that are proposed in the Field Program Plan and the data needs we identified in Sections 3 and 4, we recommend the following tradeoffs. The study design principles outlined in Section 4.1 of the Field Program Plan explained the reasons behind the proposed measurements. One of the main objectives is to generate a database for use in the performance evaluation of PM air quality models. Our recommendations for alterations of the study design are based on that objective.

Major tradeoff categories include the following:

- More detailed measurements at a few sites versus less detailed measurements at many sites.
- Time/space resolution versus time/space coverage
- Measurements of some variables versus other variables.

We discuss each of these tradeoffs below.

5.2.1 More Detailed Measurements at a Few Sites vs. Less Detailed Measurements at Many Sites

One of the study design principles (Section 4.1 of the Field Program Plan) is that "more detailed measurements at a smaller number of locations" are "of greater utility than less detailed measurements at many locations." This may not be true for model evaluation purposes. At present, the understanding of the distribution, transformation, and especially transport of PM is still limited. Although detailed information may aid in the basic understanding of the formation of secondary PM and in refining the conceptual models, the data requirements may not be completely compatible with the construction of a quality database for model execution and evaluation. It may be more important to test the model's ability to reproduce the general features of PM spatial and temporal distribution within the San Joaquin Valley rather than gain a detailed understanding of the patterns of PM formation at a few specific locations. Furthermore, whereas PM-2.5 mass measurements are relatively easy to make, some of the detailed measurements are pushing the sensitivities of current measurements (e.g., high frequency particle size distribution, NH_3 and HNO_3 measurements) and may be relatively uncertain. The quality of the data may affect their value. Good PM mass data at a large number of sites may be more useful for analysis and model evaluation than detailed data at a few locations, particularly if some of those detailed measurements have poor accuracy/precision.

Is "more frequent and more complete aerosol chemistry" really "preferable to a larger number of locations with only mass concentrations"? The argument given in Section 4.1 is that without chemical compositions, elevated mass concentrations cannot be explained and remain anomalies. We agree that determining PM chemical composition is important, however, the Field Program Plan may propose more information than required for model evaluation. In Section 4.4 of the Field Program Plan, a number of short duration (5 to 10 minutes) measurements are proposed for the annual and winter studies at the anchor sites (PM-2.5 mass, PM-10 mass, PM-2.5 carbon, PM-2.5 light scattering, and PM-2.5 light absorption, and various meteorological measurements). For example, the proposed 5 to 10 minute averaging time for the PM-2.5 measurements for the annual study will result in 105,120 data points per site per

measurement! While these measurements may be used to identify wind gusts and intermittent sources, their benefits must be weighed against the cost of acquisition, storage, quality assurance, and analysis of such a large body of data for a long-term study. Before these measurements are commissioned, one should carefully assess the expected quality of the data, the information they will yield, how they will be analyzed, and how they will be used to further our understanding of PM pollution in the San Joaquin Valley.

Although high time resolution data are useful in analyzing anomalous PM phenomena, the use of the high time resolution data in modeling is likely to be limited. First, an anomalous episode may not be a likely candidate for episodic modeling. Second, even if the anomaly is captured by the chemical composition data, it may not be captured in the meteorology and emissions data used to support the modeling exercise. Third, the time-scale of the intermittent elevated concentrations may be too short to be captured by the model, whose typical time scale is one hour. If an unexpected high PM concentration is observed, it is obviously desirable to be able to confirm and explain it. However, the cost of these "frequent" and "complete" aerosol chemistry must be weighed against the alternative cost of spatial coverage of measurements. From the point of view of model evaluation, spatial coverage with reasonable temporal resolution (e.g., 1 hour) is preferable to high time resolution data limited in spatial coverage.

In addition, resolution in time may be traded for resolution in space such that high time resolution is obtained only at a few representative sites. We recommend, instead of 10 minute PM mass data at 3 anchor sites for the annual study, hourly measurements for PM mass at anchor and selected satellite sites, with 10 minute data at one representative site.

5.2.2 Time/Space Resolution vs. Coverage

In the design of a field program, tradeoffs exist between the coverage (range) and the resolution in each of the dimensions x, y, z, and t. The spatial domain of CRPAQS extends from Chico to the South Coast Air Basin (NS) and from the Mojave Desert to 200 km west of San Francisco (EW) (see Figure 1-1). The time frame for the annual

study is December 1999 to January 2001, and December 2000 to January 2001 for the winter study (with 20 intensive days). Depending on the flexibility in the domain and the monitoring period, tradeoffs can be made between the time resolution of the measurements and the monitoring period, or the spacing of monitoring sites and the study domain.

The domain and lengths of the annual, winter, and fall studies seem reasonable. As discussed in our earlier report (Pun and Seigneur, 1998b), it is essential to include as much of the upwind emission sources as possible. Therefore, a domain that extends north to Chico and includes the San Francisco Bay Area is appropriate. The PM National Ambient Air Quality Standards (NAAQS) include both 24-hour and annual average values. Actually, the annual average value must be averaged over 3 years (it is, therefore, more a 3-year running average standard than an 1-year average). Therefore, the 1-year period planned for CRPAQS is a minimum and the success of the program will depend on that year being fairly representative of longer-term averages (i.e. 3-year averages). Twenty intensive days are planned for the winter study. This plan should allow for 4 to 5 episodes (assuming 4 to 5 days per episode). Seigneur et al. (1998) stressed the importance of evaluating the performance of 3-D air quality models for several episodes characterized by different meteorologies and atmospheric chemistry. The winter study should provide a useful database to that end. However, we recommend that other intensive measurements be conducted at other times of the year. Although high PM-2.5 concentrations occur during wintertime, we need to assess how emission control options that are beneficial for reducing wintertime PM-2.5 will affect PM-2.5 concentrations during other seasons (this is relevant to the annual standard) and O_3 concentrations during summertime (this is relevant tot he 8-hour average O_3 NAAQS).

In summary, it seems that the coverage of CRPAQS is not overstated and it would not be wise to increase time/space resolution of the measurements by reducing the coverage.

5.2.3 Measurements of Some Variables vs. Other Variables

As shown in Table 4-1, a number of measurements need to be incorporated into the Field Program Plan, based on our list of data needs for model evaluation. These measurements may be traded against redundancy (and also temporal or spatial resolution) of other measurements. They can also be traded against other measurements (which would then be eliminated from CRPAQS). The measurements that we recommend to add are listed in Table 4-1. A few suggestions of possible tradeoffs are presented in Table 5-1.

Table 5-1. Possible Tradeoffs for CRPAQS Measurements

Recommended Additional Measurements	Possible Tradeoffs
1. Measurements of NO_2 2. Ground-level measurements of key radicals (OH, NO_3, HO_2, RO_2; in order of priority) 3. Measurements of H_2O_2 4. Particulate phase ammonium (to match the resolution of sulfate and nitrate during an episode) 5. Measurements of oxygenated VOC (e.g., aldehydes) 6. Aloft measurements of gas-phase chemistry 7. Solar radiation in fog 8. Additional gas-phase measurements for the annual study (e.g., NH_3, HNO_3, SO_2, O_3, VOC) 9. Dry deposition 10. Increased spatial (x, y) resolution of aloft meteorology, especially mixing height	1. PM size distribution. 2. Special fall study of NH_3 / HNO_3 limitation. 3. Some duplicate measurements of PM2.5 mass, ions, or elements during the winter study. 4. Time resolution of component measurements. 5. Surface meteorology sites.

REFERENCES

Dye, T.S., Kwiatkowski, J.J., MacDonald, C.P., Ray S.E., Chinkin, L.R., and Lindsey, C.G., 1997. Measurement Methods Validation: Adequacy and Validation of Meteorological Measurements Aloft During IMS95. Draft Final Report. STI-997218-1766-DFR. California Air Resources Board, Sacramento, CA.

Hering, S., Eldering, E., Seinfeld, J.H., 1997. Bimodal Character of Accumulation Mode Aerosol Mass Distributions in Southern California, *Atmos. Environ.*, **31**, 1-11.

Hering, S.V. and Friedlander, S.K., 1982. Origins of Sulfur Size Distributions in the Los Angeles Basin, *Atmos. Environ.*, **16**, 2647-2656.

Meng, Z. and Seinfeld, J.H., 1994. On the Source of the Submicron Droplet Mode of Urban and Regional Aerosols, *Aerosol Sci. Tech.*, **20**, 253-265.

Pun, B. and Seigneur, C., 1998a. Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley. Draft Report CP045-1-98. Pacific Gas and Electric Company, San Ramon, CA.

Pun, B. and Seigneur, C., 1998b. Integrated Monitoring Study 95: Assessment of Mathematical Models and Associated Data Needs. Draft Report CP045-2-98. Pacific Gas and Electric Company, San Ramon, CA.

Seigneur, C., Pun, B., Pai, P., Louis, J.-F., Solomon, P., Emery, C., Morris, Zahniser, M., Worsnop, D., R., Koutrkis, P., White, W., Tombach, I., 1998. Guidance for the Performance Evaluation of Three-Dimensional Air Quality Modeling Systems for Particulate Matter and Visibility. Draft Report CP033-98-1a. American Petroleum Institute, Washington, D.C.

Watson, J.G., Dubois, D., Roth, P.M., McDade, C., Hackney, R., Niccum E., Magliano, K., Ranzieri, A., et al., 1998. Field Program Plan for the California Regional $PM_{2.5}/PM_{10}$ Air Quality Study. DRI Document #9801.1D3. California Regional $PM_{10}/PM_{2.5}$ Air Quality Technical Committee.

APPENDIX VI

SENSITIVITY OF PM NITRATE FORMATION TO PRECURSOR EMISSIONS IN THE CALIFORNIA SAN JOAQUIN VALLEY

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SENSITIVITY OF PM NITRATE FORMATION TO PRECURSOR EMISSIONS IN THE CALIFORNIA SAN JOAQUIN VALLEY

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1. INTRODUCTION

Ambient data from the 1995 Integrated Monitoring Study (IMS95) show that areas in the California San Joaquin Valley exceed the short-term $PM_{2.5}$ National Ambient Air Quality Standard (24-hour average concentration of 65 $\mu g/m^3$). Much of the $PM_{2.5}$ observed during winter is secondary in origin. Of the key components of $PM_{2.5}$, ammonium nitrate (NH_4NO_3) typically accounts for close to 20 $\mu g/m^3$ of the PM material, corresponding to 30% of urban $PM_{2.5}$ and 60% of $PM_{2.5}$ in rural areas. Therefore, it is important to investigate the PM-precursor relationships of NH_4NO_3 for the formulation of effective $PM_{2.5}$ control strategies, especially in rural areas.

In their conceptual model of PM formation, Pun and Seigneur (1999) postulated that the formation of NH_4NO_3 is limited by the availability of nitric acid (HNO_3), because ammonia (NH_3) emissions seem abundant in the San Joaquin Valley. HNO_3 is itself a secondary component, formed in the atmosphere as a product of photochemical reactions involving nitrogen dioxide (NO_2), hydroxyl radical (OH), and ozone (O_3) (the O_3 reaction involves intermediates nitrate radical, NO_3, and dinitrogen pentoxide, N_2O_5). While nitrogen oxides (NO_x) are directly emitted, the radical species are produced from precursors NO_x and volatile organic compounds (VOC). Therefore, their formation may be NO_x-sensitive or VOC-sensitive. Clearly, the chemistry regime has important implications towards the choice of effective emission controls.

This modeling study was performed to investigate the sensitivity of PM nitrate formation under conditions prevalent in the San Joaquin Valley during the winter season. This work was designed to complement any field measurements that may help unravel the details of nitrate chemistry in the ambient environment. Our objectives were to: (1) develop a box model that includes atmospheric chemistry and gas/particle thermodynamics to simulate wintertime PM formation, (2) use the box model to study the sensitivities of oxidants and PM to precursors, and (3) investigate the use of photochemical indicators (Sillman, 1995; Lu and Chang, 1998) to predict the sensitivity of wintertime PM formation.

2. FORMULATION OF THE BOX MODEL

A box model was selected to study the sensitivity of PM nitrate to NO_x and oxidants. Although a three-dimensional model should ultimately be used for this investigation, a box model, with carefully chosen initial conditions and emissions, provides valuable information on the major processes that govern the dynamics of nitrate formation during the winter PM episodes.

Winter PM accumulation is primarily associated with stagnant conditions with low wind speeds (less that 2 m/s). Therefore, advection is not treated in the box model. The box model treats the following processes:

- Emissions of precursor gases and PM
- Gas-phase chemistry using the Carbon Bond Mechanism IV (Gery et al., 1989) with isoprene chemistry
- Dilution by and entrainment of aloft air as the mixing height rises
- Dry deposition of gases and PM
- Gas/particle partitioning using SCAPE2, a thermodynamic equilibrium aerosol module (Meng et al., 1995)

Figure 2-1 depicts the dynamic processes simulated in the box model. The processes listed above are simulated using an operator splitting approach. The Carbon Bond Mechanism IV (CBM-IV) is discussed in Section 2.1. Section 2.2 provides an overview of the thermodynamic module SCAPE2. Emissions files were obtained from the California Air Resources Board (ARB) for both gaseous and particulate species. Dilution and entrainment were modeled based on the observed diurnal variations of the mixing layer height and aloft concentrations of pollutants retained from the previous afternoon. Dry deposition velocities for sulfur dioxide (SO_2), NO_2, O_3, HNO_3, hydrogen peroxide (H_2O_2), formaldehyde, higher aldehydes, and sulfate were obtained from the SARMAP air quality model (SAQM); while the diurnal dry deposition velocity profile for NH_3 was obtained from Models-3. The dry deposition velocity of sulfate was used for all particulate species in the simulation. Due to the dependence of dry deposition on

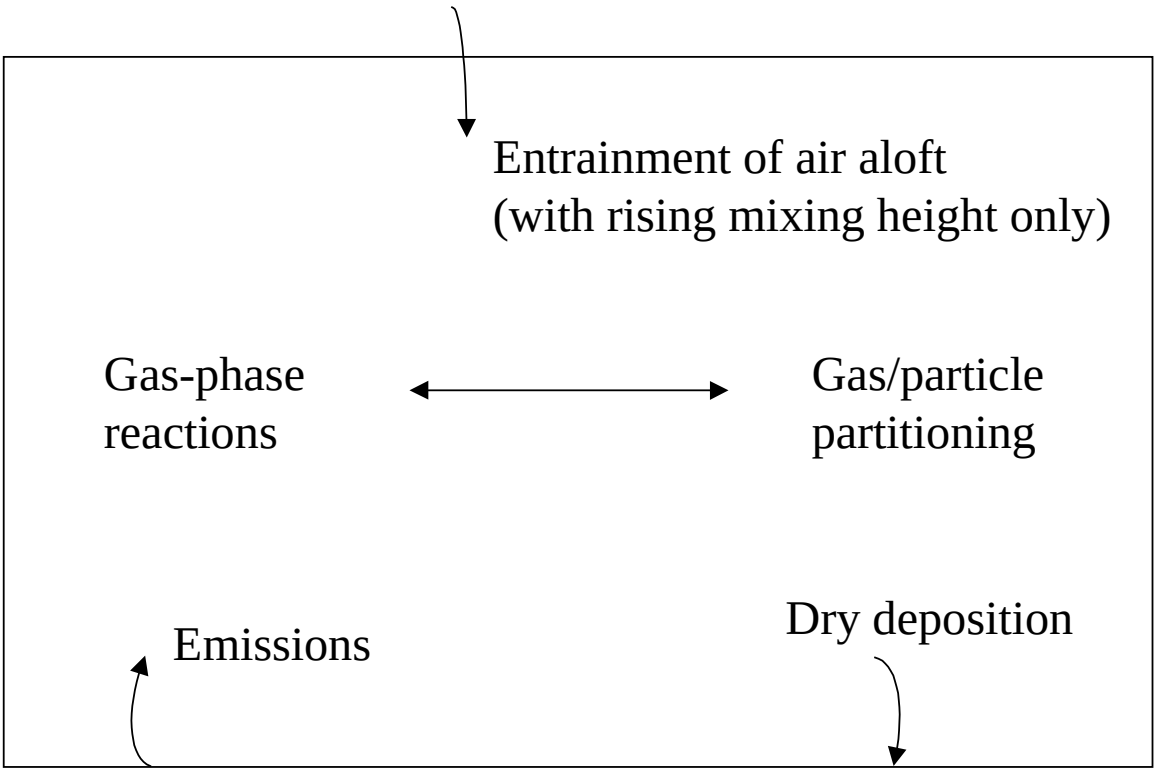

Figure 2-1. Dynamic Processes Simulated in the Box Model.

atmospheric and surface conditions, significant uncertainty is likely associated with our estimates of wintertime dry deposition values.

2.1 Gas-phase Chemistry

The key feature of the CBM-IV mechanism is the lumping of organic compounds based on their molecular structures (model species represent paraffin bonds, olefin bonds, etc). Inorganic reactions represented in the CBM-IV mechanism are similar to those used in the other gas-phase mechanisms, such as SAPRC and RADM. The list of gas-phase reactions is presented by Gery et al. (1989) and is not reproduced here. Due to the abundance of biogenic emissions in the San Joaquin Valley, the most recent treatment for isoprene chemistry was implemented to ensure the proper representation of gas-phase chemistry. A new species, ISPD, was added to represent a surrogate isoprene reaction product, which may undergo photolysis or react with OH, O_3, and NO_3. Table 2-1 shows the isoprene chemistry update implemented in this study. Therefore, the CBM-IV mechanism used in this study simulates the chemistry of 34 species (25 molecular species and 9 radicals) with 88 reactions.

The gas-phase chemical kinetic equations are solved using the Young and Boris (1977) ordinary differential equation solver. Pseudo-steady-state assumptions are made for all radical species (with the exception of NO_3, whose reaction time scale dictates whether or not steady state is assumed at any time). This approach provides a good balance between numerical robustness and computational efficiency.

Aqueous-phase/fog chemistry was not included as part of the model. Fog chemistry affects the production of sulfate and nitrate. The omission of aqueous-phase sulfur chemistry is not expected to have significant impacts on the simulation, since SO_2/sulfate chemistry has little effect on nitrate formation in an ammonia-rich and sulfate-poor environment. The effects of the aqueous reaction forming HNO_3 from N_2O_5 + H_2O was tested by increasing the reaction rate of the gas-phase reaction in a sensitivity simulation.

Table 2-1. Updated Isoprene Chemistry Included in the CBM-IV Mechanism.

Modified Reactions	
(72) O + ISOP $\longrightarrow$	0.75 ISPD + 0.50 FORM + 0.25 XO2 + 0.25 HO2 + 0.25 C2O3 + 0.25 PAR
(73) OH + ISOP $\longrightarrow$	0.912 ISPD + 0.629 FORM + 0.991 XO2 + 0.912 HO2 + 0.088 XO2N
(74) O3 + ISOP $\longrightarrow$	0.65 ISPD + 0.60 FORM + 0.20 XO2 + 0.066 HO2 + 0.266 OH + 0.20 C2O3 + 0.15 ALD2 + 0.35 PAR + 0.066 CO
(75) NO3 + ISOP $\longrightarrow$	0.2 ISPD + 0.80 ORNIT[(1)] + 1.0 XO2 + 0.80 HO2 + 0.20 NO2 + 0.80 ALD2 + 2.40 PAR
New Reactions	
(84) OH + ISPD $\longrightarrow$	1.565 PAR + 0.167 FORM + 0.273 ALD2 + 0.503 HO2 + 0.713 XO2 + 0.498 C2O3 + 0.334 CO + 0.168 MGLY
(85) O3 + ISPD $\longrightarrow$	0.36 PAR + 0.15 FORM + 0.02 ALD2 + 0.154 HO2 + 0.064 XO2 + 0.114 C2O3 + 0.225 CO + 0.85 MGLY + 0.268 OH
(86) NO3 + ISPD $\longrightarrow$	1.282 PAR + 0.282 FORM + 0.357 ALD2 + 0.925 HO2 + 0.075 XO2 + 0.075 CO23 + 0.634 CO + 0.85 ORNIT + 0.075 HNO3
(87) ISPD $\xrightarrow{hv}$	0.832 PAR + 0.90 FORM + 0.067 ALD2 + 1.033 HO2 + 0.70 XO2 + 0.967 C2O3 + 0.333 CO
(88) NO2 +ISOP $\longrightarrow$	0.2 ISPD + 1.0 XO2 + 0.8 HO2 + 0.2 NO2 + 0.8 ALD2 + 2.4 PAR + 0.8 ORNIT

[(1)] ORNIT not represented in current implementation.

2.2 Gas/Particle Partitioning

SCAPE2 simulates the composition of atmospheric particles at equilibrium given the total (i.e., gas and particulate) amounts of sulfate, nitrate, ammonium, sodium, and chloride. At each time step, the concentrations of NH_3, sodium, chloride, and sulfate change as a result of direct emissions. In addition, sulfuric acid and HNO_3 are formed from chemical reactions in the gas phase. For each time step, SCAPE2 inputs include the total mass of each species (gas and particulate phases), temperature, and relative humidity (RH). SCAPE2 calculates the distribution of each species in the gas and particulate phases based on the thermodynamic properties of the gas/particulate system. The outputs of interest are the gaseous concentrations of NH_3, HNO_3, and hydrogen chloride (HCl), and particulate concentrations of sodium, sulfate, ammonium, nitrate, and chloride.

3. BASE CASE SIMULATION

3.1 Emissions Data

The box model requires emissions of NH_3, NO_x, and VOC, which are the precursors of PM nitrate and oxidants. ARB prepared gridded emission inputs from the IMS95 inventories, which were evaluated by Haste et al. (1998). The emission files obtained from ARB contained gaseous species NO_x, VOC (speciated), NH_3, SO_2, and several particulate species, including sodium, chloride, sulfate, organic carbon (OC), elemental carbon (EC), and a category representing all other particulate compounds. Hourly emissions in the modeling domain were calculated by adding point and area source emissions. The diurnal emission profiles of NO_x, NH_3, and VOC for the entire IMS95 domain are shown in Figure 3-1. The eight classes of VOC (2 alkanes, 2 aromatics, 4 olefins) were converted to the lumped CBM-IV structure groups (PAR, TOL, XYL, OLE) and isoprene for use in the box model (see Table 3-1).

3.2 Meteorological Data

For the purpose of our box model simulations, only diurnal profiles of temperature, RH, and mixing layer height are needed to define the meteorological conditions. Temperature and RH are used in both the gas-phase chemistry and aerosol thermodynamics calculations. The mixing layer height is used to define the dilution and entrainment characteristics of the modeling domain. Meteorological data were downloaded from the ARB-maintained IMS95 data base (http://www.arb.ca.gov/themis). Mixing layer heights were determined from the vertical temperature profiles at four stations (Corcora, El Nido, Bakersfield, and Fresno) within the San Joaquin Valley for the January 1996 episode (Ajith Kaduwela, ARB, personal communication, 1999). Spatially-averaged mixing height profiles were used in this study to represent typical episode conditions. Figure 3-2 shows the diurnal variations of temperature, RH, and mixing layer height.

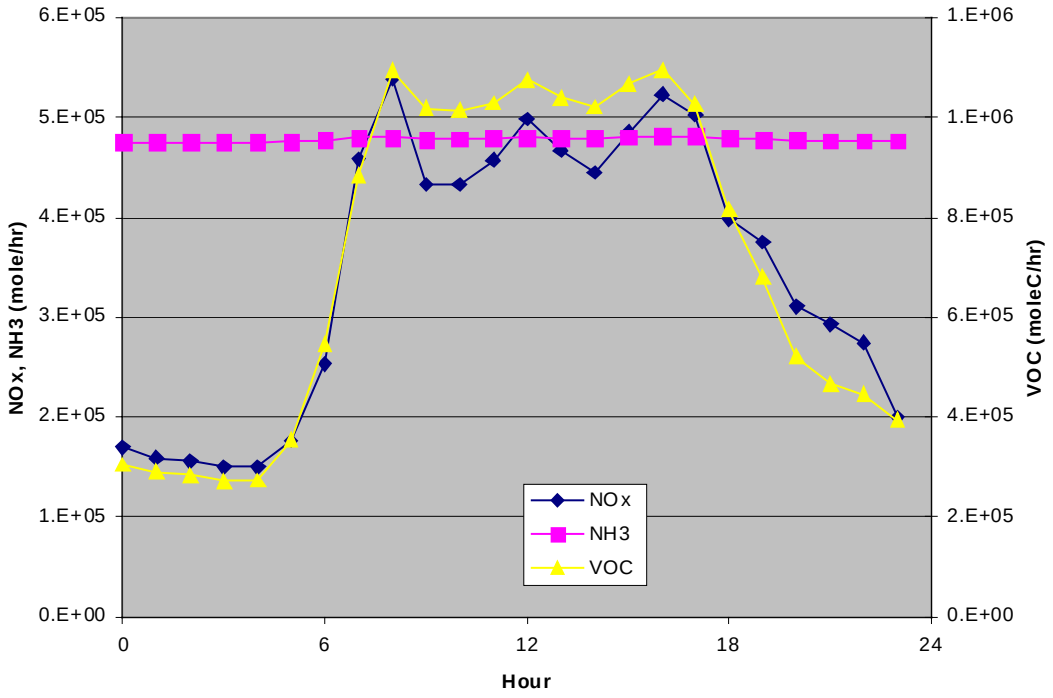

Figure 3-1. Diurnal Emissions of NO_x, NH_3, and VOC in the IMS95 Domain, January 6, 1996 (Source: ARB, 1999).

Table 3-1. Conversion of ARB Emissions Species to CBM-IV Species.

Emission Species	CBM-IV Species
ALK1	3 PAR
ALK2	7 PAR
ARO1	TOL
ARO2	XYL
ALK1	OLE + 2 PAR
ALK2	OLE + 5 PAR
ALK3	OLE + 7 PAR
ALK4	ISOP

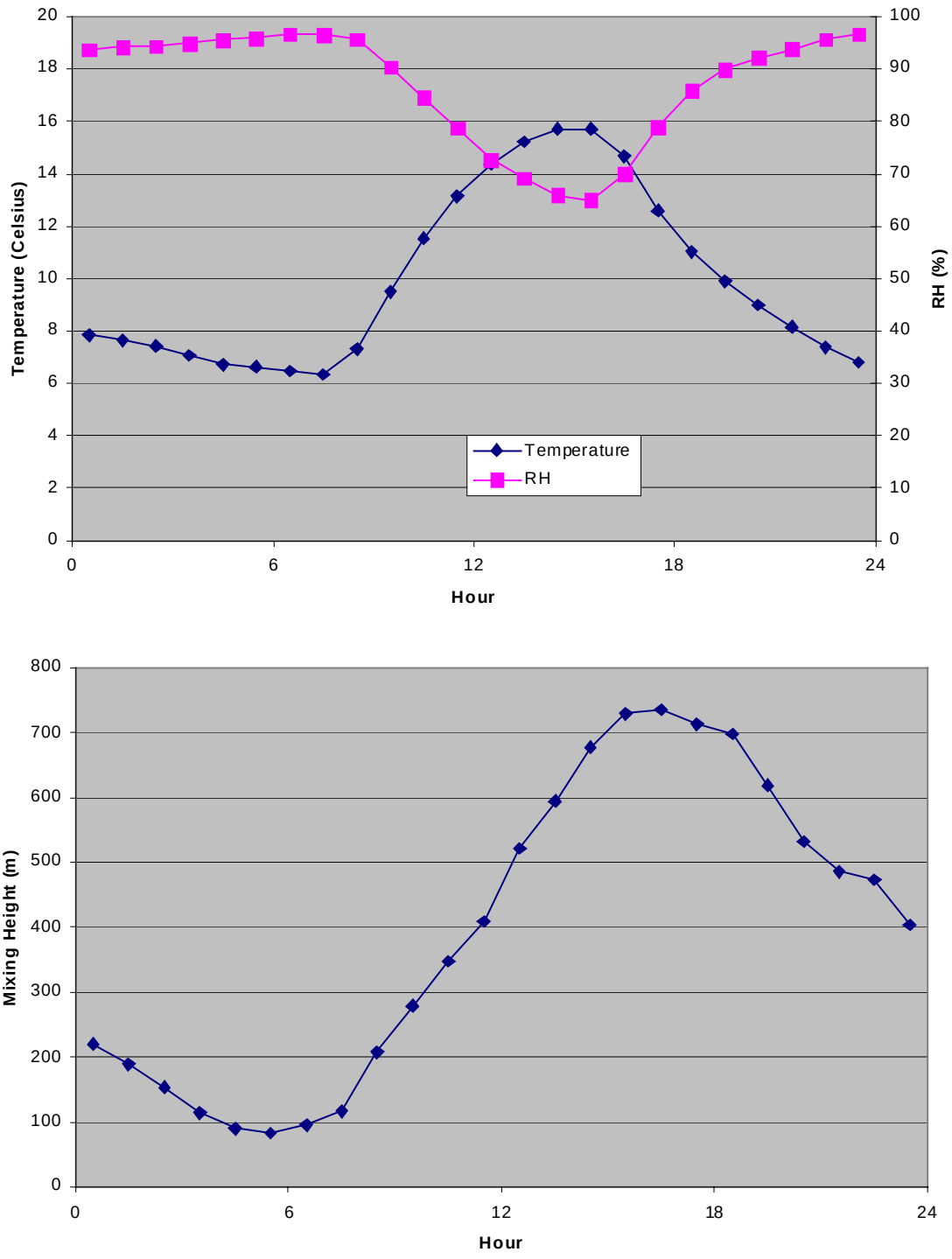

Figure 3-2. Typical Diurnal Profiles of Meteorological Measurements. Temperature and RH are averaged over 44 and 27 sites, respectively; mixing heights are averaged over four sites.

Photolysis rates were calculated based on cloud-free conditions, although fog sometimes persisted after sunrise.

3.3 Observed Concentrations

Observed concentrations were obtained from the IMS95 data base. Ambient concentrations were used in two ways: (1) to drive the box model as initial conditions and (2) to provide an indication of the accuracy of the box model predictions. Figure 3-3 shows the spatially averaged concentrations of O_3, NO, and NO_2 during the January 4-6, 1996 episode. The average night-time O_3 concentrations were a few ppb during this episode, despite the lack of O_3 production at night. At urban sites, O_3 was depleted at night by NO titration; however, in rural areas, O_3 persisted because the evening NO_x emissions were not sufficient to remove all O_3. NO exhibited strong spatial and temporal variability, as is characteristic of primary pollutants. NO_2 typically varied within the range of 10 to 40 ppb. Daily average concentrations of other species are shown in Table 3-2.

Haste et al. (1998) found significant uncertainties in the emissions inventory (e.g., underestimation by a factor of 4 for NMOC/NO_x) based on comparisons of inventory ratios of VOC/NO_x, NH_3/NO_x, and PM/NO_x to ambient values. For the box model simulations, the emissions of VOC were adjusted within the stated uncertainty range to obtain a base case that best matches the magnitudes of the ambient concentrations (see Section 3.5).

3.4 Modeling Domain

A 44 km x 44 km area around Fresno was chosen for the box model simulations. Based on Haste et al. (1998), the ambient NH_3/NO_x ratio compared well with the emissions inventory values over a 25 km radius of the monitoring station (i.e., an area of about 2000 km^2). Simulations with domains of 4 km x 4 km (urban scale) and 216 km x 288 km (entire IMS95 domain) were also performed for the base case selection. These simulations showed chemical dynamics that were not characteristic of the San Joaquin

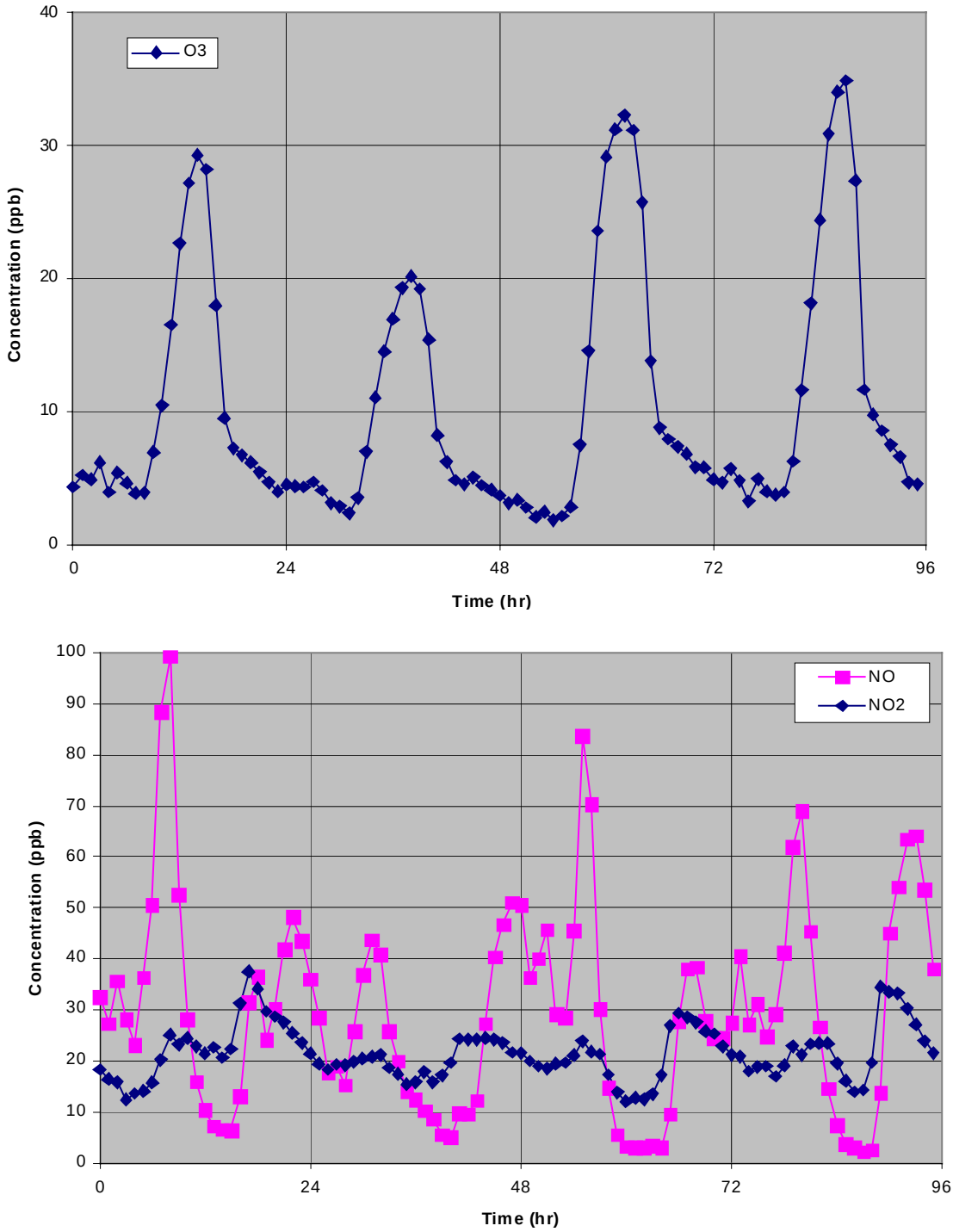

Figure 3-3. Averaged Ambient Concentrations of All San Joaquin Valley Monitoring Sites, January 4-6, 1996.

Table 3-2. Daily Average Concentrations in the Fresno Area (Source: Kumar et al., 1998).

Chemical Species	Average Concentration
HNO_3(1)	1.9 ppb
NH_3(1)	6.6 ppb
SO_2(1)	2.6 ppb
VOC(2)	0.445 ppmC
PM sulfate(1)	2.9 $\mu g/m^3$
PM nitrate(1)	19.5 $\mu g/m^3$
PM ammonium(1)	6.3 $\mu g/m^3$

(1) January 4-6, 1996

(2) December 9-10, 26-28, 1995 and January 4-6, 1996

Valley. Because of high emissions concentrated over a small area without advection flow, the urban scale simulation resulted in significant build-up of pollutants, such as NO_x, VOC, and PM, and a depletion of NH_3 within a couple of simulated days, which was not observed during IMS95. The chemical dynamics of the regional scale simulation indicated that the oxidant chemistry was too slow (because of the dilution of emissions over a large area) in rural areas to account for the observed PM nitrate and oxidant concentrations. Therefore, the 44 km x 44 km domain was selected for the box model simulations.

3.5 Base Case Simulation

A 3-day simulation was performed for the Fresno domain, based loosely on the conditions found during the January 1996 episode. The initial conditions used in the simulation are listed in Table 3-3 for a midnight start time. We assumed that pollutants are trapped and preserved aloft when the nocturnal inversion isolates the surface from the aloft layer. Therefore, the modeled aloft concentrations on each day are equal to the concentrations of pollutants in the previous afternoon at the time of maximum mixing height. Aloft concentrations are also required for the first of the modeled days. Since aloft concentrations were not measured during IMS95, characteristic aged emissions (the concentrations on the third day of a simulation without initial conditions) were assigned as the initial set of aloft concentrations.

Based on the results of Haste et al. (1998) regarding uncertainties in the VOC emissions inventory (underestimation by a factor of 4 for VOC/NO_x), the emissions of organics were adjusted to obtain a base case that best matches the ambient concentrations. In the base case simulation, the organic emissions were doubled from 1.7 x 10^7 mole C/day to 3.4 x 10^7 mole C/day within the domain in order to produce VOC and O_3 concentrations similar to those observed in the San Joaquin Valley.

The base case results for O_3, NO, and NO_2 are shown in Figure 3-4. Note that rapid titration of O_3 by NO occurs at the start of the simulation. The first day is treated as a “spin-up” period, since the first 10 hours of the simulation are strongly affected by the initial conditions. Therefore, only the results of the second and third days are analyzed.

Table 3-3. Initial Conditions for Box Model Simulations.

Chemical Species	Concentration
NO	36 ppb
NO_2	22 ppb
O_3	8 ppb
NH_3	4 ppb
SO_2	1.6 ppb
CO	1.9 ppm
HNO_3	1.2 ppb
VOC	218 ppbC
PM chloride	0.32 ppb (0.49 $\mu g/m^3$)
PM sulfate	0.54 ppb (2.2 $\mu g/m^3$)
PM ammonium	5.5 ppb (4.3 $\mu g/m^3$)
PM nitrate	4.4 ppb (11.7 $\mu g/m^3$)

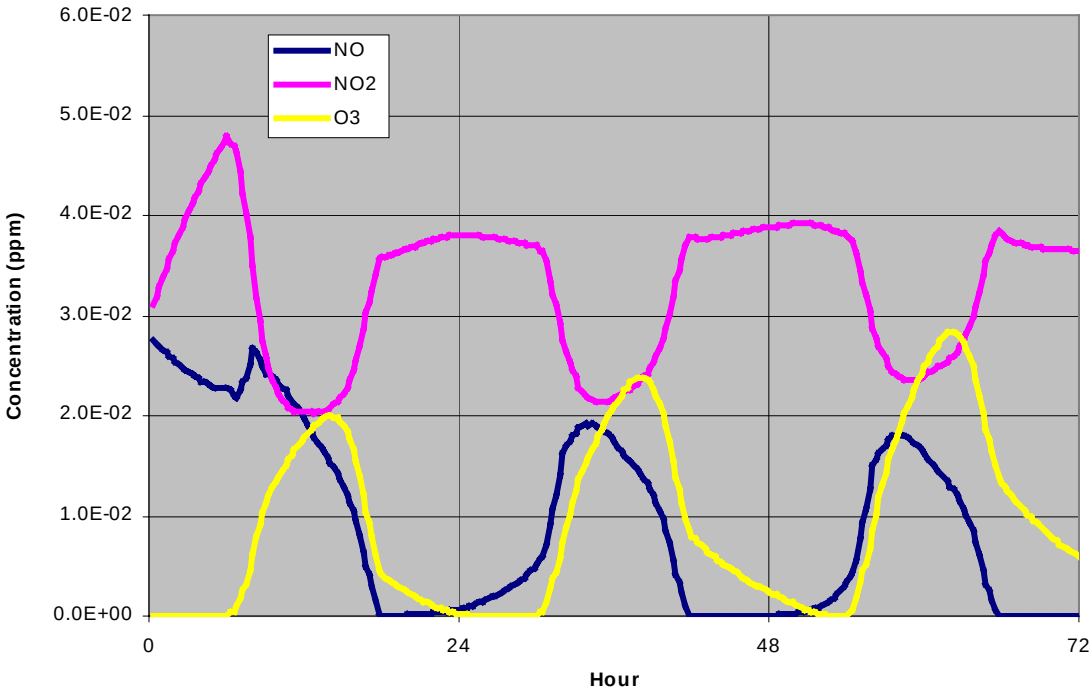

Figure 3-4. Base Case Simulation: O_3, NO, and NO_2 Concentrations.

The O_3 concentration peaks at 2 p.m. (observed peaks occurred between 2 to 3 p.m. during the January episode) on both the second and third days, with values of 24 and 28 ppb, respectively. The simulated concentrations of O_3 are within the range of values observed during the January 1996 episode of IMS95.

The NO_x concentration profiles, on the other hand, do not match the observed concentrations as well. The ambient data for NO typically displays a peak value (60 – 100 ppb) between 8 and 9 a.m. and high concentrations (30 – 50 ppb) throughout the night (see Figure 3-3). The box model is unable to reproduce this profile. A morning maximum concentration of about 20 ppb is predicted at about 10 a.m., and NO concentrations are typically low during the night. The diurnal range of observed NO_2 concentrations is smaller than that of NO concentrations. NO_2 concentrations fluctuate between 10 and 30 ppb, with a midday minimum slightly before the time of maximum O_3. The simulated NO_2 concentrations are typically 10 ppb higher than the observed values. However, the midday minimum mentioned above agrees with the observations. In general, the simulated concentrations of NO_x seem too low compared to the observations. Since all emissions are well mixed in a box model, one possible explanation of the discrepancy is that the size of the modeling domain is too large to represent some of the more local variability in NO_x concentrations, especially for the primary pollutant NO.

The 24-hour average PM concentrations and chemical composition are summarized in Table 3-4. Note that chloride, EC, OC, and the category titled “all other species” are of primary origin. Secondary organic aerosol formation is not modeled in the current study. Particulate chloride emissions may participate in thermodynamic partition and result in gaseous HCl concentrations. Particulate water is not reported here, since it was not measured during IMS95; note that significant amounts of water may be associated with the inorganic compounds. The base case concentrations of the secondary inorganic components, sulfate, nitrate, and ammonium, are quite similar to those reported by Kumar et al. (1998) (Table 3-2).

The diurnal profiles of particulate ammonium and nitrate, as well as their precursors, NH_3 and HNO_3 are shown in Figure 3-5. The concentration of HNO_3 predicted by the model is much lower than the IMS95 observations (Table 3-2). This

Table 3-4. Simulated PM Concentrations and Chemical Composition.

Chemical Species	**Day 2 ($\mu g/m^3$)**	**Day 3 ($\mu g/m^3$)**
Sulfate	2.5	2.7
Nitrate	18	25
Ammonium	6.6	8.8
Sodium	0.4	0.6
Chloride	1.4	2.0
Elemental carbon	1.4	1.9
Organic carbon	1.8	2.5
All other species	0.5	0.7
Total	33	44

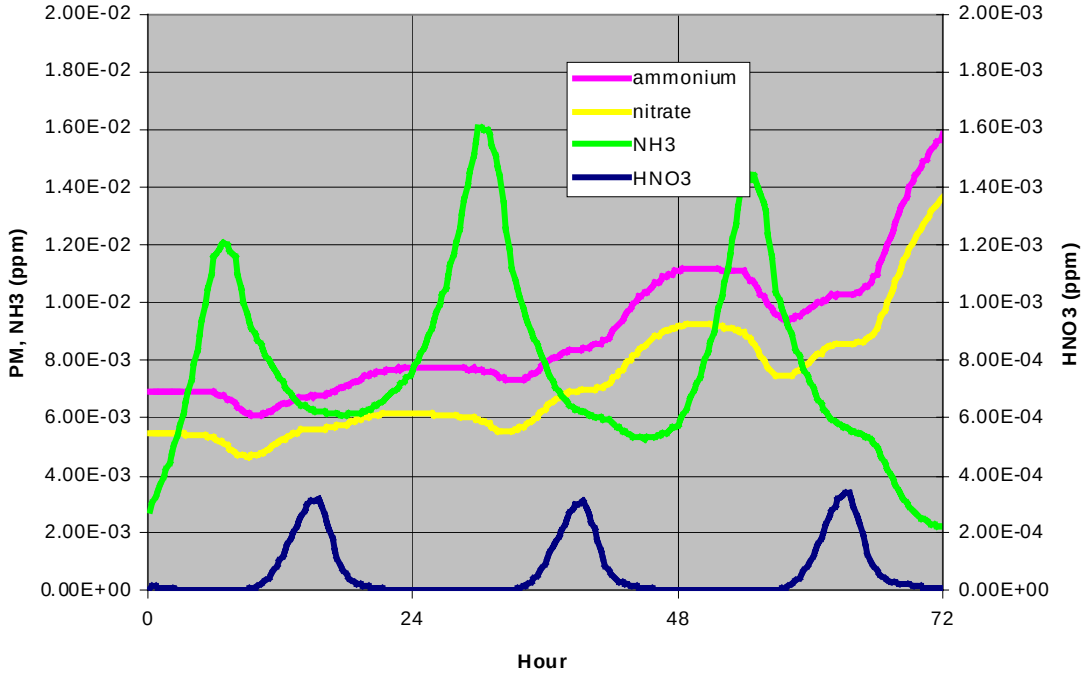

Figure 3-5. Base Case Simulation: PM Ammonium and Nitrate, and Gaseous NH_3 and HNO_3 Concentrations.

result is consistent with the modeling results of Kumar et al. (1998), who alluded to measurement difficulties for HNO_3. Some PM nitrate seems to be formed during the day; however, much of the accumulation of PM nitrate and ammonium takes place in the evening, probably as a result of favorable partitioning of inorganic nitrate toward the particulate phase (due to colder temperatures and higher RH), as well as chemical production via the reaction of NO_2 with O_3. The relatively high concentrations of NH_3 (an order of magnitude higher than HNO_3 at all times) and the build-up of NH_3 during the night (especially early morning) indicate that the formation of particulate nitrate is limited by the availability of HNO_3. Since the increase in PM nitrate in the evening greatly exceeds the available HNO_3 in the gas phase for partitioning (the day time peak of HNO_3 is about 0.3 ppb), we conclude that the chemical production of nitric acid and PM nitrate is significant in the evening. Two chemical pathways exist for the production of HNO_3. The OH pathway takes place primarily during the day, when OH is more abundant.

$$OH + NO_2 \rightarrow HNO_3 \tag{1}$$

The N_2O_5 pathway consists of 3 steps.

$$NO_2 + O_3 \rightarrow NO_3 \tag{2}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{3}$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \tag{4}$$

Reaction 4 is favored when the RH is high and when lower temperatures increase the stability of the combination product N_2O_5. The conclusion that the N_2O_5 pathway plays a significant role in PM production is supported by the predicted concentrations of the intermediates N_2O_5 and NO_3 during the evening. The production of PM nitrate via the N_2O_5 pathway ceased at night when N_2O_5 and NO_3 are depleted, because O_3, a key ingredient of NO_3 (Reaction 2), is depleted.

Since Reaction 4 also takes place in the aqueous-phase with an increased rate, a simulation with an increased reaction rate for the hydrolysis serves as a test to estimate

the effects on PM nitrate due to the omission of the aqueous-phase reaction. It was found that increasing the reaction rate constant of Reaction 4 by a factor of 10 increases the nitrate production by 13 to 18%, and accelerates the PM nitrate build-up at night. Therefore, this sensitivity test highlights the importance of the N_2O_5 pathway as a nitrate formation route.

4. SENSITIVITY SIMULATIONS

Two simulations were conducted to test the changes in $PM_{2.5}$ concentrations resulting from changes in the emissions of NO_x and VOC within the modeling domain. The results of a sensitivity simulation with a 50% reduction in VOC are discussed in Section 4.1. The 50% NO_x reduction simulation is analyzed in Section 4.2.

4.1 VOC Emission Reduction

A 50% reduction in VOC from the base case is equivalent to using the emissions estimates directly from the official inventory. Figures 4-1 and 4-2 show the O_3-NO_x dynamics and the PM and precursor time series, respectively.

The key result is that the 24-hour average PM nitrate concentration is reduced from 18.2 and 25.0 $\mu g/m^3$ on days 2 and 3 in the base case (Table 3-4) to 15.5 and 17.4 $\mu g/m^3$, respectively. Given that the initial condition is 14.7 $\mu g/m^3$, the production of secondary PM is greatly reduced when the VOC emissions are halved. Particulate ammonium, which neutralizes particulate nitrate, is also reduced (24-hour average concentrations are 5.8 and 6.6 $\mu g/m^3$ on days 2 and 3, respectively; down from the base case values of 6.6 and 8.8 $\mu g/m^3$, respectively).

Figure 4-2 shows that, as in the base case, NH_3 is abundant in the system relative to HNO_3. In fact, the gaseous concentrations of HNO_3 are lower in this sensitivity simulation than in the base case. The general features of Figure 4-1 are quite similar to those of the base case (Figure 3-4). O_3 concentrations are lower (maximum O_3 concentrations reduced from 24 and 28 ppb on days 2 and 3 in the base case to about 20 ppb in this sensitivity simulation), and NO_x concentrations are generally higher, consistent with slower chemical removal of NO_x by oxidation. Because of lower oxidation rates, NO_2, the nitrogen-containing reagent in Reactions 1 and 2, is always more abundant in the 50% VOC simulation than in the base case. The reduction in PM is therefore caused by the limited availability of oxidants, OH and O_3. Figures 4-3 and 4-4 compare the concentrations of OH, O_3, and N_2O_5 between the base case and the 50% VOC reduction case. A 50% reduction of VOC emissions reduces OH and O_3

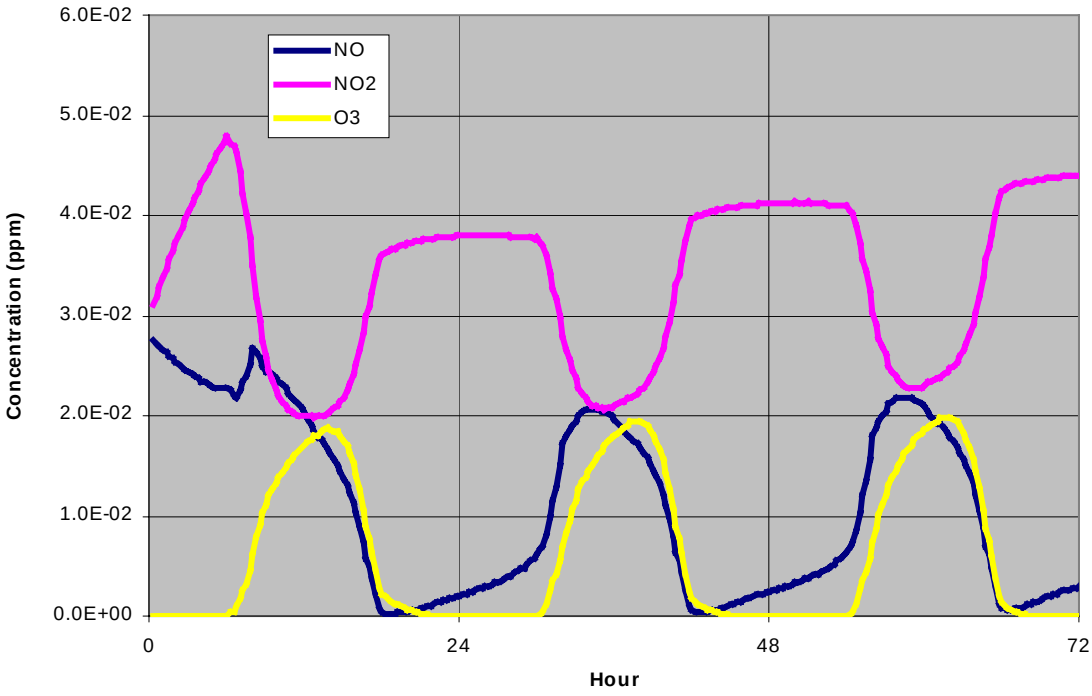

Figure 4-1. Sensitivity Simulation, 50% VOC Reduction: O_3, NO, and NO_2 Concentrations.

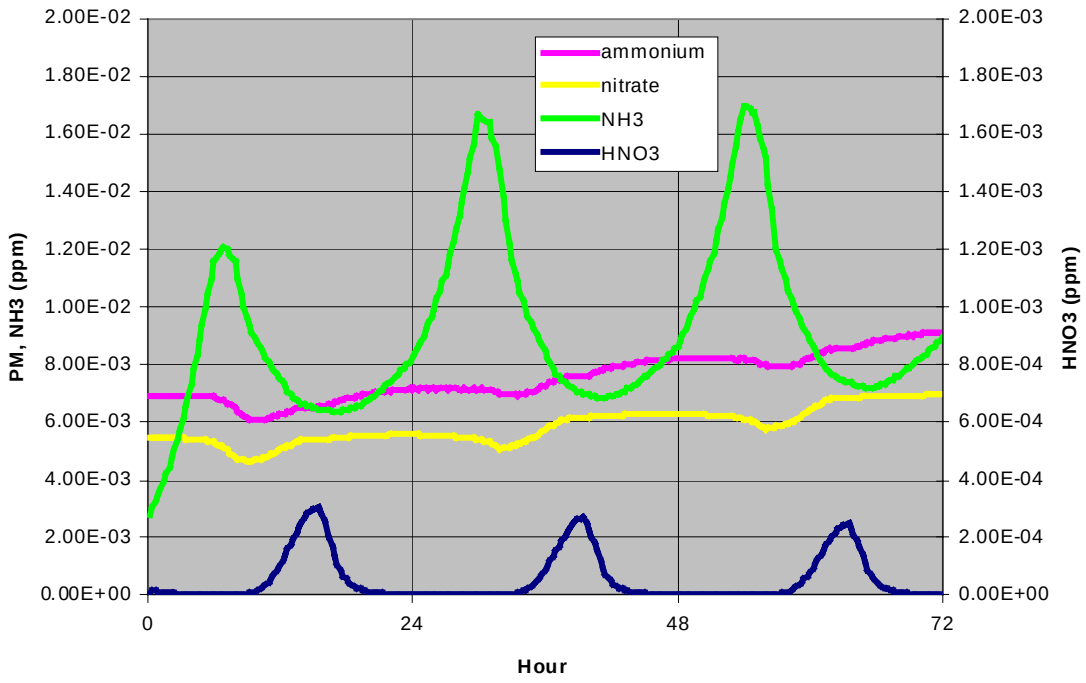

Figure 4-2. Sensitivity Case with 50% VOC Reductions: PM Ammonium and Nitrate, and Gaseous NH_3 and HNO_3 Concentrations.

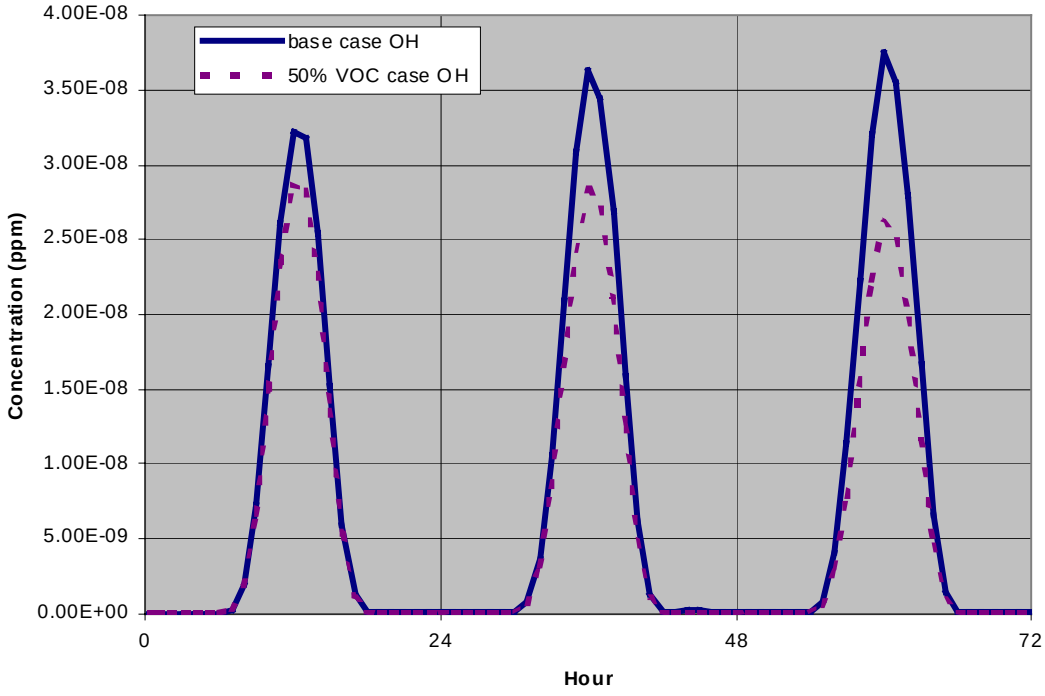

Figure 4-3. Comparison of OH Concentrations Simulated in the Base Case and the 50% VOC Reduction Case.

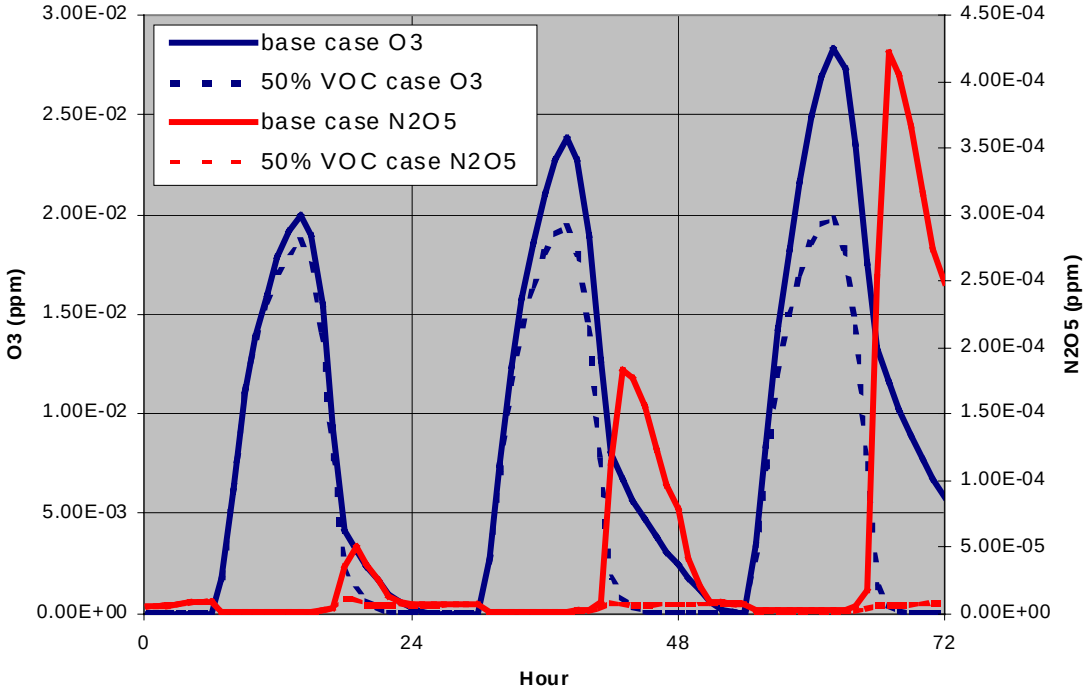

Figure 4-4. Comparison of O_3 and N_2O_5 Concentrations Simulated in the Base Case and the 50% VOC Reduction Case.

concentrations by as much as 28%. The resulting N_2O_5 concentrations are more than proportionately reduced, and consequently, the rate of HNO_3 production by this pathway is considerably reduced. Since the N_2O_5 route contributes significantly to the production of HNO_3 in the base case, PM nitrate is similarly reduced. The change in the relative importance of Reaction 1 vs. Reactions 2-4 is reflected in the difference in the PM nitrate build-up pattern between the base case and the 50% VOC case. The base case shows a relatively small increase in the nitrate concentrations following the day-time minimum that resulted from the entrainment of cleaner air, followed by a substantial increase in PM nitrate after sunset. In the reduced VOC case, PM nitrate increased gradually from mid morning to the mid afternoon due to the NO_2 + OH reaction. On the other hand, little nitrate formation takes place at night because, by sunset, O_3 has been nearly depleted; therefore, the N_2O_5 pathway for nitrate formation (which depends on O_3) is negligible in this case. This is a major difference from the base case.

4.2 NO_x Emission Reduction

The results of the 50% NO_x emission reduction case are presented in Figures 4-5 through 4-8. Figure 4-5 shows the dynamics of O_3 and NO_x. As is quite frequently the case with VOC-sensitive regimes, reducing NO_x actually increases the formation of O_3 because less NO is available to titrate O_3. The maximum O_3 concentrations are 31 and 43 ppb on days 2 and 3, higher than those observed in the San Joaquin Valley in the wintertime. The night-time NO_2 concentrations decreased from 40 ppb in the base case to 27 and 22 ppb on the first two nights. NO concentrations are also low, even during the morning rush hour.

Despite the lower concentrations of NO_x, more PM nitrate is formed, as shown in Figure 4-6. Twenty-four hour average PM nitrate concentrations rose from 23.8 to 34.4 from day 2 to day 3, a 30% increase over the base case values. Although this result seems counter-intuitive, it is easily explained if one considers the dynamics of the VOC-sensitive chemistry.

The NO_2 concentrations are always higher in the base case than in the sensitivity case. As shown in Figure 4-7, the concentration of OH radicals during the day is about

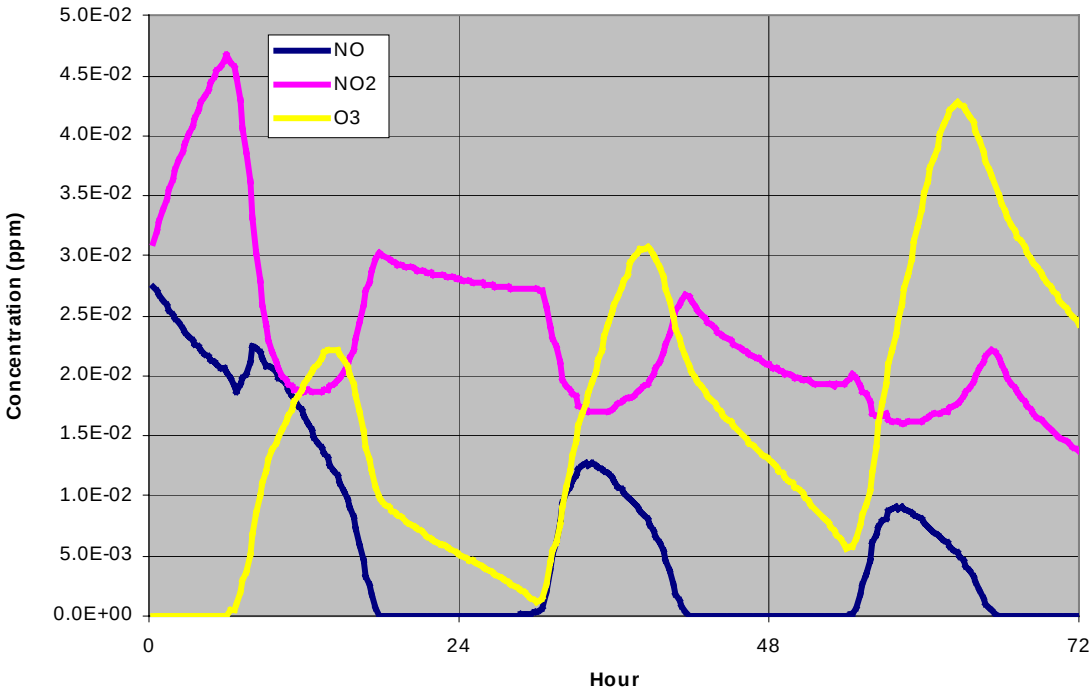

Figure 4-5. Sensitivity Simulation, 50% NO_x Reduction: O_3, NO, and NO_2 Concentrations.

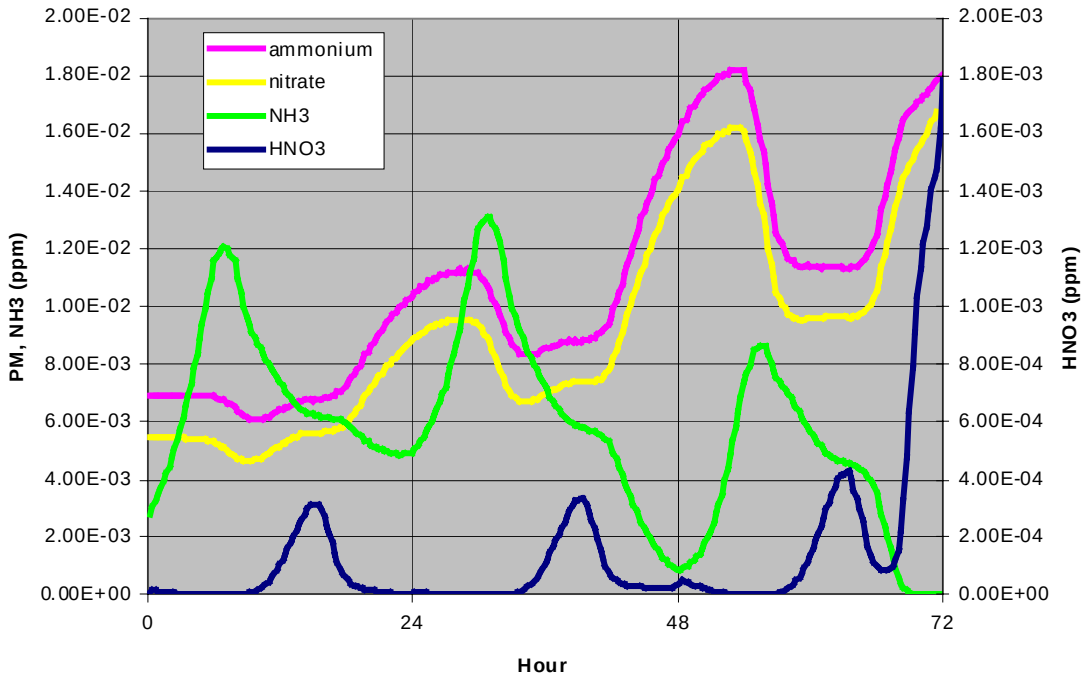

Figure 4-6. Sensitivity Case with 50% NO_x Reductions: PM Ammonium and Nitrate, and Gaseous NH_3 and HNO_3 Concentrations.

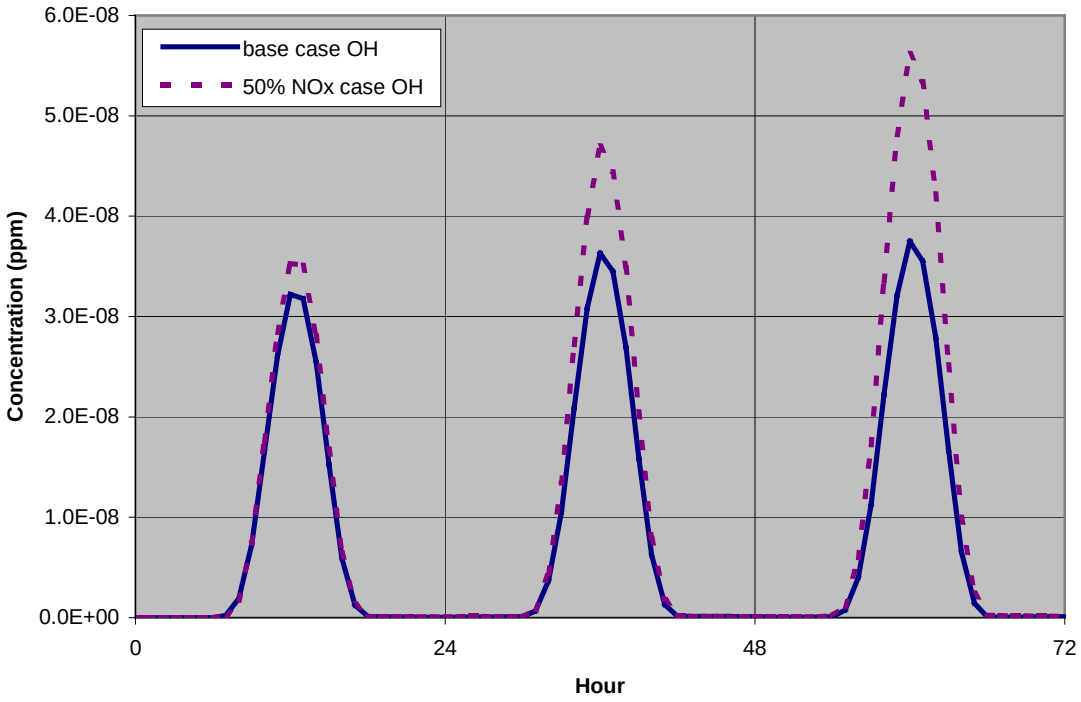

Figure 4-7. Comparison of OH Concentrations Simulated in the Base Case and the 50% NO_x Reduction Case.

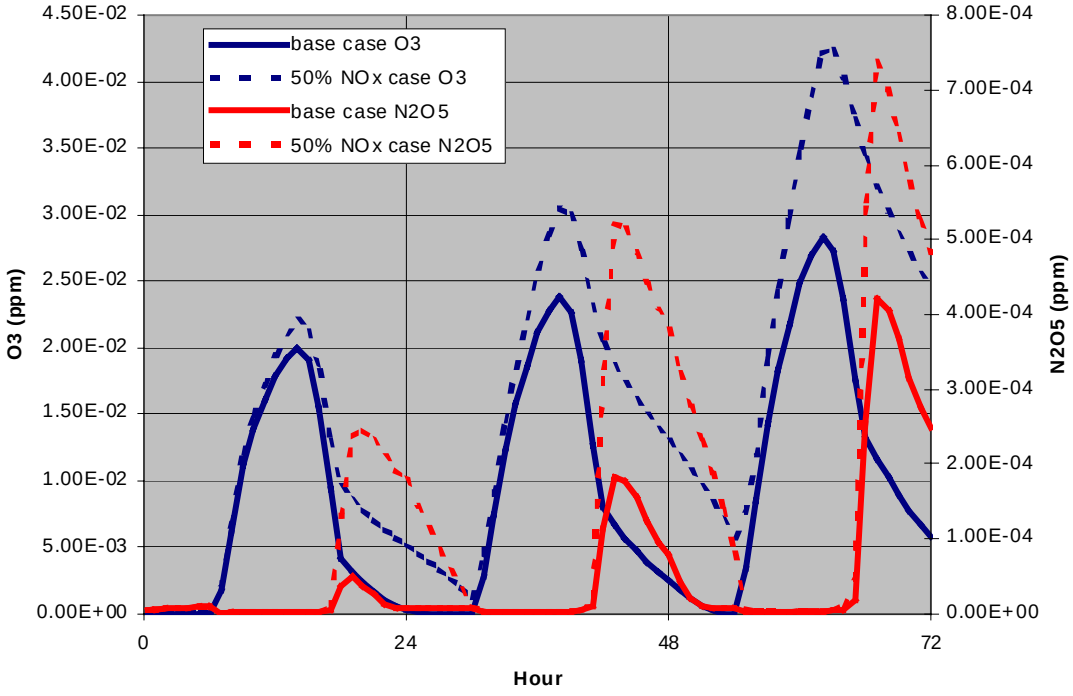

Figure 4-8. Comparison of O_3 and N_2O_5 Concentrations Simulated in the Base Case and the 50% NO_x Reduction Case.

30% higher in the 50% NO_x reduction case than in the base case. The increase in the radical concentration occurs because less NO_x is available for oxidation. As shown in Figure 4-6, daytime formation of HNO_3 increased slightly with respect to the base case because the decrease in NO_2 concentrations (Figure 4-5) is compensated by the increase in OH concentrations (Figure 4-7). The concentration of N_2O_5 is about 50% higher in the evening compared to the base case. In the previous section, we have shown that a decrease in O_3 results in a more than linear reduction in N_2O_5. The converse is also true, because the increase in O_3 in the reduced NO_x simulation relative to the base case triggers a more than linear increase in N_2O_5 in the evening (Figure 4-8). Indeed, significant PM nitrate formation is observed at night, indicating the importance of the N_2O_5 pathway in this system. The midnight increase of gaseous HNO_3 on the last day follows a depletion of NH_3, which is converted to particulate ammonium to neutralize the particulate nitrate. Once NH_3 is depleted, the pH of the droplet quickly drops (to 1.2 at the conclusion of the simulation), preventing further partitioning of HNO_3 from the gas phase into the particles.

5. PHOTOCHEMICAL INDICATORS

5.1 Sensitivity of Oxidant Production to Precursors

Several photochemical indicators have been proposed to determine the sensitivity of oxidants to VOC vs. NO_x. These indicators include H_2O_2/HNO_3, NO_y, $HCHO/NO_y$, $O_3/(NO_y - NO_x)$ and $(NO_y - NO_x)/NO_y$ (Sillman, 1995; Lu and Chang, 1998). Although the use of indicators is well accepted for the analysis of summer O_3, the approach has not been evaluated for winter conditions. The box model results were analyzed in terms of the concentrations of the indicators listed above to determine if any of the indicator species correlate well with the sensitivity of oxidants to the precursors.

Lu and Chang (1998) proposed numerical criteria for the above photochemical indicators, that characterize the threshold between VOC-sensitive and NO_x-sensitive regimes (see Table 5-1). The ratio H_2O_2/HNO_3 represents the competition of the HO_2 radical termination product (H_2O_2 dominant when VOC is abundant or NO_x-sensitive) and the OH + NO_2 termination product (HNO_3 dominant in VOC-sensitive chemistry). Since HNO_3 partitions between the gas and particle phases, it is logical to include PM nitrate and HNO_3 together in the denominator of the ratio. NO_y is total oxidized nitrogen (except N_2O). The higher the NO_y concentrations, the more VOC-sensitive the oxidant system. HCHO is an oxidation product of VOC, higher HCHO relative to NO_y indicates VOC abundance and NO_x sensitivity. $(NO_y - NO_x)$ is a measure of the amount of NO_x oxidation products (HNO_3, HNO_2, PAN, etc.). The ratio of O_3 and $(NO_y - NO_x)$ is an indication of the chain length of the radical reaction, i.e., the propagation reactions that produce O_3 vs. the termination reactions that remove radicals and NO_x from the system. Higher ratios mean more NO-to-NO_2 conversions for each termination, and an abundance of radicals. Therefore, lower ratios indicate VOC sensitivity (NO_x abundance). The ratio of $(NO_y - NO_x)$ to NO_y indicates the aging of NO_x emissions, and is anti-correlated with NO_y.

O_3 was found to decrease with decreasing VOC and increase with decreasing NO_x, and is, therefore, VOC sensitive. The indicator ratios/species as a function of time are presented in Figures 5-1 through 5-5. Our simulations show that for the VOC-

Table 5-1. Indicator Thresholds and San Joaquin Valley Simulation Results.

Indicator Species	**Threshold (Lu and Chang, 1998)**	**San Joaquin Valley Winter Simulation**
H_2O_2/HNO_3 or $H_2O_2/(HNO_3$ + PM nitrate)	0.9	H_2O_2/HNO_3 ratio less than 0.9 except at night, but $H_2O_2/(HNO_3$ + PM nitrate) always substantially less than 0.9
NO_y	4.5 ppb	NO_y > 40 ppb at all times
$HCHO/NO_y$	0.6	$HCHO/NO_y$ is around 0.2, because of the abundance of NO_y
$O_3/(NO_y - NO_x)$	27.5	$O_3/(NO_y - NO_x) < 3.5$ because O_3 is typically quite low
$(NO_y - NO_x)/NO_y$	0.55	$(NO_y - NO_x)/NO_y$ ratio less than 0.3 throughout simulation

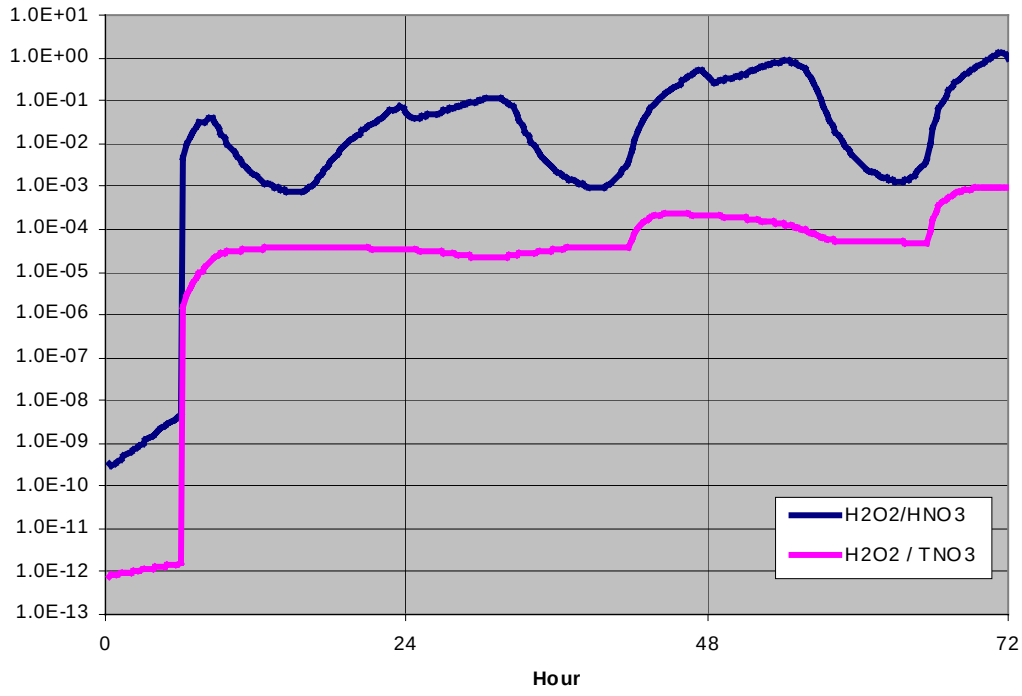

Figure 5-1. H_2O_2/HNO_3 and H_2O_2/Total Nitrate as a Function of Time.

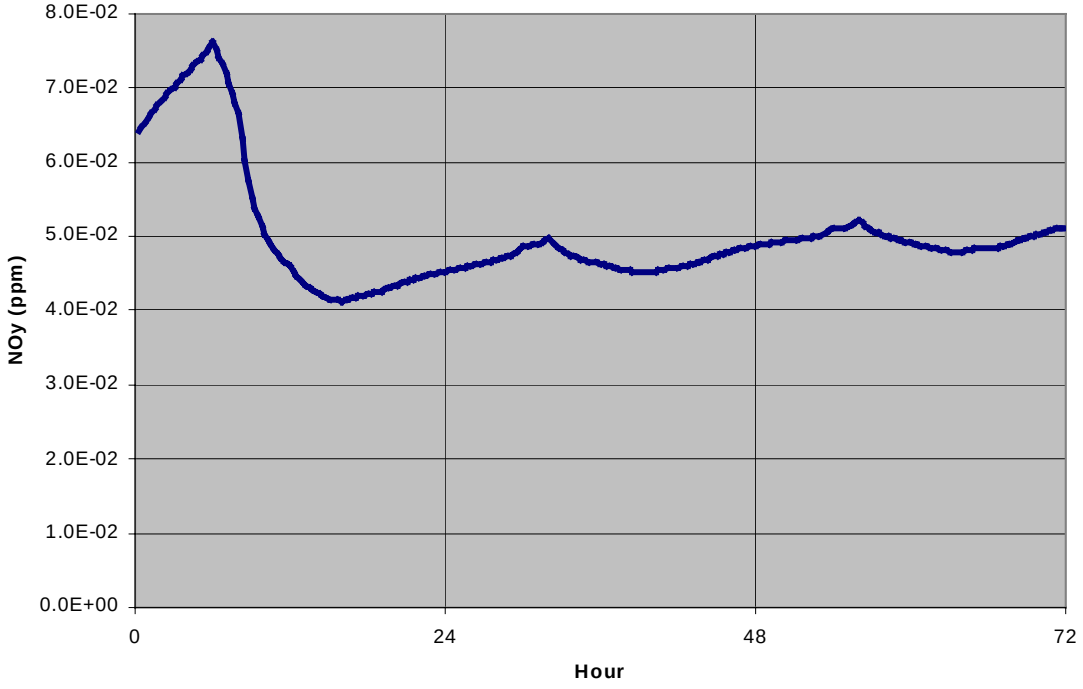

Figure 5-2. NO_y as a Function of Time.

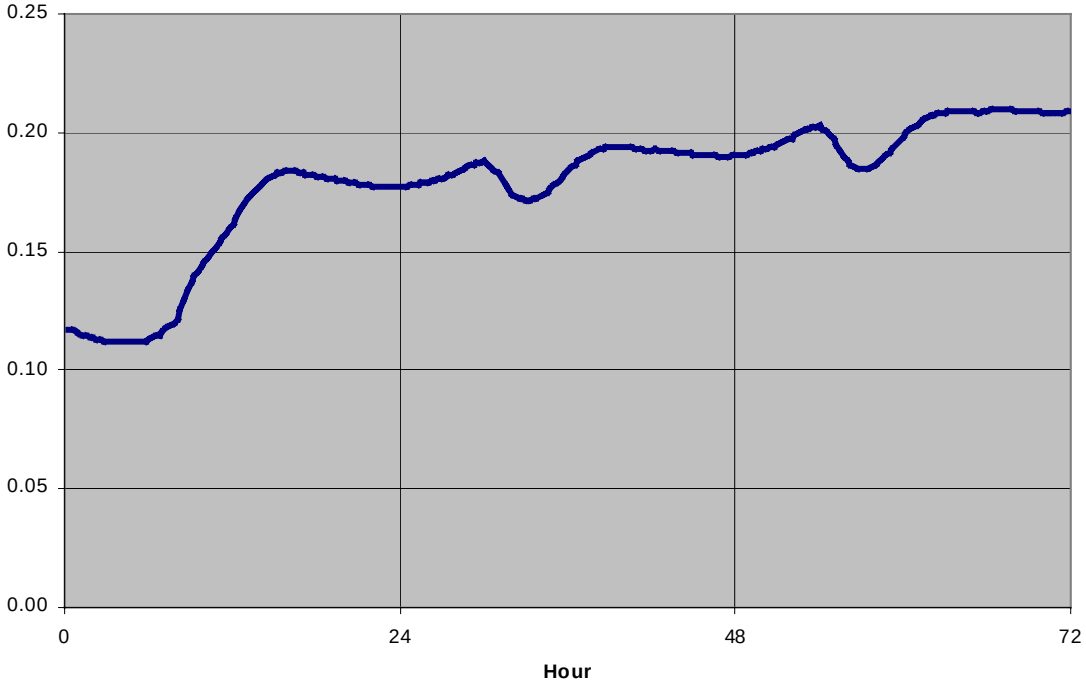

Figure 5-3. HCHO/NO_y as a Function of Time.

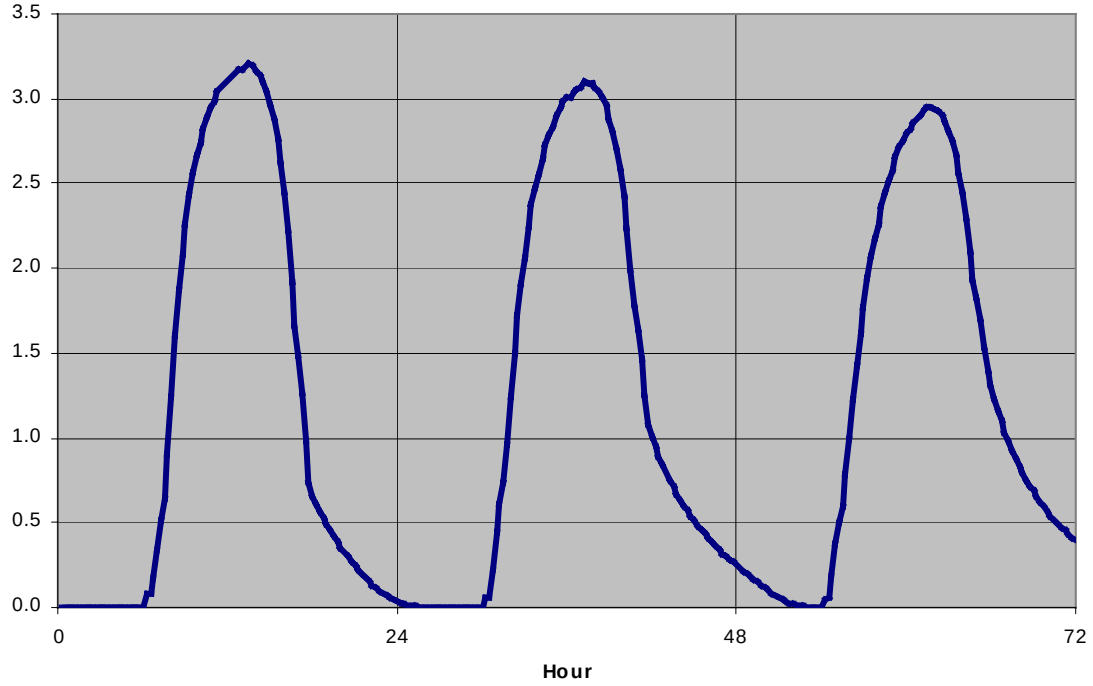

Figure 5-4. $O_3/(NO_y - NO_x)$ as a Function of Time.

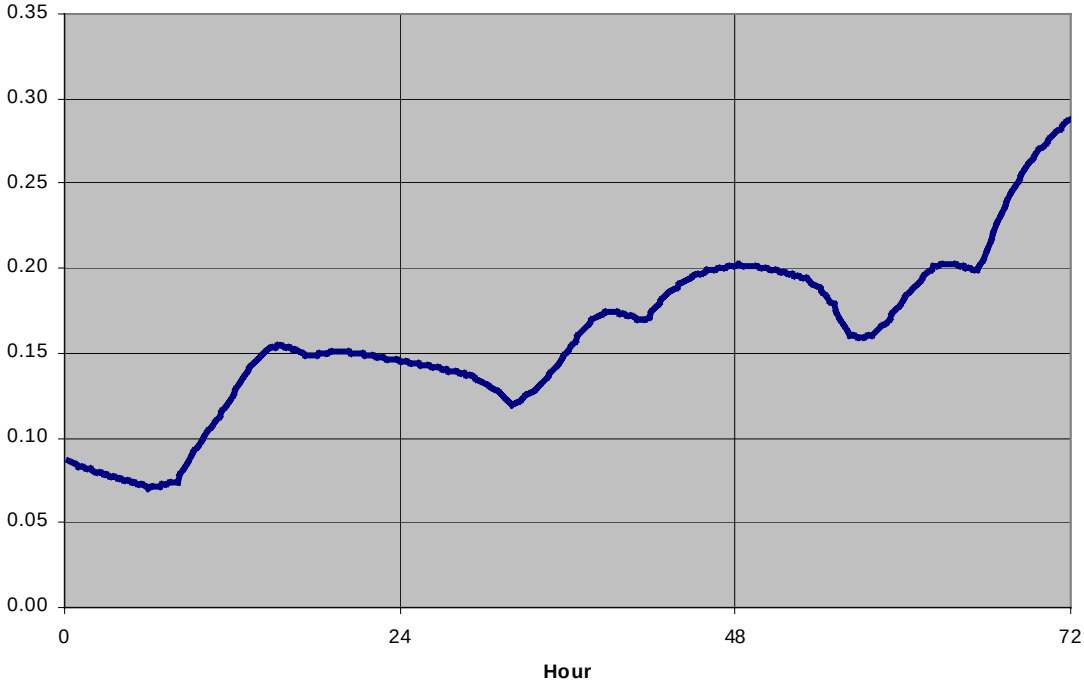

Figure 5-5. $(NO_y - NO_x)/NO_x$ as a Function of Time.

sensitive base case, H_2O_2/total nitrate is lower than the threshold value of 0.9, NO_y is higher than the threshold value of 4.5 ppb, HCHO/NO_y is lower than 0.6, $O_3/(NO_y - NO_x)$ is lower than 27.3, and $(NO_y - NO_x)/NO_y$ is lower than 0.55. These findings are consistent with the summertime model study performed by Lu and Chang using the three-dimensional model SAQM. Further simulations would be required to test whether the numerical thresholds used by Lu and Chang for summertime conditions hold for wintertime conditions as well.

5.2 Sensitivity of PM Nitrate Production to Precursors

The indicator species proposed by Lu and Chang are consistent with the fact that our box model simulations point to oxidant concentrations being VOC-sensitive. This result was further extended in our simulations to the fact that inorganic nitrate production (i.e., HNO_3) is also VOC-sensitive. We can now explore whether our results for the sensitivity of PM nitrate formation from its precursors, HNO_3 and NH_3, are consistent with the generic analysis conducted by Ansari and Pandis (1998). Ansari and Pandis defined five variables that govern the inorganic PM formation system:

- Free ammonia (NH_3^F) which is equal to (total ammonia – (2 x sulfate)), i.e., ammonia available to neutralize HNO_3
- Total inorganic nitrate (HNO_3^T) which is the sum of gaseous and particulate inorganic nitrate.
- Gas ratio which is defined as $[NH_3^F]/[HNO_3^T]$
- Temperature
- Relative humidity

Using these variables, Ansari and Pandis categorized the results of their model simulations into three regimes: (1) no response of inorganic PM to precursor, (2) nonlinear response, and (3) very sensitive response.

The values of these variables for the IMS95 box model simulations are summarized in Table 5-2. According to Figure 7 of Ansari and Pandis (1998), PM

Table 5-2. Range of PM Sensitivity Variables for IMS95 (based on base case simulation results, see Section 3).

Sensitivity Variables	**Range of Values**
NH_3^F	9 to 25 ppb
HNO_3^T	5 to 14 ppb
GR	1.3 to 3.9
Temperature	279 to 289 K (low)
RH	65 to 95% (high)

concentrations should be very sensitive to a change in HNO_3 concentrations. This result is consistent with our simulation results. Furthermore, Figure 5 of Ansari and Pandis (1998) indicates that wintertime PM concentrations should not be sensitive to NH_3 concentrations.

6. CONCLUSIONS

A box model was developed and used to investigate the response of PM nitrate to reductions in precursor emissions. The formation of nitric acid and particulate nitrate was found to be sensitive to oxidants and to VOC emissions. In fact, a decrease in NO_x emissions leads to an increase in PM due primarily to an increase in O_3 concentrations.

Our model simulations point to the fact that PM formation in the San Joaquin Valley during winter is HNO_3-sensitive, that HNO_3 formation is oxidant-sensitive, and that oxidant formation is VOC-sensitive. The conclusion that PM formation is HNO_3-sensitive is also obtained if one uses the generic analysis of Ansari and Pandis (1998). The indicator species of Lu and Chang (1998), although developed for summertime conditions, also indicate that oxidant formation is VOC-sensitive.

It should be noted that the box model represents some domain-averaged chemistry but cannot characterize the locally specific chemical regimes. Further work should extend this box model analysis to a three-dimensional modeling study so that the transport processes can be simulated and spatial variability within the valley can be addressed.

REFERENCES

Ansari, A.S. and S.N. Pandis, 1998. Response of Inorganic PM to Precursor Concentrations, *Environ. Sci Technol.*, **32**, 2706-2714.

Carter, W.P.L., D. Lu, I.L. Malkina, 1997. Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment. Report prepared for the California Air Resources Board, Sacramento, CA, Contract 92-345, Coordinating Research Council Atlanta, GA, Project M-9, and the National Renewable Energy Laboratory, Contract ZF-2-12252-07

Gery, M.W., G.Z. Whitten, J.P. Killus, M.C. Dodge, 1989. A Photochemical Kinetics Mechanism for Urban and Regional Scale Computer Modeling, *J. Geophys. Res.* **94**, 12925-12926.

Haste, T.L, L.R Chinkin., N. Kumar, F.W. Lurmann, and S.B. Hurwitt, 1998. Use of Ambient Data Collected During IMS 95 to Evaluate a Regional Emission Inventory for the San Joaquin Valley, Draft Final Report, STI-997211-1800-DFR. California Air Resources Board, Sacramento, CA.

Kumar, K., F.W. Lurmann, and S. Pandis, 1998. Analysis of Atmospheric Chemistry During 195 Integrated Monitoring Study, Draft Final Report STI-997214-1791-DFR, California Air Resources Board, Sacramento, CA.

Lu, C.H. and J.S. Chang, 1998. On the Indicator-Based Approach to Assess Ozone Sensitivities and Emissions Features, *J. Geophys. Res.*, **103**, 3453-3462.

Meng, Z, J.H. Seinfeld, P. Saxena, Y.P. Kim, 1995. Atmospheric Gas-Aerosol Equilibrium: IV. Thermodynamics of Carbonates, *Aerosol Sci. Technol.*, **23**, 131-154.

Pun, B.K. and C. Seigneur, 1999. Understanding Particulate Matter Pollution in the California San Joaquin Valley: Conceptual Model and Data Needs, Submitted to *Atmos. Environ*.

Sillman, S., 1995. The Use of NO_y, H_2O_2, and HNO_3 as Indicators for Ozone-NO_x-Hydrocarbon Sensitivity in Urban Locations, *J. Geophys. Res.*, **100**, 14175-14188.

Young T.R. and J.P. Boris, 1977. A numerical technique for solving stiff ordinary differential equations associated with the chemical kinetics of reactive-flow problems, *J. Phys. Chem.*, **81,** 25.

TES

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1995 Integrated Monitoring Study
Design, Operations,
Measurements, and Post-Field
Activities

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EXECUTIVE SUMMARY

The California Regional PM_{10} Air Quality Study (CRPAQS) is a multiyear program of meteorological and air quality monitoring, emissions inventory development, data analysis, air quality source and receptor modeling, and studies demonstrating the effectiveness of potential control strategies. The initial CRPAQS planning activities include Technical Support Studies (TSSs), demonstration studies of possible control techniques, preliminary modeling and analysis of historical data, and the development of detailed plans for each study component and for the field program, data analysis, emissions inventory, and modeling plans.

Six field-related TSSs formed the basis for developing a "mini" field program known as the 1995 Integrated Monitoring Study (IMS95). Its purpose was to provide a state-of-the-science air quality, meteorological, and emissions database that modelers could use for initial diagnostic evaluation of emissions-based or deterministic models and, perhaps, preliminary application of such models. No such database had existed before. The use of the IMS95 database for model evaluation is considered an important outcome, because it will probably allow diagnostic model evaluation to begin 3–5 years earlier than might have been possible otherwise.

The objectives of IMS95 were to (1) develop improved conceptual models for particulate matter (PM) pollution buildup (PM <10 μm, PM < 2.5μm, and secondary aerosol precursors) in the San Joaquin Valley (SJV); (2) develop a uniform air quality, meteorological, and emissions database suitable for initial evaluations of aerosol and fog air quality models; (3) minimize the risk of not capturing an episode, as compared with the original TSS approach; (4) provide enhanced interim products to support near-term planning efforts, such as the 1997 state implementation plan; and (5) collect information for planning a fall/winter field program before the year 2000. The latter is considered the primary objective. IMS95 was designed to augment the TSS objectives considerably and thus provide substantially more information than the TSSs alone could provide. Also, the planning and design of IMS95 took potential new PM standards into consideration.

IMS95 consisted of preliminary analysis of 1988–93 air quality and meteorological data in the SJV, SJV field measurements during the fall and winter of 1995, emissions assessment, system and performance auditing, and integrated data analysis.

IMS95 benefits PG&E by providing a better scientific understanding of how to comply with present and potential U.S. Environmental Protection Agency Air Quality standards in the SJV. By performing a leading role in conducting this study, PG&E has also strengthened its ongoing collaboration with the California Air Resources Board, the San Joaquin Valley Unified Air Pollution Control District, the Bay Area Air Quality Management District, other local districts in northern California.

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Section 1

INTRODUCTION

The California Regional PM_{10} Air Quality Study (CRPAQS) is a multiyear program of meteorological and air quality monitoring, emissions inventory development, data analysis, air quality source and receptor modeling, and studies demonstrating the effectiveness of potential control strategies. Study sponsors for this collaborative program include local, state, and federal government agencies and private industry and agricultural organizations. The CRPAQS objectives are as follows: (1) improve the scientific understanding and characterization of the emissions and dynamic atmospheric processes leading to high particulate matter (PM) pollution in California's Central Valley, including particle formation and distribution; (2) develop tools (i.e., air quality modeling systems) and demonstrate emissions reduction methods that will assist decision makers in formulating and comparing candidate control strategies for meeting the current federal and state standards for PM_{10} (PM < 10μm) in Central California, as well as the new standard for $PM_{2.5}$ (PM < 2.5 μm); and (3) provide reliable means for estimating how the control strategy options developed for PM_{10} and $PM_{2.5}$ will affect visibility, toxic materials in air, acidic aerosols and attainment strategies for other regulated pollutants, notably ozone (O_3).

During the initial stage, a scoping document was prepared outlining a basic structure for CRPAQS (Roth and Watson 1993). As currently envisioned, CRPAQS consists of three phases:

- Phase 1—planning, demonstration studies, and preliminary modeling and data analysis
- Phase 2—major field programs
- Phase 3—data analysis, modeling, and control strategy options development

CRPAQS is now in Phase 1 and, depending on future funding resources, will include several major field programs during Phase 2. These programs include intensive field monitoring in the CRPAQS domain during winter-like conditions, i.e., periods with low wind speeds, fog, and high concentrations of secondary aerosols, particularly ammonium nitrate; intensive monitoring during nonwinter periods when fugitive dust is a larger component of PM; and a year of monitoring throughout the San Joaquin Valley (SJV). Any ambient field monitoring will be accompanied by substantial emissions inventory data collection and will be followed in Phase 3 by data analysis and state-of-the-science air quality modeling, including source-oriented and receptor-oriented modeling approaches.

Phase 1 planning activities include Technical Support Studies (TSSs), demonstration studies of possible control techniques, preliminary modeling and analysis of historical data, and the development of detailed plans for each study component—the field program, data analysis, emissions inventory, and modeling plans. A working draft outline of the CRPAQS protocol is in Roth and Watson (1993). The TSSs (Table 1-1) are intended to collect the needed information to effectively design the overall CRPAQS. Below is a description of the need and objectives for the six TSSs that relate directly to planning future field measurement programs.

The field measurement requirements associated with the first five of the six field-related TSSs were combined and released in a single request for proposal so that a coordinated field measurement program could take place during the fall and winter of 1995. Also, the scope of the TSSs was further enhanced by including additional air quality and meteorological monitoring to develop a "mini" field program known as the 1995 Integrated Monitoring Study (IMS95) (Solomon et al. 1996a). The TSS enhancements were made to provide a state-of-the-science air quality, meteorological, and emissions database that modelers could use for initial diagnostic evaluation of emissions-based or deterministic models and, perhaps, preliminary application of such models. No such database had existed before. The use of the IMS95 database for model evaluation is considered an important outcome of the enhancements, because it will allow diagnostic model evaluation to begin 3–5 years earlier than might have been possible otherwise.

1.1 TSS 4: Diurnal Variations and Optimal Averaging Times for PM_{10} Samples

The concentrations of PM_{10} and its chemical constituents vary over periods of less than 24 hours, owing to (1) temporal changes in emissions, (2) diurnal variations in horizontal transport and vertical mixing, and (3) meteorological influences such as temperature, relative humidity (RH), and insolation on aerosol chemistry and distribution. The 24-hour samples taken to determine PM_{10} compliance are of insufficient resolution to resolve diurnal differences for scientific assessment, model evaluation, and data analysis of winter PM_{10} episodes. Diurnal data related to particulate chemistry are needed to evaluate sample start and stop times, sample durations, and the technology required to obtain accurate and precise chemical measurements throughout the day. On the other hand, the costs of PM_{10} sampling and analysis are directly proportional to the frequency of sampling, and resources are limited. Sampling for time intervals of less than 4–6 hours also requires higher flow rates (>100 l/m) and sensitive analysis methods to detect the

Table 1-1

Technical Support Studies

No.	Title	Budget
TSS 1	Assessing the Suitability of the Summer 1990 Data Base to Support Modeling and Analysis	$40,000
TSS 2	Assessing the Merits of Expanding the Extent of the Geographical Region for the Winter Intensive	part of above
TSS 3	Assessing the Merit of Carrying Out an Autumn Intensive	part of above
TSS 4	Determining Diurnal Variations and Optimal Averaging Times for PM_{10} Samples	$270,000
TSS 5	Characterizing Micrometeorological Phenomena	$54,000
TSS 6	Evaluating the Predictive Capabilities of Equilibrium Models	$50,000
TSS 7	Establishing Uncertainties in Sampling and Analysis	$50,000
TSS 8	Determining Representativeness of Sampling and Spatial Scales of Source Influences	$270,000
TSS 9	Comparing Vertical Sounding Instrumentation for Winds and Temperature	$210,000
TSS 10	Determining the Extent of Measurements Needed to Support Modeling	$50,000
TSS 11	Investigating the Dynamics and Chemistry of Fog Formation and Dissipation (In Support of Planning a Winter-like Field Program)	$210,000
TSS 12	Identifying Rare Earth Isotopes and Single Particles in Dust as an Aid in Discriminating Between the Contributions of Fugitive Dust	$200,000
TSS 13	Feasibility of Using Rare Earth Isotope Tracers for Tracking the Fate of Primary and Secondary Aerosols from Combustion Sources	$30,000
TSS 14	Development of a Methodology for Estimating Emissions of NO_x and Ammonia from Soils	$250,000
TSS 15	Evaluation of Methods for Determining Ammonia Emissions from Selected Sources in the San Joaquin Valley	$250,000
TSS 16	SJVRPS/EPA/CARB Methods Intercomparison for Particle Samplers	$250,000

ambient concentrations of relevant species. The objectives of TSS 4 are as follows: (1) enumerate and evaluate existing sampling and analysis methods of acquiring PM_{10} and $PM_{2.5}$ data within specified time intervals; (2) modify existing sampling methods for practical application to accommodate observations of diurnal patterns in aerosol/gas concentrations; (3) acquire a database of specified precision, accuracy, and validity that is suitable for determining diurnal concentrations of elevated PM_{10}, $PM_{2.5}$, and gaseous pollutant concentrations; and (4) provide evaluations, recommendations, justifications, and cost estimates for measurement methods, sample durations, and averaging times for a larger-scale sampling network.

1.2 TSS 5A: Characterizing Micrometeorological Phenomena

The transport of air pollutants from source to receptor is governed by meteorological phenomena. The motions of the atmosphere are complex, and it is impossible to observe every significant motion. It is also impossible to completely characterize atmospheric motions via partial observations and the laws of fluid mechanics. Instead, atmospheric motions are divided into one component that describes the mean properties of the flow (namely, the wind speed and wind direction, for the larger length and time scales) and another component that describes the turbulent motions.

Classical observations and physics do not define the atmospheric turbulence—the chaotic, apparently unpredictable variations in atmospheric properties. Although no specific knowledge can be obtained for individual turbulent motions, some statistical properties of the ensemble turbulent activity can be observed or derived. These properties can then be used to predict average pollutant concentrations for length scales and/or time scales that are much larger than the corresponding scales of turbulence.

In air quality modeling, atmospheric motions are generally expressed as a sum of advection (mean transport) and dispersion (turbulent diffusion). When averaging times of 1 hour or more for pollutant concentrations are being considered, the overall transport is described by following the mean wind trajectory, to which a diffusion term is added. Since advective motions typically occur over a much larger scale than turbulent diffusion, they are usually the dominant activity when atmospheric transport of pollutants is being considered.

However, during periods of light-and-variable or near-calm wind conditions, the smaller-scale diffusive motions become equally important, and it is nearly impossible to characterize the mean transport by using hourly averages. In such cases, it may be necessary to characterize atmospheric motions by using averaging times of less than 1 hour or using shorter length scales. Typically, hourly wind measurements

from a sparse network of anemometers are used to represent the advection in air quality models. Therefore, all motions on smaller time and length scales are treated as turbulence, for which empirical relationships are used to estimate the average properties of the motions. Unfortunately, this characterization technique tends to diffuse the concentration over a broad area, which may not reflect the plume "meander" that is frequently observed for light-and-variable or near-calm winds under stable conditions.

The primary objective of TSS 5A is to improve the characterization and understanding of mixing and dispersion during periods of low wind speed. Secondary objectives include evaluating the representativeness of the TSS 5A core site and obtaining a better spatial estimate of how low the wind speeds really are in the SJV (i.e., whether low wind speeds during calm conditions are typically closer to and greater than 0.2 m/s or closer to 0.05 m/s. As part of the primary objective, TSS 5A will develop an enhanced modeling treatment of micrometeorological phenomena within the SJV that can be applied during stable atmospheric periods characterized by low wind speeds. The secondary objective will improve decisions about the type of instrumentation needed to make wind speed and wind direction measurements during calm conditions. Sensors with lower thresholds for these measurements are costlier than the standard sensors with higher thresholds. Phase III of TSS 5A includes conducting a measurement program in conjunction with IMS95 and with subsequent data and modeling analyses.

1.3 TSS 8: Representativeness of Sampling and Spatial Scales of Source Influences

PM_{10} monitors in the SJV are widely separated (typically more than 48 miles apart), and they sample only every sixth day. No data currently exist on the relative contributions from emitters that are next to a measurement site, within a few blocks of the site, or many kilometers from the site. Such data are crucial for assigning priorities to the characterization of particle emissions.

Experiments to collect such data were conducted during IMS95. The winter phase focused on the major population centers of Fresno and Bakersfield, because the highest PM_{10} concentrations have been measured from late November through January in those areas. The fall phase was conducted in the Corcoran/Hanford area, because the highest excess PM_{10} concentrations have been measured there during October and November and because that area typifies much of the rural SJV.

The purpose of the saturation sampling is to examine the variability in particle concentrations as a function of location. Specifically, it is intended to (1) determine how well existing sites where

exceedances of the 24-hour PM_{10} standard have been measured can represent concentrations in their surroundings, (2) quantify the zones of influence of emissions from different types of sources, and (3) specify the characteristics that a site must have to represent regional, urban, and neighborhood scale source contributions to 24-hour average PM_{10} concentrations.

1.4 TSS 9: Surface and Meteorological Database

During the last 10 years, deterministic mathematical models or modules that comprise larger models have been developed that describe the physics and dynamics of aerosol formation, transport, deposition, and chemistry. The CRPAQS envisions using one or several of these aerosol modules together with a general photochemical model to develop control strategies for state implementation plans (SIPs) to reduce PM levels in the SJV. Examples of general photochemical models are the urban airshed model (UAM) and the San Joaquin Valley Air Quality Study (SJVAQS)/Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) Regional Model Adaptation Project (also known as SARMAP). Both models currently have aerosol modules that supplement the photochemical modeling system allowing the overall system to model the formation, transportation, and deposition of aerosols. An important input to these photochemical/aerosol models is meteorological parameters, including wind, temperature, and RH fields developed in three spatial dimensions and in time with a maximum averaging of 1 hour. These meteorological fields can be developed via prognostic or deterministic meteorological models, depending on the available data. No suitable air quality or meteorological database exists to evaluate these or other comprehensive deterministic aerosol models.

The objective of TSS 9, therefore, is to compile a suitable three-dimensional database with the needed spatial and temporal resolution for use in developing the needed meteorological fields for the comprehensive air quality models. For IMS95 deterministic rather than prognostic meteorological modeling will be used to develop 3-D wind fields.

1.5 TSS 11: Dynamics and Chemistry of Fog Formation and Dissipation

Persistent radiation fogs often form in the SJV during periods of winter air stagnation. The fogs influence ambient aerosol concentrations by accelerating particle removal and by enhancing particle growth through aqueous phase chemical reactions. Preexisting particles that are scavenged by fog drops can be deposited at the surface by droplet removal processes, including sedimentation. Aqueous phase reactions in regional fogs have been demonstrated to produce significant quantities of particulate sulfate.

Aqueous phase nitrate formation is generally considered unimportant in typical clouds and fogs; however, SJV conditions are probably more conducive to aqueous phase nitrate formation, which warrants further investigation of the potential importance of this mechanism.

The characterization of droplet removal processes and of aqueous phase sulfate production in past studies has been hampered by a lack of information about variations in droplet composition across the fog drop size spectrum. Recent work in the SJV and elsewhere has revealed that variations in droplet composition across the drop size distribution can enhance sulfate production significantly, particularly in environments where O_3 or oxygen (catalyzed by iron and manganese) are the dominant aqueous phase S(IV) oxidants. Because droplet removal processes depend on drop size, variations in drop composition across the drop size spectrum can also bias the contributions of fog drop deposition to favor the chemical species that tend to be enriched in large fog drops. Species that are preferentially associated with small fog drops are removed with lower efficiency.

The purpose of TSS 11 is to characterize fog chemistry and physics at the surface and aloft. First, fog is sampled at multiple locations in the southern region of the SJV during the winter phase of IMS95 to examine variations in fog composition with time, space, and drop size. The results will be used to (1) investigate the effects of fogs on particulate concentrations in the region, both directly and as input to modeling activities; and (2) provide baseline data for planning a more comprehensive study in the region. Second, fog is sampled simultaneously at several elevations on a TV broadcast tower to examine vertical gradients in fog composition and pollutants above the fog layer. This will provide important information on the dynamics of fogs and the extent to which pollutants above the fog or boundary layer mix downward and then become available for chemical reactions within the fog layer.

1.6 TSS 16: Measurement Methods Evaluation

The purpose of TSS 16 is to evaluate current and new methods of measuring PM_{10}, $PM_{2.5}$, and aerosol precursors and to evaluate species-specific continuous methods; all evaluation is under winter conditions in the SJV. The specific objectives of TSS 16 are to evaluate (1) positive or negative artifacts in collecting aerosol nitrate and organic species both within the sampler and on the collection medium, (2) existing particle samplers used in past California aerosol and acid deposition programs to determine the adequacy of samplers under winter conditions, and (3) new species-specific continuous methods for elemental carbon (EC) and ammonia that have not been used before in the SJV.

Evaluating the sampler collection of organic compounds and ammonium nitrate is especially important, because they are major chemical components of the winter SJV aerosol. Other major components include EC, crustal-related elements, and ammonium sulfate. Ammonium nitrate and some fraction of the organic species, while condensed from the gas phase, have significant vapor pressures and are in "equilibrium" with their gas phase precursors. During sampling, a significant fraction of these species can be volatilized or lost from the particles collected on inert filters, thus resulting in negative artifacts. In addition, the tapered element oscillating microbalance (TEOM) continuous PM monitor has a heated inlet tube and volatilizes a fraction of these species from the aerosol particle before the particle reaches the filter. Positive artifacts may arise if more reactive filter media are used, but this problem is essentially eliminated by choosing the proper filter type. Other biases can arise through the choice of an inlet approved by the U.S. Environmental Protection Agency (EPA) but not properly maintained in the field. The Anderson-type high-volume (HiVol) inlet has a higher cutpoint than the Wedding inlet; both are within EPA criteria. During sampling, the cutpoint on both inlets tends to change, especially if sampler maintenance is inadequate. The result is differences in PM_{10} mass measurements of up to 30%–40%, and perhaps more for inlets that are not maintained properly. These changes in the cutpoint affect the coarse particle mass, but not the fine particle mass, so larger effects are observed in locations with higher crustal material concentrations. Therefore, many previous intercomparison studies occurred under dry conditions with high crustal concentrations, although several intercomparisons have occurred in the winter under conditions with high concentrations of organics from wood smoke.

TSS 16 will uniquely test a variety of samples to help ensure that future field studies in the SJV employ these newer methods with some level of confidence and with relatively good knowledge of their biases under winter conditions. Collection of "true" aerosol nitrate and organics in conjunction with the aerosol samples will provide a unique opportunity to study biases among the different aerosol samplers under winter fog conditions with high nitrate and organic carbon (OC) concentrations.

1.7 IMS95

The objectives of IMS95 were to (1) develop improved conceptual models for PM pollution buildup (PM_{10}, $PM_{2.5}$, and secondary aerosol precursors) in the SJV; (2) develop a uniform air quality, meteorological, and emissions database suitable for initial evaluations of aerosol and fog air quality models; (3) minimize the risk of not capturing an episode, as compared with the original TSS approach; (4) provide enhanced interim products to support near-term planning efforts, such as the 1997 SIP; and

(5) collect information for planning a fall/winter field program before the year 2000. The latter is considered the primary objective of IMS95; thus, the goals and objectives of the TSSs are paramount with respect to the broader goals and objectives of IMS95. However, IMS95 was designed to augment the TSS objectives considerably and thus provide substantially more information than the TSSs alone could provide. Also, the planning and design of IMS95 took potential new PM standards into consideration.

Table 1-2 shows the objectives of IMS95 in more detail. IMS95 consisted of two major field efforts: a Fall study during November 1–14, 1995 and a large Winter study from December 9, 1995 through January 6, 1996. A third component consisted of fog monitoring at several elevations at a TV tower located just west of Sacramento. Table 1-3 shows the components of both studies.

IMS95 benefits PG&E by providing a better scientific understanding of how to comply with present and potential EPs emissions standards in the SJV. By performing a leading role in conducting this study, PG&E has also strengthened its ongoing collaboration with the California Air Resources Board (ARB), the San Joaquin Valley Unified Air Quality Management District, the Bay Area Air Quality Management District, other local air quality districts in Northern California, and fulfilled an important public obligation as the major electric utility in the region.

1.7.1 Schedule

Detailed schedules for the Fall and Winter studies are in Tables 1-4 and 1-5, respectively, which show the planning and implementation schedules that had been proposed for each study in early July 1995. Flexibility in the two proposed schedules was critical to the success of IMS95, because the scope of the Fall and Winter studies continued to evolve significantly that summer from what was originally envisioned in the request for proposal.

1.7.2 Report Organization

The remainder of the present report is organized as follows. Section 2 discusses the preliminary analysis of PM_{10} data in the SJV and presents conceptual models that can account for elevated concentrations. Section 3 describes the measurement program, the siting considerations, and the field and laboratory measurements and methods. Section 4 describes the auditing program, with an emphasis on the procedures for audit standard performance audits. Section 5 outlines the database management guidelines for

Table 1-2

Specific Objectives of the IMS95 Fall and Winter Field Measurement Programs

- **Determining Representativeness of Sampling Sites and Spatial Scales of Influence of Sources (Fall and Winter)**
  - ◊ Determine how well existing sites represent their surroundings.
  - ◊ Quantify the zones of influence around different types of sources, in the fall and winter seasons.
  - ◊ Specify the characteristics of sites needed to represent regional, urban, and neighborhood scale source contributions.

- **Determining Diurnal Variations and "Optimal" Averaging Times for the Collection of PM_{10} and $PM_{2.5}$ Samples (Winter)**
  - ◊ Determine sampling durations and frequencies needed to support modeling and data analysis.
  - ◊ Evaluate the precision, accuracy, validity, and sensitivity of available monitoring technologies for short-term sampling.

- **Investigating the Dynamics, Physics, and Chemistry of Fog Formation and Dissipation (Winter)**
  - ◊ Investigate the relationship between wintertime SJV Valley fogs and PM_{10} and $PM_{2.5}$ levels and composition.
  - ◊ Identify and establish appropriate measurement methods for fogs, aerosols, and selected gases.
  - ◊ Obtain an improved understanding of the vertical dynamics within fogs and at the top and bottom of the fog layer.

- **Surface and Upper Air Meteorological Measurement Support for IMS95 (Winter)**
  - ◊ Evaluate, though a review of the literature, the performance of current upper air meteorological measurement methods during low wind speeds and foggy conditions.
  - ◊ Provide upper air meteorological measurement support that will assist with the development of wind fields through diagnostic meteorological modeling.
  - ◊ Provide surface and upper air meteorological measurement support to the fog measurements, both in the southern valley and in the northern valley during the vertical fog measurements.

- **Mixing and Dispersion During Low Wind Speeds (Winter)**
  - ◊ Determine how to measure winds during calm conditions - How low is low?
  - ◊ Determine how to model pollutant dispersion under calm conditions.

- **Measurements Evaluation (Winter)**
  - ◊ Evaluate various methods for monitoring PM and it components with an emphasis on continuous methods.

- **Collect Data to Evaluate and Apply Grid-Based Emissions Models (Winter)**
  - ◊ Consider needs for initial and boundary conditions, including upper air meteorology.
  - ◊ VOC/Carbonyl compounds for photochemistry and organic aerosol species.
  - ◊ Validate conceptual models of PM pollution episodes in the SJV.

Table 1-3

Components of the Fall and Winter IMS95 Field Programs

- **Fall Study**
  - ◊ Core Site
  - ◊ Saturation Monitoring Network
  - ◊ Daily Emissions Activity Data Collection at All Sites
  - ◊ External Quality Assurance Prior to Start of Field Program
  - ◊ Supplemental Data in the Study Area

- **Winter Study**
  - ◊ Core Sites
  - ◊ Saturation Monitoring Networks
  - ◊ Boundary and Flux Plane Sites
  - ◊ Surface and Upper Air Meteorological Network
  - ◊ Mixing and Dispersion at Low Wind Speeds Experiment
  - ◊ Vertical Fog Study
  - ◊ Daily Emissions Activity Data Collection at All Sites
  - ◊ External Quality Assurance Prior to Start of Field Program
  - ◊ Supplemental Data in the Study Area

Table 1-4

IMS95-Winter Study Schedule

Task	Date Begin	Date Finish
Provide TC with IMS95-Fall Program Plan	8/15/95	8/15/95
IMS95-F Site Procurement Complete	7/27/95	7/27/95
Determine Site Locations	7/27/95	7/27/95
Arrange for Power (PG&E) and Phones (PacBell)	7/27/95	7/27/95
Arrange for Site Lease	7/27/95	7/27/95
IMS95-F Power and Phones Installed	10/1/95	10/2/95
Perform Base Emissions Survey	10/2/95	10/15/95
IMS95-F, Install equipment	10/6/95	10/10/95
Readiness Check	10/11/95	10/11/95
System and Performance Audits by ARB	10/12/95	10/14/95
IMS95-F Field Study	10/15/95	10/27/95
Remove Equipment	10/30/95	11/1/95
Perform final emissions survey	10/30/95	11/1/95
Perform Chemical Analysis	9/1/95	10/31/95
Validate Data to Level IIa	11/1/95	11/30/95
Provide Database Manager with Final Database	12/1/95	12/1/95
Provide TC with Final Report	12/31/95	1/1/96

Table 1-5

IMS95-Winter Study Schedule

Task	Date Begin	Date Finish
Provide Draft Program Plan to TC for Review	9/1/95	9/1/95
IMS95-W Site Procurement Complete	10/1/95	10/16/95
Determine Site Locations	10/1/95	10/2/95
Arrange for Power (PG&E) and Phones (PacBell)	10/15/95	10/16/95
Arrange for Site Lease	10/15/95	10/16/95
IMS95-W Site Preparation	10/26/95	11/5/95
Install Power (PG&E) and Phone (PacBell) from Poles	10/30/95	10/31/95
Install Platform	10/30/95	10/31/95
Electrical Contractor install power	10/26/95	11/5/95
Install Fence	11/1/95	11/5/95
Contractor Perform Initial Emissions Survey	10/26/95	12/5/95
THANKSGIVING HOLIDAY	11/17/95	11/25/95
Equipment for ARB Audits	10/31/95	11/21/95
Contractors Install Equipment for ARB Audits	10/31/95	11/12/95
Calibrate Equipment for ARB Audits	11/6/95	11/12/95
Readiness Check For ARB Audits	11/10/95	11/12/95
System and Performance Audits - ARB Audits	11/13/95	11/21/95
Equipment for Contractor Audits (AQ & surf. met)	11/9/95	12/5/95
Contractors Install Equipment	11/9/95	11/17/95
Calibrate Equipment	11/15/95	11/21/95
Readiness Check	11/26/95	11/27/95
System and Performance Audits	11/27/95	12/5/95
Equipment for Contractors Audits (Upper Air Met)	11/1/95	12/3/95
Contractors Install Equipment	11/1/95	11/15/95
Calibrate Equipment	11/16/95	11/28/95
Readiness Check	11/21/95	11/21/95
System and Performance Audits (two days each)	11/17/95	12/3/95
Overall Readiness Check	12/4/95	12/4/95
IMS95-W Field Study Operations	11/8/95	1/3/96
Remove Equipment	12/28/95	1/10/96
Perform Final Emissions Survey	12/29/95	1/3/96
Tower Experiment	8/1/95	8/1/95
Move Fog Equipment to Tower	8/1/95	8/1/95
Install Equipment at Tower	8/1/95	8/1/95
Calibrate Equipment	8/1/95	8/1/95
Readiness check	8/1/95	8/1/95
System and Performance Audits	8/1/95	8/1/95
Tower Sampling	8/1/95	8/1/95
Remove Equipment	8/1/95	8/1/95
Perform Chemical Analysis All Experiments	10/5/95	3/1/96
Validate Data to Level IIa	1/31/96	3/31/96
Provide Database Manger with Final Database	3/31/96	3/31/96
Provide TC with Final Report	4/30/96	4/30/96
Air Quality and Met	4/30/96	4/30/96
Emissions Activities	4/30/96	4/30/96

contractor data submittal and defines a three-level data validation process. Section 6 describes the modeling, validation, and collection of emissions data. Section 7 describes the objectives and activities for integrated data analysis. Section 8 cites references.

Appendix A presents the CRPAQS data analysis plan's major questions and their rationale. Appendixes B, C, and D define technical terms.

Section 2

PRELIMINARY DATA ANALYSIS

Smith and Lehrman (1996) performed a comprehensive analysis of the historical air quality and meteorological data that had been collected in the SJV during 1988–93 to support the planning for CRPAQS and IMS95. The air quality database (ARB 1995a) consisted of routine air quality monitoring data from a variety of networks, including those operated by ARB, the SJV Unified Air Pollution Control District (SJVUAPCD), the Westside Operators (WSO), and the National Park Service, as well as data from special studies such as the Valley Air Quality Study (VAQS) (Chow et al. 1993a). The meteorological database consisted of data from these networks, along with data from the California Irrigation Management Information System (CIMIS), the National Weather Service (NWS), and PG&E sites. This section presents findings from Smith and Lehrman that were useful in planning IMS95.

2.1 Objectives

The principal objectives of Smith and Lehrman's data analysis were to (1) develop preliminary conceptual models, which would be refined on the basis of IMS95 measurements; (2) define the optimal temporal windows for IMS95 as well as the general study domain (e.g., north or south valley); (3) determine where current understanding is limited by lack of data; and (4) make recommendations for IMS95 data collection.

To accomplish these objectives, the following specific subobjectives were defined:

- Describe the frequency of occurrence of PM_{10} concentrations (total mass, nitrate, and sulfate) as a function of season and location within the SJV.
- Summarize the duration and spatial extent of the PM_{10} episodes and the occurrence of fogs.
- Identify the meteorological conditions associated with PM_{10} episodes and low-visibility conditions.
- Evaluate the ability of the existing and proposed Winter study meteorological network to monitor the meteorological processes expected during that study.

2.2 Key Findings

Below are key findings from the data analysis of the 1988–93 SJV air quality and meteorological data. Detailed findings are in Smith and Lehrman (1996), and most of the findings presented here are from that study.

2.2.1 Spatial, Temporal, and Chemical Characteristics of PM_{10}

Primary as well as secondary chemical compounds contribute to PM_{10} mass concentrations observed in the SJV. Primary compounds are those emitted directly from sources, whereas secondary compounds are formed in the atmosphere from primary precursor gas phase emissions. In this report, secondary PM_{10} mass is defined in broad terms by its nitrate, sulfate, and ammonium components. Primary PM_{10} mass is simply the remainder of the total mass; it includes mainly crustal material, OC, and EC, although a fraction of the OC is secondary, having been formed in the atmosphere from gas phase organic precursors.

Watson and Chow (1993a) summarized the ARB 1987 emissions inventory in the SJV. Over 90% of the primary PM_{10} emissions were from the "stationary miscellaneous processes" category that includes farming, construction and demolition, road dust, unplanned fires, and waste burning. Farming activities were responsible for over 50% of the primary PM_{10} emissions, and fugitive dust emissions from vehicular activity, both on-road and off-road, were other major sources. Since much of the SJV is tilled fields and/or exposed soil, high winds can increase the concentrations of suspended PM. Emissions of nitrogen oxides (NO_X) and sulfur dioxide (SO_2) participate in the forming of the secondary particles ammonium nitrate and ammonium sulfate. Major ammonia sources are agricultural activities such as livestock operations and fertilizing. The major SO_2 source is oil and gas production operations in Kern County. Major NO_X sources are vehicular traffic along Highway 99 and Interstate 5, both of which are major north-south corridors, and the greater Stockton, Fresno, and Bakersfield areas, where most of the valley's population lives.

2.2.1.1 PM_{10} Mass

Monthly variations in PM_{10} total mass were examined for all available SJV monitoring sites (Table 2-1). PM_{10} sampling usually occurred at 6-day intervals. Histograms showing the proportion of samples that exceeded 50, 100, and 150 $\mu g/m^3$ are in the appendix of Smith and Lehrman's 1996 study. Table 2-2 lists by month the number of days exceeding 150 $\mu g/m^3$ during the 6 year period from 1988 – 1993, while Table 2-3 lists sites where ten percent or more of the samples exceeded 150 $\mu g/m^3$. As can been seen by the data presented in these tables, the highest PM concentrations occur in the late fall and early winter.

Concentrations exceeding the 24-hour federal standard of 150 $\mu g/m^3$ occurred at virtually all SJV locations where sampling continued throughout the 6-year period. Los Banos had a peak concentration of 150 $\mu g/m^3$. Bethel Island, on the northern edge of the valley, had a peak of 141 $\mu g/m^3$. The highest PM_{10}

concentrations were 297, 288, and 287 μg/m³ at Five Points, Fresno, and Bakersfield, respectively. Most exceedances of the 24-hour PM_{10} standard occur from October through January, with the highest frequency and concentrations occurring in November and December. Only infrequent and usually isolated exceedances occur from February through September. The areas with the highest PM_{10} concentrations were principally from Fresno to Bakersfield along the southeast side of the valley.

Table 2-1

PM_{10} Monitoring Sites Used in Historical Data Analysis

Abbreviation	Site
BAK	Bakersfield
BTI	Bethel Island
COV	Corcoran
FOV	Fresno-Olive
FSF	Fresno-First Street
FPT	Five Points
HAN	Hanford
KCC	Kettleman
KRF	Kern Wildlife Refuge
MER	Merced
MLB	Madera
MOK/MIS	Modesto
OLD	Oildale
SOH	Stockton
TAC/TAN	Taft
VCS	Visalia

Year-to-year variability in PM_{10} mass concentrations was also examined over the 6-year data set. Annual average PM_{10} concentrations were substantially lower in 1992–93 (4%–7%) than in 1988–91 (13%–18%). This trend generally prevails for the urban sites within the subset, although Kettleman City did not exhibit significant year-to-year variability. The lower annual average PM_{10} concentrations in 1992–93 are believed to be due to the more frequent passage of frontal systems through the study domain, which clear out the valley and reduce PM_{10} concentrations. Also noteworthy is that the years 1988–91 were the last three years of California's 6-year drought (1986–91).

An important feature in the PM_{10} data is the annual trend of the contribution by secondary species (sulfate, nitrate, and ammonium) to total PM_{10} mass (see Table 4-1 in Smith and Lehrman 1996). In general, secondary species contribute a substantial fraction (10%–50%) to the total PM_{10} mass when PM_{10} concentrations are high (>100 μg/m³) during the fog/high-humidity and winter season from November

Table 2-2

Number of Days > 150 ug/m^3 (1988-93)

Month	Number of Days	No. Days at Multiple Sites
January	5	2
February	2	1
March	2	0
April	1	0
May	1	0
June	1	0
July	1	0
August	0	0
September	2	1
October	8	4
November	15	9
December	13	7
Total	51	

Table 2-3

Ten Percent or More Samples Exceeded 150 ug/m^3

Location	Month	Frequency (%)
Bakersfield	November	25
	December	27
Fresno	November	14
	December	32
Five Points	November	12
Taft	December	10
Hanford	October	10
	November	22
	December	11
Corcoran	October	16
	November	26
	December	12
Visalia	November	11
	December	12
Oildale	November	15
	December	18

through February. However, these species are only minor contributors to PM_{10} mass from April through September or during dry hotter months in Central California. During the latter period, PM_{10} mass consists primarily of aerosol related to activities that generate crustal-related material, such as wind-driven soil erosion and on-road and off-road motor vehicle traffic. October and March appear to be transition periods between the two regimes. As an example, the secondaries at Five Points constitute an average of 23% of the total mass during the November–February period, whereas secondaries constitute only 4.5% of the total mass during the April–September period. There are also noteworthy exceptions to this generalization. Major PM_{10} events with low fractions of secondaries can occur in November (such as November 23, 1988 and November 14, 1991) as a result of high winds associated with frontal systems that produce little or no precipitation, but increase the amount of crusted material in the air.

2.2.1.2 Nitrate Concentrations

Frequency distributions of PM_{10} nitrate concentrations are in the appendix of Smith and Lehrman's 1996 study. Nitrate concentrations exceeding 30 $\mu g/m^3$ occurred at all locations in the valley in the 6-year period, with most occurrences in November and December, primarily along the southeast side of the valley. In samples where PM_{10} total mass concentrations were above 150 $\mu g/m^3$, nitrates contributed at least 25% of the total PM_{10} mass, or they contributed only 5% or less. The samples in which nitrates were 5% or less had been taken throughout the year, except for August (in which there were no events above 150 $\mu g/m^3$), November, and December. Nitrate ratios of 6%–10% were most frequent in October, which was the transition month. The peak frequency month gradually shifted to later in the year as the ratio of nitrates increased. Most of the ratios above 25% were in December samples.

2.2.1.3 Sulfate Concentrations

Frequency distributions of PM_{10} sulfate concentrations are in the appendix of Smith and Lehrman's 1996 study. The data are in frequencies of mass exceeding 3, 6, and 9 $\mu g/m^3$. The highest frequencies of sulfate concentrations exceeding 9 $\mu g/m^3$ occurred in December; at Oildale.

2.2.1.4 Hourly Measurements

In Sections 2.2.1.1 through 2.2.1.3, the focus was on PM_{10} samples collected according to the regulatory protocol of one 24-hour integrated sample every 6 days, typically via the standard PM_{10} HiVol sampler. However, hourly average PM_{10} measurements were made at Bakersfield with the TEOM during October–December 1993.

For comparison with HiVol data, the TEOM hourly data were averaged over corresponding 24-hour periods. There is a strong correlation ($r = 0.86$) between daily average PM_{10} concentrations from the two samplers; overall, however, the TEOM concentrations were 40% lower than HiVol concentrations, as inferred from the regression analysis. This observation is in excellent agreement with the findings of an ARB study (Peters 1995) conducted in Rubidoux, California. The differences were attributed to the volatilization of ammonium nitrate and possibly semi-volatile organic species that occurs during sampling due to heating of the sampled air in the inlet before collection of the aerosol on the TEOM filter.

The average diurnal variation of the hourly TEOM measurements shows two distinct maxima occurring in the morning and in the early evening that probably correspond to traffic peaks. On weekdays the morning peak occurred, on the average, during 0700-0900 Pacific Standard Time (PST), and the evening peak occurred during 1900–2100 PST. On weekends, the morning peak occurred 1–2 hours later and was more spread out. Not surprisingly, the diurnal variation was lower on the weekend than on weekdays.

2.2.2 Correlations between PM_{10} and Other Variables

A wide variety of correlations were calculated, including spatial comparisons and relationships to meteorological parameters and other pollutants, to obtain perspectives on the extent and causes of variations in PM_{10} concentrations. A major objective of this analysis was to determine which parameters might serve as surrogates for determining the duration of PM_{10} episodes, since only routine 6-day sampling constitutes the bulk of the historical PM_{10} database. Because of the preponderance of exceedances of the 24-hour standard in November and December, most of the analysis performed in the following sections considers only the every-sixth-day data collected during those months.

2.2.2.1 Valley Locations

Correlations were calculated to compare daily concentrations at various locations in the valley. November and December 6-day data were combined, making a maximum of 61 data points available for the period 1988–93. Results indicate a reasonable correlation ($r > 0.7$) north to south along the east and west sides of the valley (from Bakersfield to Madera and from Kettleman City to Five Points) and relatively poor correlations across the valley (particularly from Fresno to Five Points and from Fresno to Kettleman City). The poor correlations appear to result from occasional high PM_{10} concentrations at Fresno without corresponding high concentrations at Five Points, and vice versa. The correlations

between the east side of the valley and the north tend to be somewhat better than between the west side and the north.

2.2.2.2 Meteorological and Pollutant Parameters

Correlations were calculated between PM_{10} concentrations and a variety of meteorological and pollutant parameters during November–December for 1988–93 for every-sixth-day sampling and October–December 1993 for continuous sampling via the TEOM. The correlation matrix included the following parameters:

- The 850-mb temperature at 0400 PST on the day of the exceedance;
- The average 850-mb temperature for 6 days before and including the day of the exceedance;
- Pressure gradients from San Francisco to Reno and from San Francisco to Las Vegas, both at 0400 PST;
- Average visibility during the sampling day;
- Average RH during the sampling day;
- Peak hour average NO_x concentration, PM_{10} nitrate, sulfate, and ammonium;
- Peak hourly average carbon.

These meteorological parameters relate to (1) the stability of the atmosphere, because a more stable atmosphere allows greater buildup of pollutants and thus higher PM_{10} concentrations; or (2) the presence of fog, by inference from RH.

Although the correlations were not particularly high, some useful trends were discerned and are discussed in detail in Smith and Lehrman (1996). The highest correlations were between PM_{10} and temperatures aloft and the height of the 850-mb pressure surface. Temperatures aloft and pressure-height surfaces are indicators of atmospheric stability; higher temperatures aloft and lower 850 mb heights represent a more stable air mass. Regional pressure gradients (San Francisco to Reno or Las Vegas) indicate lateral dispersion, and negative (east-to-west or offshore flow) or weak gradients result in poor dispersion and allow PM_{10} concentrations to increase. Some differences were noted between the northern and southern portions of the valley. NO_x also seems to be well correlated with PM_{10} in the valley.

2.2.2.3 Areal Coverage

On numerous occasions during November and December, based on the 1988–93 database, a large number of sampling sites in the valley simultaneously recorded PM_{10} concentrations above 100 $\mu g/m^3$.

The greatest degree of areal coverage occurred when there were warm temperatures aloft and offshore (negative) pressure gradients between Nevada and San Francisco. A value of about 12°C at 850 mb provides a useful threshold for identifying the probability of broad areal coverage of PM_{10} concentrations above 100 μg/m³.

Table 2-4 shows major episodes of PM_{10} concentrations above 150 μg/m³ in which at least five locations in the valley had 24-hour average concentrations above 150 μg/m³.

Table 2-4

Major Episodes of PM_{10} Concentrations above 150 μg/m³

Date	Number of Locations
November 12, 1989	5
November 24, 1989	6
November 13, 1990	7
December 6, 1989	6
December 18, 1989	6
December 7, 1990	13
December 31, 1990	6

Marked year-to-year differences are implied by these data, because all the major episodes occurred in 1989 or 1990, and no major episodes occurred during other years in the 1988–93 database.

2.3 Meteorological Influences on PM_{10}

PM_{10} concentrations in the SJV are strongly influenced by particle sources and meteorological conditions. The meteorological factors are discussed in more detail below, including interbasin and intrabasin transport, atmospheric stability, and high humidity (which drives aqueous chemistry mechanisms).

Two widely different meteorological scenarios contribute to high PM_{10} concentrations. In the first scenario, high winds lead to soil erosion and locally high PM_{10} concentrations. At locations where erosion is not a problem, the conditions that produce the high winds result in rapid ventilation of the valley and unusually low PM_{10} concentrations.

In the second scenario, warm temperatures aloft lead to light winds and the trapping of pollutants in the near-surface layers. Poor ventilation of the valley can result in a buildup of PM_{10} concentrations over a period of days. This scenario can occur in Central California throughout the year—resulting, for

example, in high O_3 during the summer (Smith 1994). However, the following sections primarily concern periods when PM_{10} concentrations are high, so the data analysis is limited to the November–December period in the 1988–93 database. The occurrence of high wind is considered in Section 2.7.2.

2.3.1 Warm Temperatures Aloft

As discussed in Section 2.2.2.2, warm temperatures aloft provide the necessary stability for trapping airborne material in the surface boundary layer. This stability is an essential feature of the periods of high PM_{10} concentrations in which chemical formation mechanisms play a key role. The temperature at 850 mb (about 5,000 ft) has frequently been used as an indicator of this temperature aloft and hence of atmospheric stability.

2.3.2 Surface Pressure Gradients

Surface pressure gradients affecting the SJV are not independent of the aloft temperature structure. Warm temperatures aloft tend to be associated with weak or offshore pressure gradients. Moderate-to-strong onshore gradients occur with lower temperatures. Two pressure gradients that have proved useful in evaluating the gradient effects on the valley are those between San Francisco (SFO) and Reno (RNO) and between SFO and Las Vegas (LAS). In both cases, higher pressures at SFO are considered positive gradients.

The role of the pressure gradients within a warm episode is to modulate the effects of the warm temperature stability, generally affecting only portions of the valley. Major trough passages with colder temperatures are required to clear out the entire valley.

2.3.3 Duration of Warm Temperature Episodes

Twenty-five warm temperature episodes, from 2 to 22 days long, were identified in the November–December 1988–93 database. Because PM_{10} measurements are made at 6-day intervals, duration was determined primarily by reference to two more frequently measured parameters that were shown to be highly correlated with PM_{10}—namely, ambient temperature aloft (at 850 mb) and daily-average NO_X. Smith and Lehrman (1996) identified 25 PM_{10} episodes in the historical database, most of which lasted for 8 days or less. Nine episodes encompassed multiple 6-day PM_{10} sampling intervals. In each of the 9 episodes, the average PM_{10} concentration in the valley increased during the episode, with the highest concentration occurring near the end of the episode.

The conclusions are that PM_{10} concentrations build up during a warm temperature episode, and the duration of the episode influences the average concentration in the valley.

2.3.4 Ventilation of the Valley

Ventilation of the valley is controlled primarily by synoptic changes in regional meteorology and by diurnal changes in slope flows.

Weak low-pressure troughs occasionally move through the area even within the framework of a warm temperature episode. A brief period of onshore flow may result, followed by a return to a weak or offshore pressure gradient. Typically, the upvalley flow, which occurs when weak low-pressure troughs and onshore flow occur, is not strong enough to clear out the valley even during peak flow periods. Examples of such an event are in Smith and Lehrman (1996).

Despite the semi-stagnant conditions in the valley on high PM_{10} days, there is substantial upslope and downslope flow along the sides of the valley. In a manner similar to the summer pattern, but with reduced magnitudes, upslope flow occurs during the daytime on each side of the valley with drainage (downslope) flow at night. In addition, there is frequently an influx of air during the day to the northern part of the valley and an outflow at night.

These synoptic and diurnal variations in flow patterns represent mixing of the valley air with the cleaner environment outside the valley. Because the indicated flows, under the semi-stagnant conditions, tend to be relatively weak, the cleaner air generally mixes with valley air to produce a diluting rather than a cleansing impact, with the principal effects observed at the northern end and at the edges of the valley.

2.3.5 Horizontal Mixing

The ventilation characteristics described in Section 2.3.4 also mix PM_{10} suspended mass throughout the valley. Crossvalley components, averaged over high PM_{10} days (>150 $\mu g/m^3$), indicate a maximum transport of 25–30 km before flow reversal occurs with comparable transport in another direction (which is not necessarily 180° from the initial direction). Local sources would be diluted, particularly, by wind shifts and accompanying changes in trajectory under the light wind conditions. The diurnal nature of the upvalley component also contributes to the sloshing and dilution of airborne material in the valley. Because of horizontal transport effects, it is not possible to identify the source of given parcels of air after a few days of travel.

2.3.6 Fog

The 1988–93 database is not well suited for examining fog effects on PM_{10} concentrations. Fog in the valley is frequently patchy and is not well documented.

Fog or high humidity is assumed to increase the concentrations of secondary aerosols through aqueous chemistry mechanisms, although long-duration fog events may result in substantial deposition of large fog droplets, which results in a leveling off of PM_{10} concentrations (formation equals deposition) (TSS 11 literature review, Pandis et al. 1995). When days that have high secondaries are compared with apparent foggy periods (as determined by using high RH as a surrogate along with observations of fog in the valley), significantly greater secondary aerosol concentrations are evident during apparent/assumed foggy periods.

Another indirect fog effect occurs when fog forms during warm temperatures aloft. Findings suggest that poor visibility may cause numerous people to stay home, which substantially decreases traffic-generated pollutants (secondary aerosol precursor species, NO_x, and organics), and, despite the relatively warm temperatures aloft, pollutant concentrations can be quite low. Several examples of this effect are described in Smith and Lehrman (1996).

2.3.7 Depth of Boundary Layer

The depth of the mixed layer in the valley is of great importance in determining PM_{10} concentrations. This depth is strongly influenced by the subsidence that generates the warm temperatures aloft. Unfortunately, there is little historical information available on mixed-layer depths under stable winter conditions. However, occasional airport observations suggest an average height of about 305 m, but with a considerable range. It is essential that more specific data be obtained for planning future field programs.

2.4 Evaluation of Routine Surface Wind Measurements

High PM_{10} concentrations occur frequently in the SJV during the winter. Although some of these episodes can be attributed to fugitive soil particles caused by strong winds, most episodes occur during extended periods of relatively stagnant flows that allow the buildup of primary and secondary PM from mobile, urban, agriculture, and industrial SJV sources. Therefore, it is essential to accurately measure these low wind velocities to understand the transport and dispersion processes during PM_{10} episodes that occur in the November-January timeframe. Secondary aerosol formation is governed by two meteorological parameters—humidity and temperature. When fog or low clouds occur, RH and

temperature are often characterized by inhomogeneity within the valley, and thus it is important to document conditions at representative locations throughout the valley. Also important are measurements of conditions aloft that, at the minimum, define the boundary layer temperature structure and winds.

As input to the IMS95 planning process, the existing network of routinely acquired surface wind measurements was evaluated for its adequacy in defining the flow field during periods with light winds. The evaluation included sensor sensitivity, data of a known quality, and areal coverage. Operators of the identified sites were contacted, and information was gathered on the types of wind monitors used and the quality control (QC) and quality assurance (QA) procedures employed. Sites were identified that were judged to yield data of a known high quality suitable for use in IMS95 and other future studies. For a number of these sites, statistics on the frequency of low wind speeds were compiled to evaluate whether the threshold of standard propeller-type anemometers (0.5 m/s) was adequate to define wind fields for the low wind speed conditions in winter and to identify SJV regions where winds were particularly light.

2.4.1 Potential Sites

Table 2-5 lists the SJV meteorological networks and includes measurement descriptions, performance specifications, QA/QC procedures, and any changes in the equipment or sites before or during IMS95. In this table, the networks that are in compliance with the prevention of significant deterioration (PSD) or the equivalent are expected to yield the optimum data that are possible from standard-purpose meteorological equipment. Procedures at these sites require scheduled calibrations and maintenance to ensure that the equipment is operating within established specifications. In the study domain, the sites meeting these criteria are operated by the ARB, SJVUAPCD (the "District"), PG&E, CIMIS, and WSO. Data from other sites may be of high quality but were not included in the historical or IMS95 data archive, because the needed documentation (i.e., QA/QC procedures and results) to verify data quality was lacking.

2.4.2 Qualified Sites

Figure 2-1 shows the locations of the meteorological sites in the ARB/District, PG&E, CIMIS, and WSO networks where documentation exists to ensure data of known quality. CIMIS sites are the most numerous, followed by ARB sites. CIMIS sites are typically in rural areas, complementing ARB and

Table 2-5

Catalog of Existing Meteorological Measurement Sites Within the IMS95 Study Domain

Met Network	Type of Instrument	Averaging Time	Starting Threshold	Approx. Accuracy	QA/QC	Maintenance/Daily and Scheduled	New Sites for 1995
Air Resources Board	WS, WD, T, RH, neph,	all hourly averaged	0.5 m/s	PSD Specs	2 audits yearly per PSD by internal QA section	None except operator looks at daily readings	Jerseydale
Pacific Gas and Electric Company	WS, WD, T, RH, SR, uses Met One Package	all hourly averaged	0.5 m/s	PSD Specs	2 audits yearly per PSD by external QA contractor	Daily review and corrections/replacements if needed	No change
CA Dept of Water Resources, CIMIS	WS, WD, T, RH, SR, uses Met One Package	all hourly averaged	0.5 m/s	PSD Specs	2 calibrations and self audits	Daily review and yearly change out of bearings and pyrometer	Panoche
Bay Area AQMD	WS, WD, T, RH, SR,	all hourly averaged	0.5 m/s	PSD Specs	2 audits yearly by internal QA section	Daily review-immediate response to out of bound conditions	Spike Peak, Pacecho Pass, and Cement Hill - installed
National Weather Service	WS, WD, T, RH, weather conditions, precip	met is hourly averaged	1 m/s	None	No audits	Self calibrated yearly, but may not be done)	No change
Remote Automated Weather System-mainly USFS, CDF, BLM	WS, WD, T - all instantaneous and not taken on a precise hourly schedule	not confirmed	1 m/s	None	No audits	Eyeball look at measurements to see if they are ok	No change
Westside Operators - Texaco & Chevron	WS, WD, T, RH by RM Young system	all hourly averaged	0.5 m/s	PSD specs	2 audits by external contractor every quarter	Daily review and corrections if needed	All sites removed before IMS95 except KRG, FEL
Offshore Buoy Data	WS, WD, T, RH, SR, stability	not confirmed	0.5 m/s	PSD specs	not confirmed	not confirmed	not confirmed

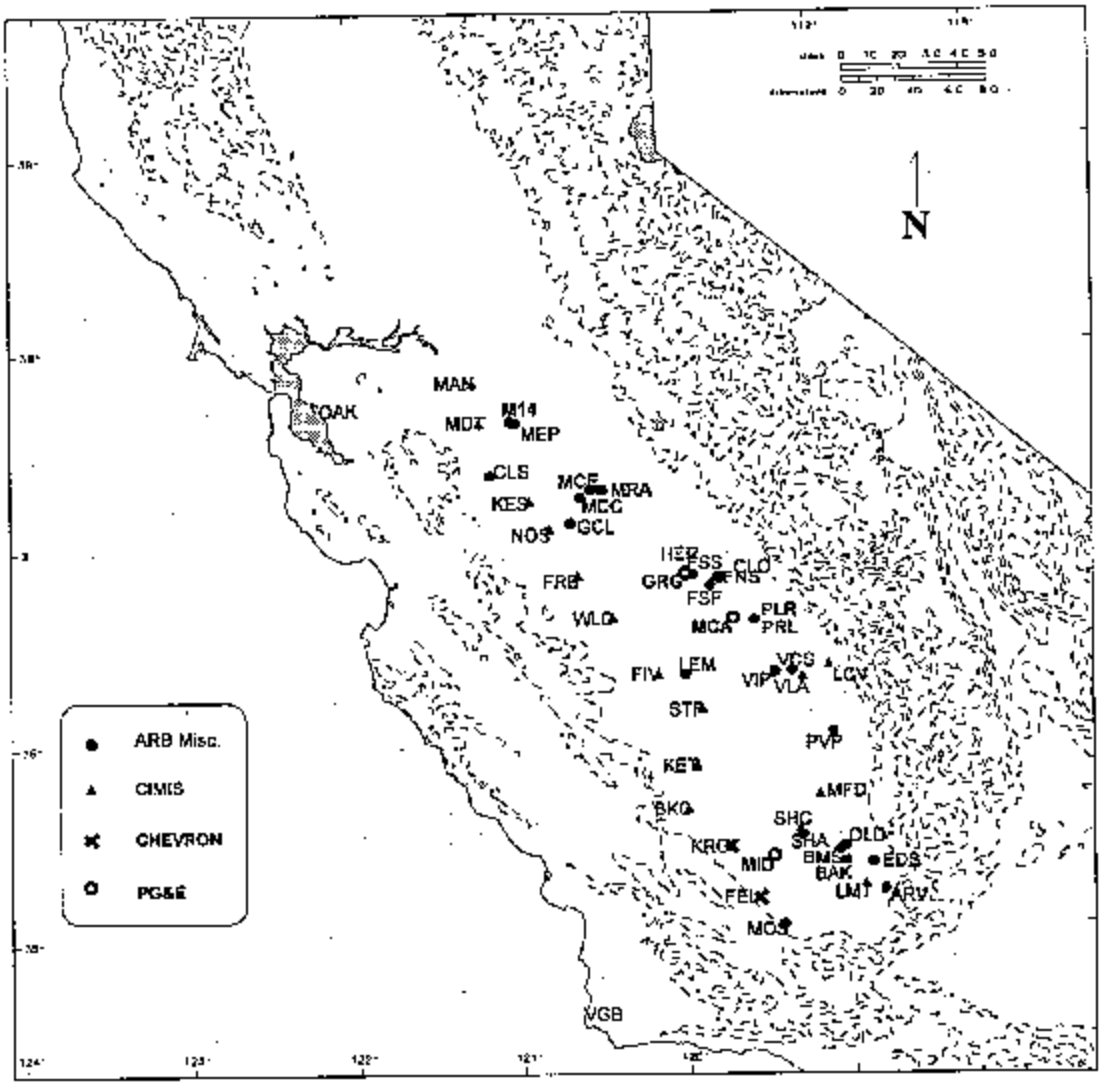


Figure 2-1. Meteorological Sites with Known Data Quality.

District sites; the latter two kinds are usually in urban areas. However, wind sensors at CIMIS sites are at a nonstandard height above the ground—2 m, as opposed to a standard 10-m tower. There is some question as to how well winds at the two heights compare under light wind conditions. However, Thuillier (1995) has shown that, during the summer, when wind speeds may be somewhat higher, either of these heights can represent regional or subregional wind speeds and direction. Thuillier indicated that spatial variability over scales of kilometers is greater than the vertical variability between the two heights.

The westside foothill region has good coverage in the southern end of the SJV by the WSO sites, the CIMIS sites at Blackwells Corner and Kernridge, and an ARB site at Maricopa. WSO closed three of its five sites before IMS95 but kept Fellows and Kernridge operational to provide coverage in the southern end of the study domain in support of IMS95. ARB/District and CIMIS sites provide reasonable coverage from Shafter south to Arvin. Coverage is very sparse in the center of the valley between Visalia and Shafter. The central and northern westside foothill region has only one representative site (Panoche), although westside coverage is very good east of Interstate 5. Coverage in the northeastern areas of the SJV is limited to ARB/District sites along Highway 99. The only eastside foothill site is at Lindcove, where unfortunately the local terrain effects probably dominate the winds when synoptic pressure gradients are weak.

Wind speed and wind direction are sampled frequently (1–5s), and averaged data are stored—typically, they are averaged hourly. Data are averaged via two algorithms that cannot be interpreted as being the same. One algorithm produces a vector-average wind speed and wind direction, and the other algorithm produces a scalar average wind speed and unit-vector average wind direction. Except for ARB sites, wind measurements in this group are averaged via the latter algorithm. ARB produces vector averages.

All CIMIS, PG&E, and WSO sites measure temperature and humidity, subject to standard QA/QC procedures as specified. All the ARB and District sites measure temperature, but fewer than half of them measure RH.

2.4.3 Frequency of Low Wind Speeds

To investigate the frequency of occurrence of low wind speeds, they were defined at two thresholds: 0.5 m/s and 1.0 m/s. In the PG&E, CIMIS, and WSO networks, measurements were examined from 22 sites, all of which could provide scalar-averaged wind speeds of known accuracy down to at least 0.5

m/s. This analysis used hourly averaged data for five months (November 1992–January 1993 and November–December 1993), without regard to air quality.

Low wind speed frequencies varied considerably between months and between sites. Nevertheless, in general, wind speeds during November—especially, November 1993—were lower than during December and January. The higher wind speeds in December and January are consistent with the higher occurrence of winter-type (frontal passage) weather systems.

At the WSO sites in the southwest corner of the SJV, from Kernridge to Maricopa, calm winds (≤ 0.5 m/s) were very infrequent during the months examined. At nearby Midland (a PG&E site to the east), calm winds were significantly more frequent then at WSO sites, but yet consistent with the measurements at Shafter (SHC), which is in the center of the SJV at an equal distance further east. This finding may be due to the influence of the slopes along the southwest edge of the valley. Overall, winds at or below 0.5 m/s were the least frequent at the WSO sites, and 30%–50% of those occurrences were during January 1993. At most of the other sites, such winds occurred only a few times, except for Herndon (HER), Westland (WLC), and Midland (MID), where stagnant wind conditions occurred about 10% of the time. This evaluation shows that the occurrence of calm winds is not an overwhelming feature of the SJV wind field but may be of significance at some locations.

Wind speeds at or below 1.0 m/s are frequent throughout the SJV, with notable exceptions in the WSO network due to their location in the valley. The highest frequencies of such winds are in the Visalia-Lindcove (VLA-LCV) area.

2.4.4 Measurements Aloft

Meteorological measurements aloft are very sparse in the SJV. There are no routine measurements of winds or RH. Balloon soundings measuring temperature and RH (rawinsondes) are made twice daily from the Oakland (OAK) and Vandenberg (VBG) airports (see Figure 2-1 for locations of sites). However, low-level measurements at either site are not representative of SJV boundary layer conditions. In support of special operations, rawinsondes are made from Lemoore Naval Air Station, within the SJV, but these measurements are infrequent and unscheduled.

The ARB makes daily airplane temperature soundings at 0600 PST from Stockton, Fresno, and Bakersfield. Airplane soundings are made over Columbia on an as-needed basis. These are crude but useful measurements that the pilot takes for every 152 m of altitude via the airplane's outside air temperature (OAT) indicator. Unfortunately, fog and/or low ceilings—which often accompany high

PM_{10} concentrations in the winter—can restrict aircraft operations. Thus, data may be missing for significant periods of time when conditions are conducive for high PM_{10} concentrations.

2.4.5 Summary of Routine Measurements

In summary, a great many SJV sites use low-threshold standard meteorological sensors and record WS and WD data of known accuracy and precision. However, many of those sites measure winds at nonstandard heights. Although in general there is good surface wind areal coverage, there are important gaps, most notably in the Sierra foothill region and in the south central area. Wind speeds below 0.5 m/s may occur with significant frequency during periods when high PM_{10} concentrations are measured. This raises the question of whether standard cup- or propeller-type anemometers are adequate. There also is a requirement to standardize the averaging and computational methods used in collecting and summarizing data. For wind averaging, the scalar and vector averaging methods discussed earlier are useful, and hourly averages that use both methods should be part of the database. There are no routine measurements of winds aloft in the SJV. The ARB makes scheduled temperature soundings via aircraft at three SJV locations during the fall and winter; however, aircraft measurements are curtailed when the visibility decreases or the ceiling descends below the airport minimum.

2.5 Recommendations for IMS95 Meteorological Measurement Network

Additional meteorological monitoring sites collecting temperature, RH, and wind speed and direction (scalar and vector) data should be established and operated during IMS95. Standard vane-propeller and sonic anemometer wind monitors were employed. The standard wind monitors were the fast-response and low-threshold type that can accurately measure wind speeds as low as 0.5 m/s. Manufacturers of sonic anemometers claim a wind direction accuracy of $\pm$ 0.1° and a wind speed accuracy of $\pm$ 0.05 m/s. At sites employing standard monitors, data were stored both as 5-minute and hourly averages. Sonic anemometers collect data at 10 Hz, and those too were stored as 5-minute and hourly averages.

The recommended locations of the meteorological sites were based on several factors, including the requirement for meteorological coverage at critical chemistry measurement sites, the requirement for supplementing upper air measurements with surface data, and the need for measurements that provide information about key meteorological features. Of the 14 sites established, 5 used sonic anemometers, and 9 used standard systems.

The information gathered from this network is important not only for understanding the causes of high PM in the SJV, but also for determining monitoring requirements for future SJV field studies. Some of

the major objectives of these measurements were to determine the adequacy of (1) standard low-threshold anemometers, with thresholds of about 0.5 m/s, for defining winter wind fields when calm conditions prevail; (2) the spatial coverage of sites needed to define winter wind, temperature, and moisture fields; and (3) the time resolution required to accurately determine dispersion and transport conditions.

Sections 2.5.1 and 2.5.2 list the 14 sites and summarize the primary reasons why these sites were included in IMS95.

2.5.1 Sonic Anemometer Sites

2.5.1.1 Panoche (PAN)

This site is influenced by flows near the northern boundary of the IMS95 study domain and is also likely to be influenced by the western hills terrain. This site has been collocated at a CIMIS site so that the sensitivity of standard monitors at a height of 2 m can be compared with the sonic anemometer at 2 m. This comparison is especially important, because CIMIS sites provide the major wind data on the west side of the SJV.

2.5.1.2 North of Madera (NMD)

This site is located to measure the influence of terrain-driven slope flows on the general flow in the SJV and has been aligned with three other sites to provide data along the northern boundary of the study domain.

2.5.1.3 Porterville Airport (PVA)

This site is at the east end of an east-west sequence of chemistry and meteorology measurement sites and in an area where very light flows are likely. Data from this site, along with data from the following two sites, are important in defining fluxes in the southern section of the SJV.

2.5.1.4 Pixley Wildlife Refuge (PWR)

This site is at the center of the southern flux plane measurements and should be representative of air flow along the central axis of the valley.

2.5.1.5 Lost Hills Airport (LHA)

This site is at the west end of the southern flux plane measurements and should be representative of the west side flows, because it should be influenced by the western hills terrain.

2.5.2 Standard Wind Monitor Sites

2.5.2.1 Southwest of Chowchilla (SWC)

This is a core site, where it is critical to measure site-specific meteorology. This site is aligned with three other sites to provide data along the northern boundary of the study domain.

2.5.2.2 El Nido (ELN)

This site supports radar wind profiler (RWP) (winds aloft) operations and is aligned with three other sites to provide data along the northern boundary of the study domain.

2.5.2.3 Fresno/Einstein Park (FEP)

This site is located to support chemistry measurements at the Fresno core sampling site.

2.5.2.4 Mouth of the Kings River (MKR)

This site supports RWP operations. Even without the RWP, this site is critical for assessing the effect of a major airshed drainage—namely, the Kings River Canyon drainage—on the dispersion and transport from Fresno, which is a major emissions area.

2.5.2.5 Caruthers (CAR)

This site is located in the central region of the valley, which is often likely to be downwind of the greater Fresno area. Previous meteorological measurements at this site are sparse.

2.5.2.6 Corcoran (COR)

This site supports RWP (winds aloft) operations and is aligned in the center of the valley along the axis of the two other RWP sites.

2.5.2.7 Kern Wildlife Refuge (KWR)

This site is located to support chemistry measurements at the core sampling site.

2.5.2.8 Bakersfield/Van Horn School (BAV)

This site is located to support chemistry measurements at the core sampling site.

2.5.2.9 Mettler (MTL)

This site is useful mainly for augmenting RWP operations. It is in the southern end of the valley, near one of the major passes (Tejon), in an area where previous data are sparse.

2.6 Conclusions From Historical Data Analysis

Below are conclusions from Smith and Lehrman (1996) and from others whose data are not documented in reports but were presented at the February1994 CRPAQS data analysis workshop:

- The optimal sampling period for the Fall study is from September 15 to November 15, depending on the schedule for cotton harvesting in 1995.
- The duration of fall episodes depends on meteorological conditions, with shorter episodes occurring when frontal systems move through the valley more frequently and higher PM concentrations occurring when stagnation and associated calm conditions prevail. Episode durations of several days to one week are typical.
- The highest PM concentrations during the fall, and in fact during the year, occur in the Corcoran area, extending north to Hanford and south into the Tulare Lake bed to Kettleman City.
- The optimal sampling period for the Winter study is from December 1 to January 10.
- The duration of winter episodes depends on the meteorological conditions. Lower PM concentrations occur if low-pressure troughs are more frequent, as they were in the winters of 1992 and 1993. Higher PM concentrations occur if long periods of stagnation occur, with resulting calm winds and associated fog. Episodes typically last about 7 days, but they may range from a few days to 20 days.
- The highest winter PM concentrations occur in the southern half of the valley, with a dividing line somewhere between the San Joaquin River and the Merced River. Bakersfield and Fresno typically experience the highest winter PM concentrations, as compared with rural areas. However, during the winter, rural and urban areas typically experience the same trends in high and low PM_{10} concentrations, because the winter episodes are more regional than episodes during other seasons (Chow et al. 1993a, Smith and Lehrman 1996). PM_{10} components during high-concentration days include significant amounts (10%–50%) of secondary aerosols, consisting of sulfate, nitrate, and ammonium. Most of the remaining PM_{10} mass consists of primary crustal material and primary and secondary organic material (Chow et al. 1993a).
- The meteorological conditions most associated with high PM concentrations in the fall and winter are high temperatures aloft (>12° C) and weak pressure gradients from Nevada (Las Vegas or Reno) to San Francisco; the most favorable conditions occur when the gradient is actually negative, with a resulting offshore flow. Although fog may persist in the valley for long periods, from several days to three weeks, it is often patchy at the surface. However, data the on fog coverage, duration, and the height of the top and bottom of the fog layer are, at best, extremely poor.
- The routine surface meteorological monitoring network provides fairly good coverage in most of the southern portion of the valley, with a few notable exceptions—the center of the valley between Shafter and Visalia, the area along the eastern foothill region, and the area west of

Interstate 5 in the western foothill region. As a result of this analysis, nine standard meteorological systems were installed. Although most systems were placed so as to be associated with core sites or upper air meteorological sites, they all filled gaps in the routine meteorological monitoring network. Five sonic anemometer sites were also installed for IMS95 at locations throughout the valley where low flows would be expected. The sonic anemometers were placed to provide information on how low the wind speeds are during calm conditions and assist in estimating the representativeness of the TSS 5A experiment (Gray et al. 1996).

- Routine upper air meteorological measurements are lacking in the valley, although some special measurements are made. The upper air data used in the historical analysis were from the twice-daily Oakland and Vandenberg airport rawinsonde soundings. Although these data probably provided reasonable synoptic information, upper air boundary layer information was not transferable from these coastal areas to the valley.
- Winds tend to be light during high winter PM episodes, because stagnation periods are conducive to pollution buildup. However, at least regionally, two types of flow regimes occur. One regime is up (south) and down (north) the axis of the valley, and the other is east and west across the valley. The latter develops because of daytime upslope flows and nighttime downslope flows, into and out of the mountains on the east and west sides of the valley.

2.7 Conceptual Models of PM_{10} in Central California

Conceptual models provide a framework for understanding elevated PM_{10} concentrations in the SJV. They state hypotheses that must be verified, refined, or refuted by interpreting measurements or applying quantitative chemical and physical principles. Conceptual models identify all the dominant emissions, meteorological, transformation, and deposition mechanisms that affect PM_{10} concentrations, and such models eliminate mechanisms from consideration that are minor causes of the elevated concentrations. Conceptual models must be perfected before performing mathematical modeling for quantitative source apportionment. Only phenomena that are part of the conceptual model need to be included in the quantitative modeling.

Initial analysis of the historical data indicates four situations in which PM_{10} concentrations above 150 $\mu g/m^3$ occur (Watson et al. 1997, Smith and Lehrman 1996). For each situation, a corresponding preliminary conceptual model was initially developed by Watson et al. (1996), as described in Sections 2.7.1 through 2.7.4. The Winter study is intended to refine conceptual model 4, and the Fall study is intended to refine conceptual model 1 and/or 3. Each of these models is based on observations of air quality and meteorological data, with little direct evidence of the relationships between activities at sources and pollutant concentrations measured at receptor sites. However, the models represent the best current thinking by drawing upon the historical data analysis, the ARB emissions inventory, general knowledge of emissions activities, an understanding of atmospheric chemistry, and common sense. The

conceptual models will be refined, as needed, on the basis of findings from IMS95 and future field programs.

2.7.1 Model 1: Low Wind Fugitive Dust

This conceptual model is defined by situations in which a high PM concentration is measured at a single receptor for only one day. The receptor can be in an urban or rural area. In the rural areas, nearby sources include tilled fields and unpaved roads. In urban areas, nearby sources include paved roads and construction on vacant lots or roads. These events occur during nonwinter or dry months and show no proclivity for one time period or site over another. Wind speeds are generally lower than 10 m/s, which is a reasonable threshold for dust suspension. No emissions information is available, although anecdotal observations identify potential sources—such as a pile of material that was near a sampling site but later disappeared, unpaved parking lots surrounding a sampling site, a nearby field that was untilled before the exceedance and was apparently tilled afterward, and road construction. These activities have never been conclusively related to an elevated concentration. Only a single sampling site in the compliance network is observed to exceed the standard, and its concentration is two to five times higher than PM concentrations at other SJV monitoring stations.

In this conceptual model, an intermittent activity capable of suspending surface particles in the air probably occurred within 5 km upwind of the sampling site. The activity may have been extremely intense for a few hours, such as the cloud generated by a farm implement, or it could have been at a lower level for a longer period, such as suspension of dust from a dirty street. Most of these particles are larger than 5 μm, and many of them are larger than 10 μm, but they are sampled and quantified gravimetrically, owing to the slope of sampling effectiveness curves. Inlets on routine samplers become loaded with dust, enabling particle bounce, reentrainment, and deagglomeration to occur, which increase the measured mass beyond what is inhalable; however, the amount of added material is unknown for any given sample and varies with sampler maintenance and design. In that regard, properly designed and maintained samplers would minimize this potential positive artifact.

At wind speeds less than 10 m/s PM_{10} concentrations at 5 km from the source are only 10% as large as concentrations at 10 m from the source, owing to deposition and dilution. Beyond 10 m, however, particles larger than 2.5 μm have fallen out, but the smaller particles remain suspended and mix with the overall background concentrations. The source range of influence increases with wind speed, owing to the larger vertical mixing that accompanies high winds as well as the larger transport distance. This zone

of influence is offset by the greater dilution supplied by the winds, which are lower than those needed to suspend dust.

2.7.2 Model 2: High Wind Fugitive Dust

Wind speeds associated with frontal systems can exceed the suspension threshold of approximately 10 m/s. Periods of drought in California can leave land dry and fields fallow. Winds blowing over these fields can cause particles to saltate, thereby breaking larger particles (>50 μm to 100 μm in diameter) into smaller particles (>3 μm). The smaller particles are suspended by the wind and mixed throughout the mixed layer by substantial vertical components of the wind; horizontal transport may also be substantial (tens of kilometers) because of the higher wind speeds. The highest PM concentrations are observed at one or more measurement locations closest to disturbed land—thus groupings of sites that exceed the standard are observed. Exceedances typically last for only one day. The crustal component at all SJV sites increases, though not always enough to exceed the PM_{10} standard.

Owing to the longer transport distances, a portion of this suspended material can deposit onto paved roads, where it can be resuspended by vehicles. Just as in low wind situations, poorly designed or maintained sampler inlets can become loaded with particles, allowing nonrespirable mass to be measured with the respirable fraction. As noted in Section 2.7.1, properly designed and maintained inlets will minimize the likelihood of this positive artifact.

2.7.3 Model 3: Clear Sky Stagnation

Though secondary particle contributions are highest during winter, sometimes exceeding 100 $\mu g/m^3$, they can reach 50 $\mu g/m^3$ during October and early November when there is no fog and the air is still relatively dry.

Agricultural burning, harvesting, and planting are prevalent during the fall. The flow along the SJV axis has become less persistent than during the summer, because of decreased heating in the Mojave Desert. Photochemical activity produces copious amounts of nitric acid, because of clear skies and sunlight that last for several hours longer than in December. Fog occurs rarely, but flows are weak, allowing stagnation to occur, along with its accompanying accumulation of pollutants. Once again, there is plenty of ammonia, and the lower fall temperatures push the ammonium nitrate equilibrium toward the particle phase. Though secondary aerosol is a significant contributor at most sites, it contributes less than one-third of the PM_{10} mass in samples that have the highest PM_{10} concentration, whereas it often contributes over 50% of the PM_{10} mass in such samples during winter. Field burning and harvesting contrast with

the road dust and residential burning expected during winter. However, the crustal material fraction in the fall is significant in relation to the winter fraction. PM_{10} exceedances occur on days when there is a supposition of pollutants, primary and secondary.

2.7.4 Model 4: Stagnation with Fog

The highest winter PM_{10} concentrations in the SJV result when several persistent stagnations occur and source contributions are superimposed upon each other. Secondary aerosol becomes a major contributor, accounting for 30%–50 % or more of PM_{10} mass. Secondary ammonium nitrate is typically the largest contributor, with significant and sometimes major contributions from secondary ammonium sulfate, primary dust, primary wood burning, primary emissions from steam generators, and primary emissions from diesel and gasoline internal combustion engines. Nitric acid levels are low. Ammonia concentrations are variable, but probably high, because the ammonia drives the nitric acid to the aerosol phase, especially in the cooler winter temperatures. Ammonium nitrate and ammonium sulfate concentrations are usually high and low, respectively, in the same samples throughout the SJV and even in the San Francisco Bay Area. Contributions from other sources are not correlated with the sampling location.

On the basis of current emissions inventories, most of the NO_x in the valley comes from ground-level sources, but 10%–20% comes from elevated sources that may loft plumes above the inversion layer. Ammonia is emitted everywhere but is probably highest near large concentrations of animal waste. Agricultural burning is uncommon, as are forest fires, but residential wood burning may be a significant source during the holiday season.

Wind speeds are generally low throughout the winter, often below 0.5 to 1 m/s, which is the threshold of most standard anemometers in routine SJV meteorological monitoring networks. During drought years, strong low-level inversions are common and persistent, with frequent extended periods of stagnation and nighttime ground fogs that may persist into the day through several day/night cycles. The inversion heights are typically low, approximately 300 to 400 m, and they may not break for days at a time, as evidenced by the top of the stratus cloud layer that fills the valley and is easily observed from aircraft flights over the valley. Wetter years are characterized by more frequent storms or strong fronts passing through California. Under these conditions, stagnation periods are shorter, PM concentrations are usually lower, and fogs may persist for only a few hours on several consecutive nights and dissipate by midmorning. Ground-level fogs are very patchy, although more consistency may occur several hundred meters above the valley floor.

Under stagnant conditions, a Great Basin high-pressure system settles over Nevada and Utah after a storm front. All valleys throughout the West experience extended, low-level inversions, especially valleys with snow on the ground or damp surfaces that turn surface heating into latent heat of evaporation rather than into ground heating. These inversions can persist for a week or more without breaking or until a storm front passes through the area.

As the inversion persists day after day, pollutants build up, especially near emissions sources. Though wind speeds are low below the inversion height, organized upvalley and downvalley flows and upslope and downslope flows mix pollutants together over several days. Above the inversion, the air is clear; the Sierra Nevada can be viewed from the Coastal Range. This visual range of over 100 km implies that fine particle concentrations above the inversion are below 5 mg/m^3.

When fog or low-lying stratus clouds are not the dominating features of the valley, photochemical reactions during daylight create hydroxyl radicals that oxidize SO_2 and NO_x to sulfuric acid and nitric acid, respectively. Gaseous hydrogen peroxide also forms from these reactions, and its presence before fog formation can play a major role in the oxidation of SO_2 to sulfate within the fog droplets. There is plenty of NO_x and SO_2. The NO_x reaction is 10 times faster than the SO_2 reaction, so the hydroxyl radicals are used up as fast as they can form. Most sulfuric acid formation occurs near the point of emissions, where concentrations are high. Sulfuric acid formation stops at night, but nitric acid formation continues through the reaction of N_2O_5 with water.

Plenty of ammonia from widespread livestock emissions is transported to urban areas. Sulfuric and nitric acids are immediately neutralized by ammonia, except in the west side oil fields that are protected from the transported ammonia by orographic channeling. There is little time for nitric acid to deposit before it is converted to aerosol ammonium nitrate, and the low temperatures throughout the episode keep most nitrate in the particle phase during the day and night.

Some aqueous phase chemical conversions occur within patchy fogs, but this is not the dominant mechanism for aerosol formation until fogs become widespread, intense, and persistent. SO_2 emissions are absorbed by the droplets, and O_3, hydrogen peroxide, and iron/manganese catalyzed reactions efficiently convert SO_2 to sulfate. Hydrogen peroxide and iron/manganese catalysis are the dominant pathways for conversion to sulfuric acid under these conditions. Conversion of SO_2 to sulfate in the northern SJV is limited by SO_2 availability. In the southern SJV, however, because of the more abundant emissions of SO_2 from oil production, hydrogen peroxide is depleted long before the SO_2 is converted to sulfate. Nitric acid and ammonia also dissolve in these drops, forming ammonium nitrate when the fogs

dissipate. Sulfate concentrations increase in relation to nitrate concentrations as the fog forms, but larger droplets deposit more rapidly than particles do that were present before the fog formed. Aerosol concentrations may thus stabilize and even start to decrease toward the end of a fog episode.

As the Great Basin high-pressure system breaks in response to the beginning of another storm system, the droplets evaporate, leaving enlarged particles from 0.5 to 0.7 μ. These particles mix with the small particles generated earlier to provide a bimodal size distribution from 0.1 to 1 μ. Coastal air accompanying the storm front moves into the SJV, but the precipitation cleanses the air while the vigorous transport and mixing move pollutants up into and over the Sierra Nevada.

This process repeats several times throughout the winter. No single contribution causes an exceedance of the PM_{10} standard. Exceedance results from a combination of the source emissions, the persistence of the inversion, and the formation processes for secondary aerosol that all occur simultaneously.

Section 3

MEASUREMENT PROGRAM

This section summarizes the IMS95 measurement activities. It describes the study design and siting, the field and laboratory measurement methods, and external QA.

3.1 Overview

The Fall study, conducted during November 1-14, 1995, was designed to provide data pertaining mainly to conceptual models 1 and 3 (Sections 2.7.1 and 2.7.3). The Winter study, conducted during December 9, 1995 through January 6, 1996, was much larger and was designed to provide data pertaining mainly to conceptual model 4 (Section 2.7.4).

3.1.1 Fall Study

The Fall study consisted primarily of daily sampling for PM_{10} via a saturation monitoring network of 22 sites and collection of daily emissions activity data. In general, the purpose of this network was to collect a data set consisting of spatially dense, chemically characterized PM (PM_{10} and/or $PM_{2.5}$) concentrations to determine the spatial representativeness of the core site and the general spatial influence of sources in the surrounding area.

The Fall study domain was in the central SJV, covering about 1,080 km^2 (40 km north to south and 27 km east to west). Figure 3-1 shows the study domain, and Table 3-1 shows the site codes, names, locations, coordinates, and elevations. Detailed site descriptions are in Solomon et al. (1997). The core site for this network was located at the District site in Corcoran, as shown in Figure 3-1. Saturation sampling sites using battery-powered portable PM_{10} samplers were located in and around Corcoran and as far north as Hanford. The core site (COP) and saturation site (C04) were collocated for QC purposes. Saturation sites were located near and between emissions sources. Siting rationale are given later in this section.

3.1.2 Winter Study

The Winter study consisted of daily sampling for size-fractionated PM (PM_{10} and $PM_{2.5}$), PM composition and precursor gases, fog size and composition, surface and aloft meteorological variables, and emissions activity at over 65 sites during the 4-week period from December 9, 1995 through January 6, 1996. TSS 5A and TSS 11 were conducted almost concurrently with the Winter study.

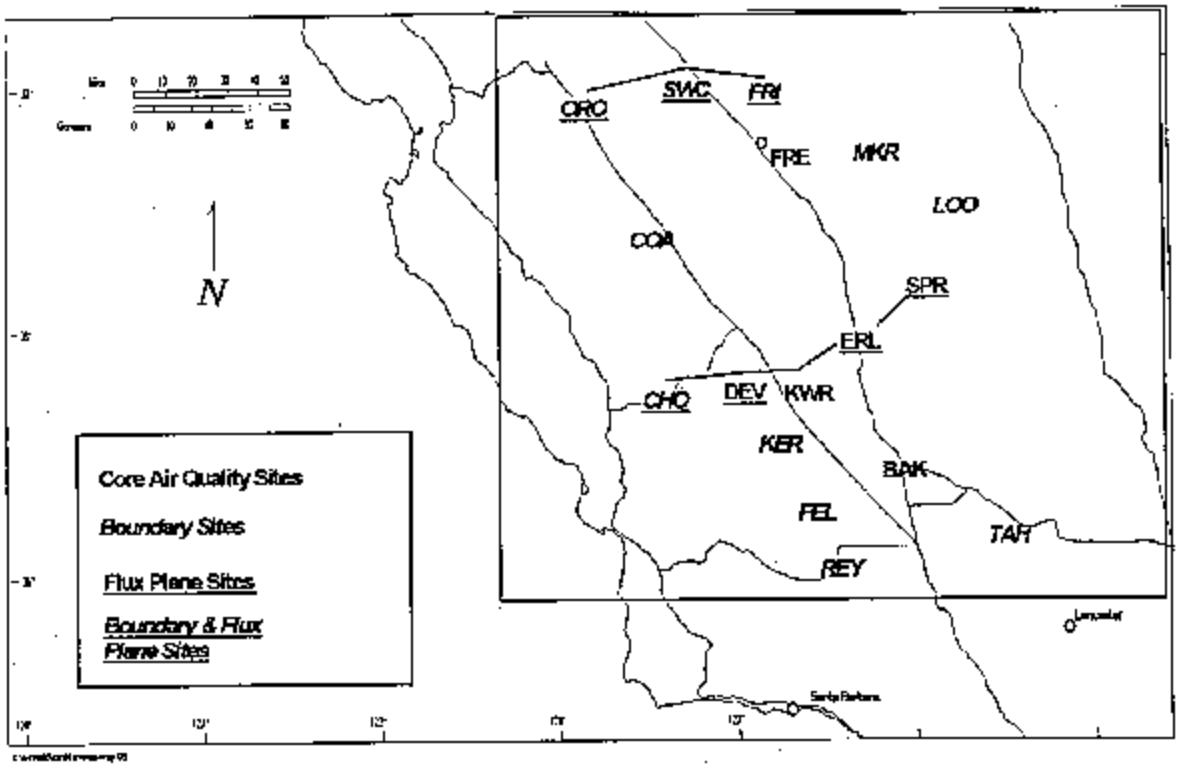


Figure 3-1. IMS95 Winter Core, Boundary, and Flux Plane Air Quality Measurement Site Locations.

Table 3-1

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Fall Study							
COP	Van Dorsten	1000 Van Dorsten and northeast corner of Zumwalt Park.	Core	36_05' 58.38" N	119_33' 50.98" W	0	
01C	Irwin	807 S. Irwin. Located at the southeast corner of the school's play yard.	Saturation	36_18' 52.90" N	119_38' 39.67" W	62	
02C	Nevada	North 0.6 miles (or 10 power poles north) of Nevada Avenue on 6th Avenue, which is west of the Corcoran Irrigation District Reservoir.	Saturation	36_08' 38.30" N	119_33' 54.31" W	61	
03C	Tulare Lake	Northwest corner of Paris and 7th Avenue on west side of 7th Avenue.	Saturation	36_04' 04.75" N	119_35' 24.36" W	41	X
04C	Van Dorsten	1000 Van Dorsten, at northeast corner of Zumwalt Park near intersection of Hanna and Van Dorsten.	Saturation	36_05' 58.38" N	119_33' 50.98" W	61	
05C	Pickrell	1st pole north of Sherman on Pickrell on the east side of the train tracks.	Saturation	36_05' 42.66" N	119_33' 14.83" W	61	X
06C	Yoder	Yoder and Patterson. Site is 2nd pole north of corner of Patterson and Yoder on east side of the street.	Saturation	36_06' 06.50" N	119_33' 29.84" W	61	X
07C	Newark	1st pole on the southeast corner of the intersection of Newark and 6½ Avenue.	Saturation	36_07' 10.80" N	119_34' 52.47" W	60	
08C	Josephine	1st pole on the northeast corner of Grable and Josephine.	Saturation	36_06' 26.50" N	119_34' 11.93" W	61	X
09C	Canal	On south side of Sherman Avenue at the intersection of Sherman and 6½ Avenue. Located on the 2nd power pole east of canal crossover that is across from the end of 6½ Avenue.	Saturation	36_05' 39.86" N	119_34' 31.59" W	55	X
10C	Jepsen	1st power pole on northeast corner of Jepsen and Chase.	Saturation	36_05' 48.95" N	119_33' 40.03" W	61	
11C	Paris	Power pole at east end of Paris, east of King and northwest of Corcoran Prison.	Saturation	36_03' 55.55" N	119_32' 14.15" W	61	X

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
12C	King	3rd pole on east side of King at the intersection of King and Ottowa.	Saturation	36_05' 00.82" N	119_33' 30.93" W	59	
14C	Zacky Farms	South of Racine Avenue at 5th. 2nd pole from entrance on south side of Racine.	Saturation	36_00' 25.67" N	119_32' 48.69" W	41	
15C	Pueblo	Corcoran Wastewater Treatment Plant at Pueblo and King, 2nd pole on north side of Pueblo, east of King.	Saturation	36_04' 48.64" N	119_33' 28.75" W	56	X
16C	Bainum	2nd power pole from the southwest corner of Bainum and King, on south side of Bainum.	Saturation	36_05' 26.84" N	119_33' 32.95" W	61	
17C	Miller	1st power pole on the northwest corner of Miller and Bell.	Saturation	36_06' 13.90" N	119_35' 00.16" W	59	
18C	Kent	1 mile east on Kent between 9 2 Avenue and Hwy. 43.	Saturation	36_13' 22.85" N	119_36' 40.10" W	60	
19C	Wastewater	Hanford Wastewater Treatment Plant. 900 S. 10th Avenue.	Saturation	36_17' 41.94" N	119_38' 48.19" W	61	X
20C	Creighton 1	Creighton Ranch Reserve. South edge of Road 48 at north end of Reserve.	Saturation	36_05' 08.57" N	119_27' 53.31" W	63	X
21C	Redding	On south side of Redding, 5 poles east of 6th.	Saturation	36_01' 17.53" N	119_33' 53.89" W	44	
22C	Creighton 2	Just north of site C20.	Saturation	36_06' 10.56" N	119_27' 52.73" W	63	
CRM	Corcoran	2202 Sherman Avenue, across the street (north) of 09C.	Surface meteorology	36_05' 43.14" N	119_34' 31.66" W	59	

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Winter Study							
Core Air Quality Monitoring Site							
BFK	Bakersfield	Van Horn School. 5501 Kleinpell Ave. SW corner of playing fields.	Core	35_21' 21.86" N	119_03' 57.15" W	116	X
FEI	Fresno-Einstein Park	Einstein Park, 3566 E. Dakota Avenue.	Core	36_41' 08.16" N	119_46' 04.19" W	365	X
KWR	Kern Wildlife Refuge	Northwest corner of Garces Hwy. and Rowlee Road.	Core	35_45' 41.18" N	119_28' 43.60" W	66	X
Boundary and Flux Plane Sites							
SWC	Southwest of Chowchilla	20513 Road 4, 2.5 miles south of Hwy. 152.	Boundary A	37_02' 56.73" N	120_28' 17.38" W	49	
CHO	Cholame	41 South just over Cottonwood Summit. ~200 feet from a road narrowing sign is a pullout with parking on the north side of 41. Site is located on north side of 41 up on dirt hill east of parking area.	Boundary B	35_46' 50.06" N	120_12' 26.34" W	640	X
COA	Coalinga	4th power pole north from the intersection of Derrick and Jayne on west side of Derrick.	Boundary B	36_08' 21.11" N	120_23' 26.89" W	254	X
ERL	Earlimart	3rd power pole on Rt. 120, north of Rt. 120 and Rt. 56 intersection located 1.5 miles west of Hwy. 99 and Rt. 56.	Boundary B	35_53' 41.03" N	119_18' 14.54" W	75	X
LOO	Lookout Point	On fence at NPS Air Quality Site behind ranger station.	Boundary B	36_25' 45.55" N	118_45' 43.25" W	1174	X
SPR	Springville	Power pole in front of 35273 Radcliff Avenue.	Boundary B	36_07' 33.36" N	118_49' 28.58" W	304	X
TEH	Tehachapi	Hwy. 58 to Broom Road scanning/ met station. At approximately 3,500, (just above elevation of Valley haze)	Boundary B	35_12' 02.85" N	118_31' 18.85" W	949	X

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Boundary and Flux Plane Sites (cont.)							
DEV	Devils Den	South of Pyramid Hills Road on West Side Hwy., take dirt road east immediately south of California Aqueduct station. Site is the third pole on south side of a row of double power poles heading to the east.	Boundary C	35_47' 46.55" N	119_59' 08.02" W	155	
FRI	Friant	10th power pole from the intersection of Hwy. 145 and Rt. 41, on the south side of Hwy. 145.	Boundary C	37_00' 36.83" N	119_47' 05.56" W	163	
MKR	Mouth of the Kings River	Belmont east to Trimmer Springs Road. The site is at the southeast corner of the Friant-Kern canal and Trimmer Springs Road.	Boundary C	36_46' 02.60" N	119_27' 14.91" W	145	
LBS	North of Los Banos	NW of Los Banos just east of the San Joaquin Valley National Cemetary.	Boundary C	37_07' 06.46" N	121_03' 05.23" W	69	
REY	Reyes Station	Second pole on east side of Cerro Noroeste Road, south of Hwy. 166/33. Approximately 200 yards north of entrance to Bitter Creek National Wildlife Refuge.	Boundary C	34_57' 35.41" N	119_26' 43.18" W	914	
FEL	Fellows	On east side of Hwy. 33, about 8 miles north of Taft.	Boundary D	35_11' 51.01" N	119_32' 40.76" W	365	X (Limited)
KRN	Kernridge	6 miles north of Lost Hills Road on Hwy. 33.	Boundary D	35_27' 07.72" N	119_43' 12.66" W	186	X (Limited)

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Bakersfield Saturation Network							
01B	Van Horn School	Van Horn School. End of Kleinpell. SW corner of playing fields.	Saturation, collocated at core site	35_21' 22.38" N	119_03' 56.86" W	116	X
02B	Chester	Chester just north of old ARB site at 225 Chester (between second and third) on west side of street.	Saturation	35_21' 28.04" N	119_01' 08.25" W	119	
03B	El Rio	Light pole in front yard of 612 North El Rio (SE corner of North El Rio and Retreiver).	Saturation	35_21' 33.21" N	119_04' 57.68" W	117	
04B	Stockdale	Stockdale Hwy. just west of Hwy. 99 in Park and Ride lot on south side of Stockdale Hwy.	Saturation	35_21' 13.69" N	119_02' 25.19" W	118	X
05B	China Grade	China Grade Loop. One mile east of Manor. Second pole west of entrance to Texaco facility at 1546 China Grade Loop on north side of road.	Saturation	35_25' 36.74" N	118_59' 35.72" W	164	X
06B	Santa Fe	0.3 miles south of Renfro on Santa Fe. Take dirt road to west. Third power pole on south side of road.	Saturation	35_24' 31.69" N	119_09' 45.35" W	105	
07B	Truxtun	At intersection of Mohawk and Truxtun. 2nd power pole to the north on the north side of Truxtun in unpaved riverfront park area.	Saturation	35_21' 53.02" N	119_03' 56.82" W	118	X
08B	Edison	ARB site at Johnston Orange Farm. 0.2 miles east of last building in downtown Edison on Edison Hwy. North on dirt road across railroad track then immediately go east on dirt road, then north on dirt road just before orchard and after vineyard through vineyard into storage/junk area.	Saturation	35_20' 44.00" N	118_51' 04.06" W	198	

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Bakersfield Saturation Network (Cont.)							
09B	Mohawk	First pole on Mohawk, north of Krebs on east side of road.	Saturation	35_23' 55.02" N	119_03' 55.09" W	122	X
10B	Warren	Third pole west of Plymouth on south side of Warren. Across from 320 Warren.	Saturation	35_24' 42.94" N	119_01' 38.65" W	151	X
11B	Fairway	Power pole in front yard of house at 401 Fairway (SW corner of Fairway and Mt. Shasta), next to stop sign.	Saturation	35_20' 56.00" N	119_04' 34.82" W	115	
12B	Van Horn School	Van Horn School. End of Kleinpell. SW corner of playing fields.	Saturation, collocated at core site	35_21' 22.38" N	119_03' 56.36" W	116	X
Kern Wildlife Refuge Saturation Network							
13K	Gun Club	Paso Robles Road east to Gun Club Road. North on Gun Club Road onto unpaved segment to where road dead ends at Pond Road. Turn east on Pond Road. Second pole on north side of Pond Rd.	Saturation	35_43' 02.57" N	119_30' 24.23" W	67	
14K	Core KWR	NW corner of Garces Hwy. and Rowlee.	Saturation	35_45' 40.72" N	119_28' 44.59" W	66	
15K	Kern National Wildlife Refuge	Third pole north of entrance to KNWR on west side of Corcoran Avenue. Approximately 200 yards east of old Westside Operators site.	Saturation	35_46' 00.41" N	119_34' 46.95" W	65	X
16K	Garces	3.3 miles east of Rowlee on Garces Hwy. and west of Scofield Rd. On south side of road across the street from a sign at dirt road leading to Chevron McKesson Gas Facility.	Saturation	35_45' 38.90" N	119_25' 08.93" W	71	
17K	Rowlee	Take Rowlee north from Garces to where it deadends, go west 100 m to power pole at north edge of Rowlee at beginning of ditch.	Saturation	35_47' 26.07" N	119_28' 25.12" W	66	

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Fresno Saturation Network							
18F	Cornelia	Southwest corner of W. Jensen and S. Cornelia. Traveling south on Cornelia, turn west at the first gravel road on the west towards PG&E substation gate. Power pole is located in the open field and about 50 ft. to the east of the PG&E substation gate.	Saturation	36_42' 22.01" N	119_52' 52.21" W	60	
19F	Nielson	North of the corner of N. Marks and W. Nielson, on Marks, second power pole north of railroad tracks.	Saturation	36_44' 52.65" N	119_50' 39.32" W	72	
20F	Swift	Power pole located in front of 3395 Swift. 2nd pole on north side of intersection of intersection of Swift and Bond.	Saturation	36_47' 46.43" N	119_46' 03.33" W	91	
21F	Einstein Park	Einstein Park on Dakota Ave. Site is 1/2 mile east of First Street on south side of Dakota Avenue and west side of Einstein Park. Enter to the south just east of Church into parking lot for park. Site is at southern end of parking lot.	Saturation	36_47' 08.52" N	119_46' 03.68" W	91	
22F	Hyde	Northeast corner of W. Florence and S. Fruit. At southwest end of Hyde Park. Power pole is on the SE corner of the intersection.	Saturation	36_43' 01.56" N	119_49' 03.59" W	69	
23F	Fresno Air Terminal	East corner of Anderson Ave. and N. Air Fresno Dr. West of airport runway. On city light pole at the parking lot on Anderson, near sign for "Western Pipeline Sales".	Saturation	36_46' 32.84" N	119_43' 40.65" W	91	
24F	Meridien	Power pole on the right side of the driveway for 3630 Meridien Avenue.	Saturation	36_47' 00.96" N	119_44' 45.77" W	91	X

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Fresno Saturation Network (Cont.)							
25F	Library	2nd pole north of intersection of Keats and Barton on Barton. Light pole 3S94M in front of Henry Madon Library at Cal State Fresno.	Saturation	36_48' 39.75" N	119_44' 57.16" W	91	
26F	Coventry	Pole in front of 1433 Coventry Avenue. Near corner of Coventry and Dennis. Major intersection is Shaw and Locan. New housing development.	Saturation	36_48' 49.80" N	119_39' 33.40" W	103	
27F	Hwy. 41	N. side of Shields, at the intersection of Shields and Hwy. 41 overpass. Heading west on Shields from First St. the site is on city light pole on barrier island west of 41 overpass at the northbound entrance for Hwy. 41.	Saturation	36_46' 47.02" N	119_47' 05.15" W	91	X
28F	Fresno	1st light pole east of the intersection of L Street and Fresno. Across from old jailhouse, about 50' east of bus pullout.	Saturation	36_44' 14.91" N	119_47' 23.87" W	80	X
29F	Browning	Pole in front of 1683 Browning. At southeast corner of Browning Avenue and Channing Way.	Saturation	36_48' 08.32" N	119_49' 25.70" W	91	X
30F	Shields	3rd power pole northwest of the corner of W. Shields and N. Weber on N. Weber. Outside railroad yard fence, southwest of RRX control tower.	Saturation	36_46' 47.26" N	119_50' 33.66" W	87	X
31F	Kings Canyon	Southeast corner of S. Maple and E. Kings Canyon Road. At NW corner of Burger King parking lot. On city light pole.	Saturation	36_44' 08.41" N	119_44' 43.17" W	91	X
32F	Illinois	Power pole located in front of 4856 E. Illinois Ave. At southeast corner of intersection of Illinois and Garden.	Saturation	36_44' 40.73" N	119_44' 02.58" W	91	X

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Fresno Saturation Network (Cont.)							
33F	Barstow	At CSUF Dairy/Farm. Third power pole east from the intersection of Barstow and Woodrow on south side of Barstow.	Saturation	36_48' 56.04" N	119_44' 23.71" W	91	X
34F	Floral	On Floral between Bryan and Hayes (south of Rasin City). Fourth power pole heading east from the intersection of Byran and Floral on the north side of Floral.	Saturation	36_34' 32.46" N	119_54' 12.93" W	60	
35F	Jensen	Traveling south on Marks from Jensen Ave. go about 3/4 mile past 3-4 houses in front of the dairy and on east side of Marks Ave. Turn east on to dirt road into dairy. Pole is at the northwest side of gate in the dairy farm.	Saturation	36_42' 04.79" N	119_50' 30.50" W	66	X
36F	Grantland	0.2 miles south of Manning on Grantland Ave. Site is at 1st power pole on dirt road inside the vineyard to the east (left) of Grantland. On corner of dirt road and Grantland Avenue is an irrigation pump.	Saturation	36_36' 03.27" N	119_54' 57.50" W	60	
37F	Deleted	---	---	—	—	---	
38F	Shaw	5th light pole east of Clovis Avenue on Shaw Avenue and NW of the Red Robin restaurant in the Target/Mervyns Shopping Center.. In front of handicapped parking spot in the Red Robin parking area.	Saturation	36_48' 29.84" N	119_41' 53.31" W	103	X
39F	Palm	6th light pole northwest of intersection of North Street and Palm. Next to fire hydrant.	Saturation	36_44' 51.65" N	119_48' 33.77" W	80	X
40F	Malaga	Hwy. 99 south to North Street. Head east on Willow. First pole north on Willow on west side of street.	Saturation	36_41' 36.50" N	119_43' 38.15" W	83	X

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Fresno Saturation Network (Cont.)							
41F	Weldon	Power pole in front of 3410 Weldon Drive. At northwest corner of Norris Drive and Weldon Avenue.	Saturation	36_46' 08.23" N	119_46' 04.21" W	91	X
42F	Jensen	4th power pole south of Jensen on first unpaved road east of Marks Ave. The site is close to the NE corner of the Dairy where site 35 is located.	Saturation	36_42' 18.97" N	119_50' 06.82" W	71	
43F	Barton	2nd power pole on the west side of Barton, north of the intersection of Barton and Dayton. The site is just east of the school yard (Duncan Polytech High School) on Barton Ave.	Saturation	36_47' 03.54" N	119_44' 59.01" W	91	
Meteorological Measurement Network							
ELN	El Nido	West on Sandy Mush Road behind El Nido Jail.	Surface/upper air	37_11' 24.01" N	120_31' 48.18" W	41	
MKR	Mouth of the Kings River	Belmont east to Trimmer Springs Road. The site is at the southeast corner of the Friant-Kern canal and Trimmer Springs Rd.	Surface/upper air	36_46' 02.60" N	119_27' 14.91" W	145	
COR	Corcoran	East of the Orange Avenue and Avenue 71/2 intersection.	Surface/upper air	36_06' 32.40" N	119_35' 48.78" W	59	
MTL	Mettler	Private airport west of Hwy. 99, north of Valpredo Road.	Surface/upper air	35_04' 47.93" N	118_59' 24.00" W	139	
CRT	Caruthers	Behind school district office at 1 Tiller Road.	Surface	36_32' 16.83" N	119_49' 53.52" W	60	

Table 3-1 (continued)

Location of Fall and Winter Monitoring Sites

Site Code	Site Name	Location	Site Type	Latitude	Longitude	Elevation (m MSL)	Chemistry
Meteorological Measurement Network (Cont.)							
TS5	TSS5A Special Study Site	10 miles north and 2 miles east of Corcorann	Surface	36_14' 07.93" N	119_31' 33.63" W	61	
NMD	North of Madera	North of Madera at the southeast corner of Road 26 and Avenue 23.	Sonic anemometer	37_04' 57.77" N	120_04' 10.50" W	91	
PAN	Panoche Water District	3 miles northeast of Hwy. I-5 on the Merced/Fresno County line.	Sonic anemometer	36_53' 24.74" N	120_43' 57.58" W	56	
PVA	Porterville Airport	Porterville Airport	Sonic anemometer	36_01' 40.16" N	119_04' 13.00" W	132	
PWR	Pixley Wildlife Refuge	1.5 miles north of Road 56 and east of Road 88.	Sonic anemometer	35_55' 20.07" N	119_22' 35.64" W	72	
LHA	Lost Hills Airport	SW of Lost Hills Airport at refueling station	Sonic anemometer	35_37' 21.44" N	119_41' 04.64" W	88	

The Winter study domain covered about 78, 400 km² (280 km north to south and 280 km east to west), extending from about 100 km north of Fresno to 60 km south of Bakersfield and from about 900 m agl in the Sierra Nevada to about 600 m agl at the crest of the Coastal Range. Table 3-1 shows the site codes, names, locations, coordinates, and elevations. Detailed site descriptions are in Solomon et al. (1997). The land use in this domain is mixed, consisting of agriculture, oil production, major urban areas (Fresno and Bakersfield), and a number of smaller, fairly isolated cities. The northern two thirds of the domain is dominated by agriculture, and the southern third of the domain is dominated by oil production. The sampling sites consisted of core sites, boundary and flux plane sites, saturation monitoring sites, and surface and upper air meteorological measurement sites (Figures 3-2 to 3-6).

3.1.2.1 Core Site Measurements

Three core sites were established during the Winter study—in Fresno (FEI), Bakersfield (BFK), and about 9 km east of the Kern Wildlife Refuge (KWR). Figure 3-2 shows these sites, and Table 3-1 shows their coordinates and elevations. At these core sites, PM_{10} and $PM_{2.5}$ mass and chemical composition, HNO_3, and NH_3 data were collected on a 3-hour sampling frequency via sequential filter samplers (SFSs) and sequential gas samplers (SGSs), the latter using denuder difference technology for HNO_3, and NH_3 (Chow and Egami 1997). Measurements of fog and fog composition in several size ranges were obtained at the three core sites on an event basis. Hourly averaged concentrations of O_3 and other criteria pollutants were measured continuously throughout the study period at the KWR core site or at the ARB sites adjacent to the BFK and FEI core sites. Continuous PM_{10} and/or $PM_{2.5}$ mass samples were obtained at the core sites as well. Speciated organic aerosol precursors (C_2–C_{20} volatile organic compounds and up to C_2-C_7 carbonyl compounds) and organic species reaction products (speciated organic aerosols) were collected twice a day at BFK and three times a day at FEI. The third sample at FEI was a 24-hour average sample, whereas the other two samples at both sites were 3-hour integrated samples during the morning and evening rush hours (0600–0900 PST and 1500–1800 PST). Visibility-related parameters were measured at each core site, whereas highly resolved size-segregated aerosol samples were collected only at BFK. Continuous PM_{10} and/or $PM_{2.5}$ mass samples were obtained at the core sites as well.

For comparison purposes, several special samplers also were operated at BFK. These include the College of Engineering Center for Environmental Research and Technology (CE-CERT) denuder

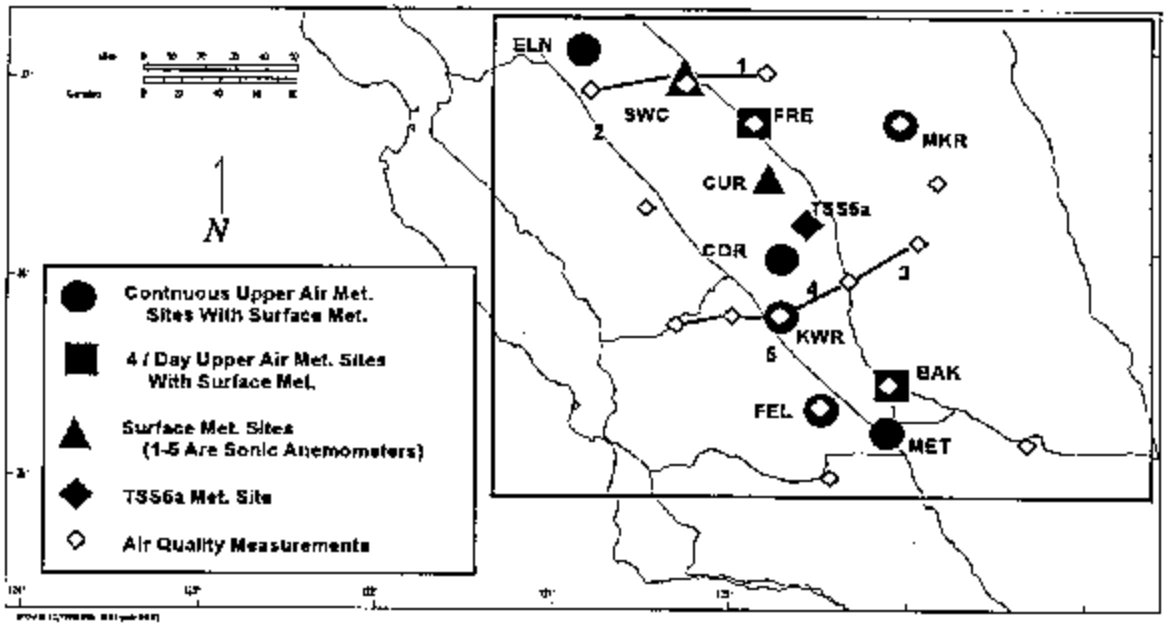


Figure 3-2. IMS95 Winter Meteorological Measurement Site Locations by Site Type.

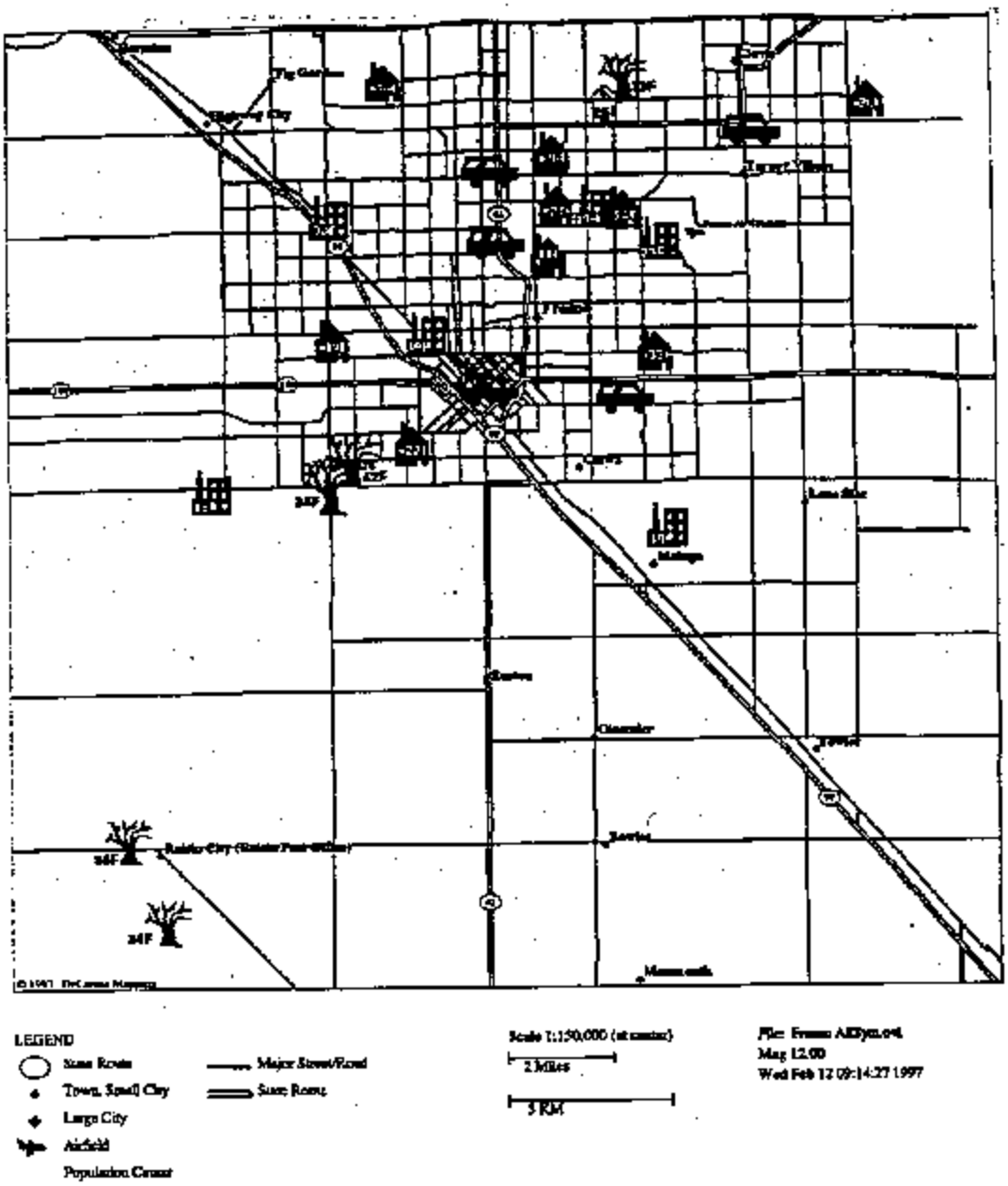


Figure 3-3. Saturation sampling sites, by type, in the Fresno area for the Winter study. Major source influences anticipated are given by the symbol on the map: house – residential; car – automotive; factory – industrial; tree – agricultural.

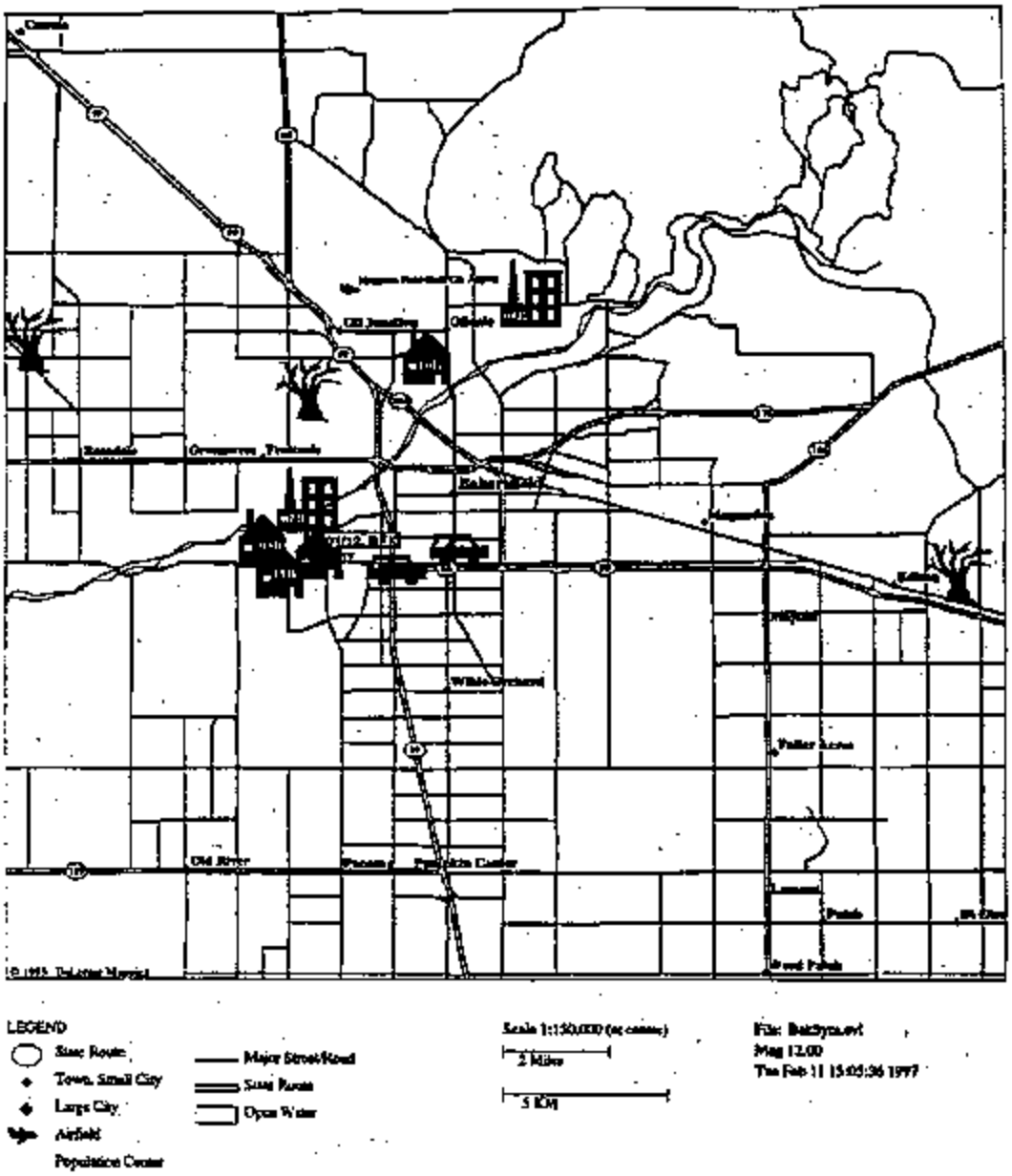


Figure 3-4. Saturation sampling sites, by type, in the Bakersfield area for the Winter study. Major source influences anticipated are given by the symbol on the map: house – residential; car – automotive; factory – industrial; tree – agricultural.

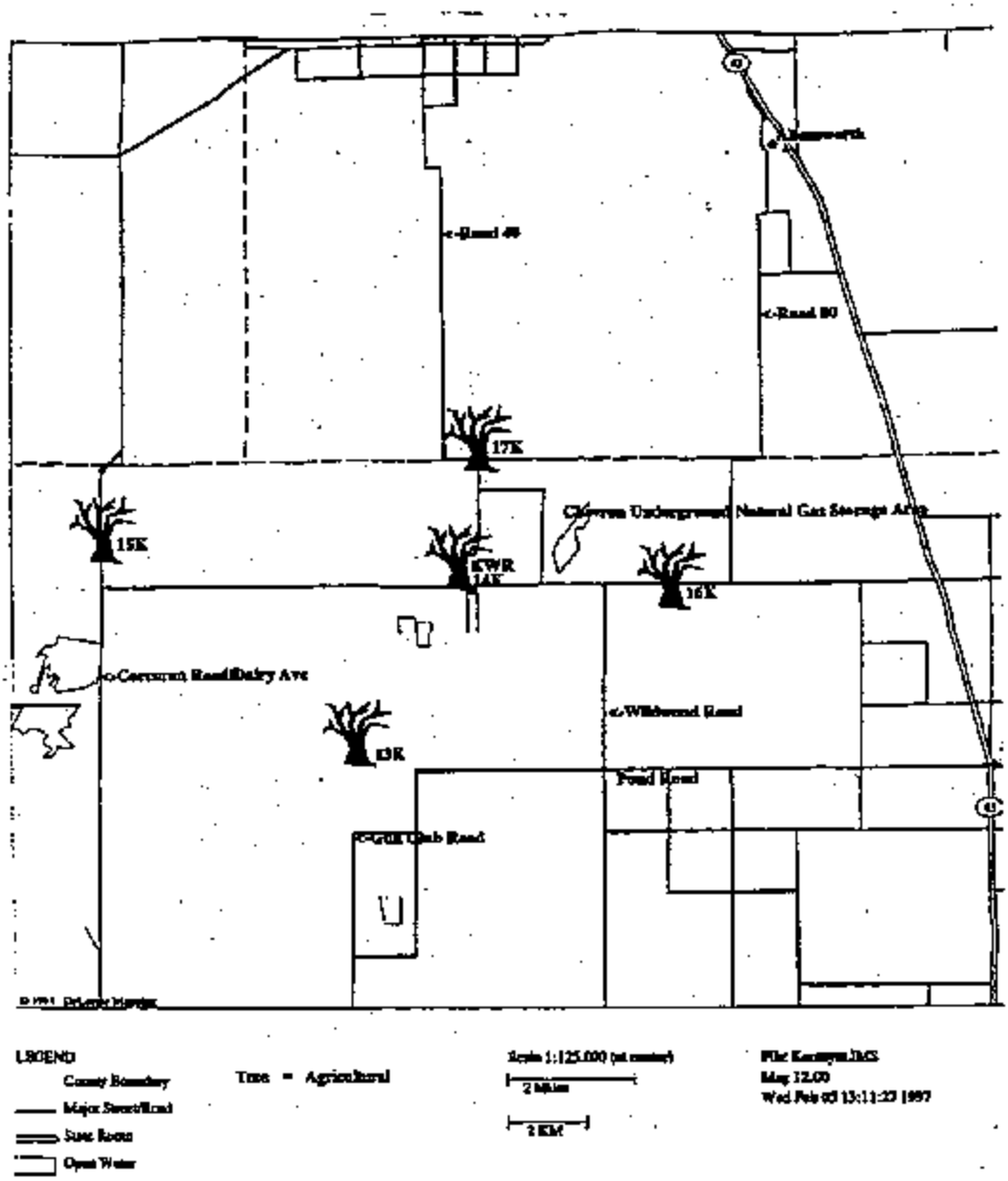


Figure 3-5. Saturation sampling sites, by type, in the Kern Wildlife Refuge area for the Winter study. Agriculture or in this case native vegetation (trees) is the major source of influence.

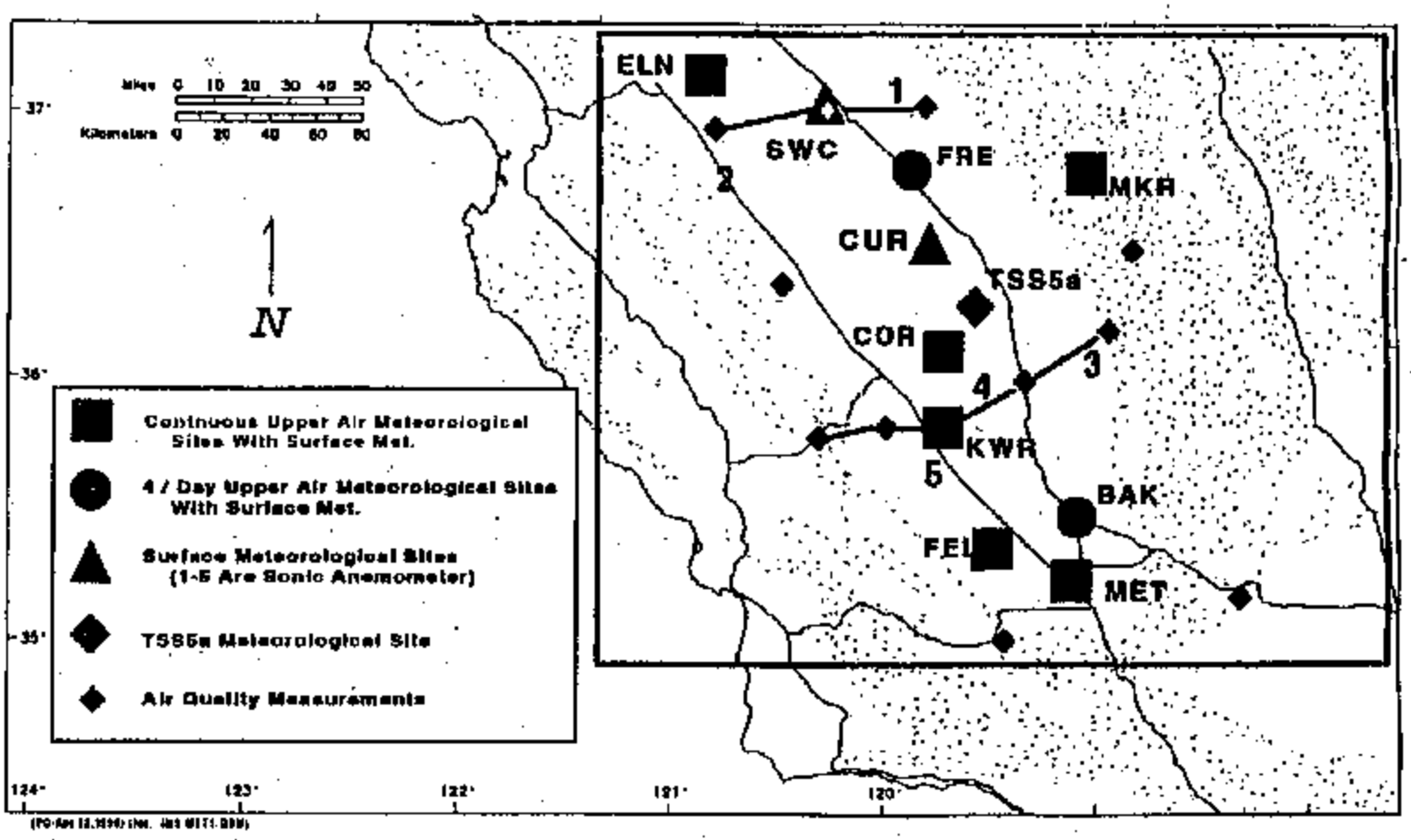


Figure 3-6. Meteorological measurement sites for the Winter study.

supplied by EPA for QA purposes, all of which were collocated on the platforms at BFK. Continuous ammonia sampling via a recently available commercial method was also performed at BFK. Other special measurements for fog and aerosols were performed at FEI and KWR.

Data from these core sites provide information about the temporal nature of PM_{10} episodes as well as the impact of fog formation and dissipation on elevated PM_{10} concentrations in the study domain under winter conditions.

3.1.2.2 Boundary and Flux Plane Air Quality Measurements

Four types of boundary/flux plane sites were established (Table 3-1) on the basis of the types of measurements performed at the site. Many of these sites served multiple purposes, as shown in Figure 3-2, which also shows their general location. Three-hour samples were collected at SWC, which is the Boundary A site in the center of the northern flux plane. Measurements at SWC were similar to those at the core sites but excluded the fog and organic species measurements. SWC provided information on the temporal variability of PM and related species that pass across the northern boundary/flux of the study domain.

Twenty-four-hour average PM_{10} samples were collected at 11 boundary/flux plane sites (Figure 3-2) via battery-powered portable samplers, to assess the concentrations of PM and precursor gases at the boundaries of the region and between the core air quality sites. Samples were collected at all sites for PM_{10} mass and NH_3 (Boundary B and C sites, Table 3-1), and additional samples were collected at six of those sites to determine PM_{10} chemical composition, HNO_3, and $PM_{2.5}$ mass (Boundary B sites, Table 3-1). Two additional sites once operated by WSO, Fellows (FEL) and Kernridge (KRN), were reactivated for this study (Boundary D sites, Table 3-1). PM_{10} mass and sulfate were measured at those sites, along with criteria pollutant gases and meteorological variables. Results from the boundary/flux plane network provide insight into the nature of pollution buildup in the valley, transport across the northern boundary of the study domain and in and out of the valley through mountain passes, and the effect of slope flows associated with the Sierra Nevada and the Coastal Range.

3.1.2.3 Saturation Sampling Sites

Forty-two saturation monitoring sites using battery-powered portable PM_{10} monitors were placed at or around the three core air quality monitoring sites. Twenty-five sites were in the Fresno area, 12 were in the Bakersfield area, and 5 were near the KWR site (Figures 3-3 through 3-5). Table 3-1 shows the coordinates and elevations for these sites. Section 3.2.3 describes specifics of the siting approach and the rationale for siting the saturation monitors. Samples were collected at all saturation sites for PM_{10} mass

and NH_3, and additional samples were collected at half the sites (identified in Table 3-1) to determine PM_{10} chemical composition and HNO_3. Data from these monitors can be used to assess the representativeness of the core sites, determine whether elevated PM_{10} concentrations are local or regional in nature, and evaluate the influence of sources (such as ammonia, vehicular, oil, or dust) on their surroundings over a 24-hour average period.

3.1.2.4 Upper Air Meteorological Measurements

Surface air quality monitoring throughout the study domain was accompanied by measurements of upper air meteorological parameters at eight sites to characterize air flow in the southern valley. Figure 3-6 shows these sites, and Table 3-1 shows their coordinates and elevations. RWPs with radio acoustic sounding systems (RASSs) were operated at four locations to measure wind speed and direction continuously from near the surface (at a minimum of about 110 m above ground level [agl] to about 4,000 m agl) and to measure temperature (from about 110 m agl to about 1,500 m agl). A Doppler acoustic sounder (DAS) was located at KWR to measure wind speed and direction up to about 600 m, and an acoustic sounder was located at FEL to obtain mixing height data. Rawinsondes were launched four times per day at FEI and BFK to collect data on wind speed and direction, temperature, and RH from the surface to about 5,000 m. These upper air meteorological measurements will provide valuable information on the types of meteorological conditions associated with winter PM episodes. These sites are likely to also provide information about the homogeneity of the fog and an estimate of the height of the top of the fog layer and the mixed layer. Finally, this relatively dense upper air meteorological measurement network provides a rich database for the development of wind fields through diagnostic and perhaps limited prognostic meteorological modeling. Unfortunately, limited resources did not allow valleywide measurements of meteorological variables that are needed for full prognostic meteorological modeling with four-dimensional data assimilation (Thuillier and Seaman 1995).

3.1.2.5 Surface Meteorological Measurements

Surface meteorological measurement sites were added to fill gaps in the existing network of surface meteorological monitors, as shown in Figure 3-6 and Table 3-1. Ten standard surface meteorological sensors measuring wind speed and direction, RH, and temperature were placed at the four RWP sites and at SWC, FEI, KWR, FEL, KRN, and Caruthers (CRT). The thresholds for this study's wind speed sensors were 0.2 to 0.5 m/s, although most routinely placed standard sensors typically have cutoff thresholds of about 0.5 to 1 m/s; differences are often due to the level of maintenance. Because winter wind speeds in the valley are often below the threshold of standard sensors, five meteorological

measurement sites were located throughout the study domain that use very-low-threshold wind speed sensors (sonic anemometers) with wind speed thresholds of 0.05 m/s. These sensors measure wind speed and direction at low windspeeds and will help improve the understanding of flow dynamics in the valley and define the need to use low-threshold and more expensive sensors in future studies.

3.1.2.6 Monitor Evaluation Study

Several kinds of monitors were evaluated at BFK during the Winter study (Table 3-2), because of the foggy cool conditions that occur in the SJV during the winter. The CE-CERT denuder sampler, a newly developed acid deposition monitor, was included by the ARB Research Division to compare it with the CADMP sampler, which has been used in California for several years. The TEOM and beta attenuation monitor (BAM) were included to evaluate the two widely used continuous aerosol mass monitors under the high-RH conditions that occur in the SJV during the winter. In addition, TEOMs were operated at lower temperatures (30° C) and at lower flow rates (1 l/min) than their normal operating conditions, to minimize the loss of semivolatile components (nitrate and organic species). Normal operating conditions for the TEOMs are 50° C and 3 l/min. The two continuous analyzers were included to evaluate recently developed monitors that can provide continuous species-specific concentration data. The VAPS was included because it has been used in a number of past studies and will be used for QA of some of the aerosol measurements, specifically to check the PM mass and x-ray fluorescence (XRF) data collected by the PM_{10} SFS.

This was considered important because a new configuration was used for the SFS and gas samplers. The results from the high-volume dichotomous virtual impactor (HVDVI) (Solomon et al. 198a) allow first-time measurements of ambient concentrations of organic aerosol species in the SJV. These measurements are particularly useful for identifying sources of primary and secondary OC from combustion sources. This method is costly on a large-scale basis, so its evaluation here on a smaller scale provides information about its future feasibility.

3.1.2.7 External QA Program

A comprehensive external quality assurance program (EQAP) was an integral part of the Fall and Winter studies. All systems and most performance audits for field measurements occurred before the start of the measurement campaign, to minimize potential loss of data. Two groups, a private contractor and the

Table 3-2

Monitors Evaluated during Winter Study at Bakersfield Core Site

Monitor	Contractor	Sponsor	Operator	Comments
CE-CERT acid deposition sampler	Fitz	ARB-RD	ARB	Potentially new ARB acid deposition sampler
CADMP acid deposition sampler	DRI	ARB-RD	ARB	Current ARB acid deposition sampler
PM_{10} and $PM_{2.5}$ TEOM (modified)[a]	DRI/R&P and ARB	R&P	DRI/STI	Operating T = 30° C, flow rate = 1 / min-1b
PM_{10} and $PM_{2.5}$ BAM	DRI/Graseby-Andersen	Graseby-Andersen	DRI/STI	Located at SWC
Continuous $NH_3/NO/NO_x$ analyzers	Thermo Environmental	CRPAQS	ARB	Calibrated by ARB, located at BFK only
Continuous carbon black analyzers	Magee Scientific	CRPAQS	CSU	EC in aerosols and in fog droplets, at BFK
VAPS samplers	EPA/ Stevens	US EPA	ARB	XRF analysis of PM_{10}, at BFK only
HVDVI[c] for organic aerosol speciation[d]	Cass	CRPAQS	DRI/STI	Operated at 350 l/min, fine cutpoint at ~3.5 um
Various $PM_{2.5}$ samplers on roof of ARB California Street air quality site	Various	ARB-MLD	ARB	Continuation of Bakersfield 94/95 intercomparison

[a] PM_{10} TEOMs are also located at FEI and KWR.
[b] Normal operating conditions are 50° C with a flow rate of 3 l/min.
[c] High volume dichotomous virtual impactor (Solomon et al. 1989).
[d] One sampler each at BFK, FEI, and KWR.

Monitoring and Laboratory Division (MLD) of the ARB performed the systems and performance audits. Section 4 describes the details of this effort, and a summary of results is in Bush et al. (1996) and Miguel (1996). A DAS, rawinsondes, and tethered balloon were used to audit the upper air meteorological measurement systems. Audits of the air quality monitors and surface meteorological equipment were performed according to ARB and EPA protocols. Laboratory audits were performed during 1996 at the same time as the chemical analysis of the IMS95 samples. Audits of the laboratory, where aerosol samples were analyzed, were performed as part of another project, and the results are in Chow and Egami (1997). In addition, MLD coordinated and performed laboratory audits with the groups who were performing gas phase organic analysis and fog sample analysis. The final database archive includes information about the precision and accuracy of the measurements on the basis of the EQAP and the contractors' QC measurements.

3.1.2.8 Daily Emissions Activity Measurements

In a unique effort, real-time area source emissions activity data were collected concurrently with regional air quality monitoring during the Fall and Winter studies. This was a unique undertaking because, to date, few or no real-time area source emissions activity data have been collected concurrently with regional air quality sampling. Many emissions activities cannot be reconstructed after sampling programs are over, especially activities that are intermittent and infrequent. Therefore, the purpose of the measurements was to collect emissions activity data that support the ambient measurements, which in turn provides a rare opportunity for an improved understanding of ambient data interpretation and for improved evaluation of models.

These activity data describe transient land uses, traffic flows, and unusual emissions events that occurred during the sampling program. Emissions activity measurements consisted of performing daily visual surveys around each of the PM monitoring sites via videotaping and site logs, collecting traffic count data and collecting road dust samples. Full-time field observers documented visible releases of PM near saturation and core monitoring sites. At boundary and flux plane sites, site operators documented changes in the surroundings that may have resulted in PM emissions; however, daily video was not obtained at those sites. At multiple points in surrounding areas, traffic counts were monitored, and road dust samples were collected and analyzed for silt content. The EPA PM emissions database relates PM_{10} emissions from roads to silt loadings, hence the need to measure silt content.

Examples of emissions activities include farming operations, earthmoving activities, and traffic. To the extent possible, the occurrences and locations of emissions activities within 1.6 km of the monitoring

sites were documented daily. A database of the daily emissions activities and summaries of the traffic count data was created via Microsoft Access to allow simple queries of the data via a point-and-click program developed in Visual Basic (Coe and Chinkin 1996). This database, including the query capabilities, is part of the IMS95 data archive. Section 3.3.5 describes further details of the daily emissions activity measurements.

3.1.2.9 TSS 5A Measurements

TSS 5A was a 4-week study of the mixing and dispersion of microscale processes under low wind speed stable conditions, conducted from December 18, 1995 to January 17, 1996 in a large farm field about 16 km northeast of Corcoran. The study consisted of characterizing low wind speed meteorological conditions in an area of about 0.5 km^2 and to a depth of a few hundred meters. Details of the study are in Section 3.2.5 and Gray et al. (1996).

3.1.2.10 TSS 11 Measurements

TSS 11 was an 11-day vertical fog study conducted after the Winter study to obtain a better understanding of the vertical dynamics, physics, and chemistry of fogs. The following data were collected: (1) gaseous criteria pollutants (O_3, NO_y, and SO_2) and hydrogen peroxides were measured continuously at the base and top of a 430-m TV tower; (2) bulk fog samples for chemical composition were collected at the surface and at two heights on the tower—the heights varied according to the location of the fog; (3) meteorological variables were measured at several locations on a nearby tower augmented with rawinsonde launches on a forecast basis (however, radio frequency interference invalidated the rawinsonde data); and (4) size-fractionated aerosol samples for chemical composition and supporting gas phase aerosol precursor species concentrations (SO_2, HNO_3, and NH_3) were obtained at the tower's base. A videotape recording at the top of the tower documented the presence of and the top of the fog layer. Chemical measurements at the top of the tower helped to indicate whether the inclusion of oxidants into the top of the fog layer is responsible for much of the oxidation potential within the fog that allows generation of nitric acid during foggy periods. These data will also provide information on the vertical dynamics and spatial variability of water content and chemical components within the fog.

3.1.2.11 Existing or Supplemental Sites

A network of existing or supplemental sites operated by state and local government agencies and by the private sector was used to establish the study's baseline measurements. The activities at these sites included monitoring for criteria pollutants and surface meteorological parameters. Two NWS sites outside the study domain at the Vandenburg and Oakland airports provided synoptic meteorological data

twice daily. Table 3-3 shows site codes, names, and the measurements performed at each site, and Figures 3-7 through 3-16 show the existing sites by site type.

3.2 Site Rationale, Location, and Logistics

The same general siting approach and rationale were used for the Fall and Winter studies. However, as described below, not all site types were established for the Fall study, and the Winter study sites had multiple purposes.

3.2.1 Core Sites

Core sites in urban locations were chosen at or near existing ARB or District compliance monitoring networks. In rural areas, the core sites were located to minimize anthropogenic source impacts. Table 3-4 shows the purpose or siting rationale for each site, along with the sources in the general area that might influence PM concentrations at each site.

The Fall study core site (COP in Figure 3-1) was located at the District site in downtown Corcoran, which is the compliance monitoring site that has typically had the highest 24-hour average and the highest annual average PM_{10} concentrations of all sites in the valley. COP was chosen as the core site to evaluate its representativeness for estimating population exposure in the Corcoran/Hanford region. COP is in a mixed residential and commercial area of Corcoran about 1 km west of the city's industrial section. The residential/residential-commercial area of the city is only about 2.5 km by 2.5 km, with a population of less than 14,000 (U.S. Census 1994).

Figure 3-2 shows the Winter study core sites—BFK, FEI, and KWR. Bakersfield and Fresno are the two largest urban areas in the valley and have historically recorded some of the highest winter PM_{10} concentrations. The KWR site was chosen to represent regional concentrations (Chow et al. 1993a).

BFK and FEI were in mixed-land-use neighborhoods consisting of residential and commercial buildings. The population of Bakersfield is about 191,000, and the population of Fresno is about 387,000 (U.S. Census 1994). BFK was located at an elementary school next to the ARB California Street monitoring site. FEI was in a park less than 1 km northeast of the ARB First Street monitoring site. Although the two sites are both in urban areas, their potential regional source mix is expected to be somewhat different. The area surrounding Fresno is predominantly agricultural, whereas the area surrounding Bakersfield is predominantly used for oil production. Thus, the influence from the surrounding areas at the two sites may be quite different.

Table 3-3
Supplemental Measurements in Place during Fall and Winter Studies

SITE	SITE NAME	NET CODE	PURPOSE	SITE TYPE	LATITUDE	LONGITUDE	UTME	UTMN	EV_MSL (m)	O3	NX	CO	S2	BC	C4	WD	SP	TP	RH	SR	PR	WG	CH	VS	MA	SI	NI	CL	N4	TC	DI
AAR	ARROYO GRANDE-RALCOA	ARB	Routine Ambient Monitoring for AQ	SRF/AQ	35_02'58.64" N	120_34'41.00" W	720.7710	3880.3910	300				X																		
ARV	ARVIN	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_12'29.88" N	118_47'03.40" W	[illegible]	3894.0960	136	X	X					X		X	X	X	X										
ATL	ATASCADERO-LEWIS AVENUE	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_29'36.12" N	120_40'04.30" W	711.5420	3929.8140	262	X	X					X	X	X		X											
BAT	BATTLES BETTERAVIA ROAD	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	34_55'26.04" N	120_24'00.00" W	737.5090	3867.4510	91	X	X			X		X	X	X													
BGS	BAKERSFIELD-1128 GOLDEN STATE	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_23'03.60" N	119_00'32.92" W	363.0540	3921.9610	158	X	X	X		X		X		X	X	X	X				X						
BKA	BAKERSFIELD-5558 CALIFORNIA AV	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_21'22.32" N	119_02'25.08" W	359.4630	3919.3396	117	X	X	X	X		X	X		X	X	X					X	X	X	X	X	X	X
CLK	CHINA LAKE	ARB	Routine Ambient Monitoring for PM	SRF/AQ	35_41'13.10" N	117_38'06.00" W	436.6790	3951.3730	695																X	X	X	X	X	X	
CLO	CLOVIS-908 N VILLA AVENUE	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_49'30.40" N	119_42'50.40" W	793.6970	4080.2936	130	X	X	X		X		X		X	X	X	X				X	X	X	X	X		
COV	CORCORAN-VAN DORSTEN AVE	ARB	Routine Ambient Monitoring for PM	SRF/AQ	36_05'11.04" N	119_33'46.80" W	809.4950	3998.2020	62																X	X	X	X	X		X
EDI	EDISON	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_21'44.96" N	118_51'03.60" W	377.1110	3919.1580	126	X	X					X		X													
FNP	FRESNO-NORTH PERIMETER ROAD	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	37_08'16.80" N	119_30'00.12" W	873.6470	4116.5430	1735	X						X		X	X												
FSD	FRESNO-1406 E DRUMMOND	ARB	Routine Ambient Monitoring for AQ & PM	SRF/AQ	36_41'44.88" N	119_44'31.20" W	793.0170	4065.8790	187	X	X	X													X						
FSF	FRESNO-3425 FIRST STREET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_46'53.04" N	119_46'19.20" W	788.0850	4075.1620	96	X	X	X	X		X	X		X					X		X	X	X	X	X	X	X
FSS	FRESNO-SIERRA SKYPARK #2	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	36_50'26.12" N	119_52'26.40" W	778.7610	4081.6710	98	X	X	X				X															
GRL	GROVER CITY-LESAGE DRIVE	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_07'34.06" N	120_37'38.80" W	710.2815	3891.1580	4	X	X		X			X	X	X													
HAN	HANFORD-S IRWIN STREET	ARB	Routine Ambient Monitoring for PM & Met	SRF/AQ	36_18'58.56" N	119_38'34.80" W	800.6620	4025.4050	73	X	X														X	X	X	X	X		
IYA	INYOKERN AIRPORT	ARB	Routine Ambient Monitoring for PM	SRF/AQ	35_39'25.80" N	117_49'56.40" W	[illegible]	3930.1050	755																X						
KCC	KETTLEMEN CITY-CAL TRANS	ARB	Routine Ambient Monitoring for PM	SRF/AQ	36_00'24.84" N	119_57'33.40" W	774.1010	3988.7520	73																X	X	X	X	X		
MBP	MORRO BAY	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_22'24.00" N	120_50'36.00" W	694.6180	3919.3370	16	X			X			X															
MCS	MARICOPA SCHL-STANISLAUS	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_03'15.12" N	119_24'14.40" W	326.0060	3881.7725	283	X						X		X													
MER	MERCED	ARB	Routine Ambient Monitoring for PM	SRF/AQ	37_18'39.84" N	120_28'51.60" W	725.1440	4129.0670	41																X	X	X	X	X		
MED	MADERA-HEALTH DEPT	ARB	Routine Ambient Monitoring for AQ	SRF/AQ	36_57'19.08" N	120_02'07.10" W	766.1470	4093.9120	83	X																					
MLB	MADERA-LIBRARY	ARB	Routine Ambient Monitoring for PM	SRF/AQ	36_57'39.96" N	120_03'39.60" W	761.6310	4094.3910	93																X	X	X	X	X		X
MOP	MOJAVE-923 POOLE STREET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_03'46.73" N	118_09'06.60" W	941.5160	3881.1590	855	X	X					X		X							X	X	X	X	X		
MRA	MERCED-385 S COFFEE AVE	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	37_16'37.09" N	120_25'38.86" W	721.3000	4129.6970	53	X	X					X		X													
NOR	NIPOMO-1300 GUADALUPE RD	ARB	Routine Ambient Monitoring for AQ	SRF/AQ	35_01'14.88" N	120_33'41.26" W	722.4430	3877.8690	60	X			X																		
NIP	NIPOMO	ARB	Routine Ambient Monitoring for AQ	SRF/AQ/MET	35_02'30.12" N	120_30'00.00" W	728.0430	3880.1170	104	X	X		X				X														
OLD	OILDALE-3311 MANOR	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_26'20.04" N	119_00'57.60" W	363.6990	3924.1170	180	X	X		X		X	X		X					X	X	X	X	X	X	X	X	
PLR	PARLIER	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_36'00.00" N	119_30'28.80" W	813.3490	4055.9100	166	X	X					X		X	X	X	X										
PRF	PASO ROBLES-235 SANTA FE	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	35_37'34.12" N	120_41'24.00" W	708.1920	3943.3500	244	X						X		X					X								
SHA	SHAFTER	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	35_30'00.00" N	119_16'04.80" W	338.3550	3934.7030	125	X	X					X		X						X							
SLM	SAN LUIS OBISPO-MARSH	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	35_17'02.04" N	120_39'14.40" W	713.1690	3906.8530	66	X	X	X				X		X					X								
SMY	SANTA MARIA-BROADWAY	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	34_56'58.16" N	120_26'02.40" W	734.1120	3870.0930	74	X	X		X			X		X					X								
TAC	TAFT COLLEGE	ARB	Routine Ambient Monitoring for PM	SRF/AQ	35_08'33.00" N	119_27'36.00" W	321.3470	3889.3480	291																X	X	X	X	X		X
TSM	TURLOCK-900 S MINARET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	37_29'28.96" N	120_50'06.00" W	691.4100	4151.0720	38	X	X	X				X									X						
VCS	VISALIA-CHURCH STREET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_19'55.01" N	119_17'34.00" W	833.0430	4026.9870	93	X	X	X			X	X		X					X		X	X	X	X	X		X
ASV	ARVIN-EDISON	CIM	2 m tower/met variables in agricul. area	SRF/MET	35_12'32.40" N	118_44'40.00" W	344.4430	3905.8770	131							X	X	X	X	X											
BLC	BLACKWELLS CORNER	CIM	2 m tower/met variables in agricul. area	SRF/MET	35_38'39.60" N	119_51'30.60" W	773.3940	3949.3610	215							X	X	X	X	X											
CUY	CUYAMA	CIM	2 m tower/met variables in agricul. area	SRF/MET	34_55'34.00" N	119_36'17.00" W	410.1520	3870.1130	696							X	X	X	X	X											
CCO	ARROYO SECO	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_21'12.00" N	121_17'15.00" W	653.4020	4024.9110	72							X	X	X	X	X											
FIV	FIVEPOINTS/WSFS USDA	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_20'11.00" N	120_06'47.00" W	759.1230	4024.9190	87							X	X	X	X	X											
FNS	FRESNO STATE	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_49'13.00" N	119_44'33.00" W	790.6190	4078.2560	103							X	X	X	X	X											
FRB	FIREBAUGH/TELLES	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_51'04.00" N	120_35'23.00" W	714.8480	4080.2640	56							X	X	X	X	X											
GLP	GUADALUPE	CIM	2 m tower/met variables in agricul. area	SRF/MET	34_57'42.00" N	120_32'48.00" W	724.0040	3871.3440	14							X	X	X	X	X											
KCO	KING CITY-OASIS RD.	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_07'17.00" N	121_05'03.00" W	672.4410	3998.9120	165							X	X	X	X	X											
KES	KESTERSON	CIM	2 m tower/met variables in agricul. area	SRF/MET	37_13'57.00" N	120_52'48.00" W	666.0100	4121.3630	33							X	X	X	X	X											
KET	KETTLEMAN	CIM	2 m tower/met variables in agricul. area	SRF/MET	35_52'08.00" N	119_53'55.00" W	780.4340	3971.6620	104							X	X	X	X	X											
LCV	LINDCOVE	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_21'26.00" N	119_03'31.00" W	315.3110	4024.5800	146							X	X	X	X	X											

09-73-99.2

Table 3-3 (continued)
Supplemental Measurements in Place during Fall and Winter Studies

SITE	SITE NAME	NET CODE	PURPOSE	SITE TYPE	LATITUDE	LONGITUDE	UTME	UTMN	ELV_MSL (m)	O3	NOx	CO	SO2	HC	CH4	WD	SP	TP	RH	SR	PR	WE	CH	VS	MA	SA	DS	CL	NH	TC	OM
LOS	LOS BANOS	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	37_03'33.00" N	120_45'35.00" W	699.1100	4127.2860	29							X	X	X	X	X											
PXL	PARLIER	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	36_37'33.00" N	119_30'11.00" W	812.8430	4095.7430	103							X	X	X	X	X											
PSV	PANOCHE	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	36_33'35.00" N	120_43'55.00" W	702.5520	4064.0000	36							X	X	X	X	X											
SHC	SHAFTER/USDA	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	35_33'39.00" N	119_16'52.00" W	837.2250	3938.2300	110							X	X	X	X	X											
SLB	SAN LUIS OBISPO	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	35_18'22.00" N	120_39'55.00" W	282.7100	3909.5030	108							X	X	X	X	X											
STT	STRATFORD	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	36_09'27.00" N	119_31'00.00" W	783.3870	4003.8460	59							X	X	X	X	X											
STM	SANTA MARIA	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	34_57'16.00" N	120_28'03.00" W	738.6660	3830.9190	62							X	X	X	X	X											
VLA	VISALIA/CI AMERICAS	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	36_18'03.00" N	119_33'33.00" W	839.1928	4023.7790	89							X	X	X	X	X											
WLC	WESTLANDS	CIM	2 m lowerlmet variables in agricul. area	SRF/MET	36_55'00.00" N	120_32'55.00" W	734.0518	4037.1580	58							X	X	X	X	X											
FEL	FELLOWS	ESC	10 m lowerlmet variables at Westside Operation	SRF/AQ/MET	35_11'00.00" N	119_32'47.00" W	814.8460	3879.1970	370	X	X		X			X															
KRG	KERN RIDGE	ESC	10 m lowerlmet variables at Westside Operation	SRF/AQ/MET	35_27'03.00" N	119_42'33.00" W	798.9490	3927.8900	377	X	X		X			X															
BKF	BAKERSFIELD-MEADOWS FIELD	NWS	10 m lowerlmet variables at airport	SRF/MET	35_23'00.12" N	119_03'00.00" W	838.7800	3906.7200	152							X		X	X			X		X							
FAT	FRESNO AIR TERMINAL	NWS	10 m lowerlmet variables at airport	SRF/MET	36_46'39.87" N	119_43'01.20" W	763.8150	4075.6430	100							X		X	X			X		X							
BKF	BAKERSFIELD	PGE	Temp & RH in Urban Area	SRF/MET	35_19'03.00" N	119_03'22.00" W	838.3070	3913.8950	94									X	X												
BUC	POINT BUCHON	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_15'30.00" N	120_53'42.00" W	691.6900	3903.3400	12							X	X	X													
DCC	DIABLO CANYON	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_11'45.00" N	120_47'00.00" W	709.3900	3896.8400	40							X	X	X													
DLO	DELANO	PGE	10 m lowerlmet variables for monitoring	SRF/MET	35_45'44.00" N	119_28'28.00" W	818.7230	3965.3440	64							X	X	X													
FSF	FRESNO	PGE	Temp & RH in Urban Area	SRF/MET	36_47'00.00" N	119_47'52.00" W	788.9030	4068.3100	88									X	X												
GRC	GROVER CITY	PGE	10 m lowerlmet variables for monitoring	SRF/MET	35_07'28.00" N	120_37'54.00" W	765.8000	3849.2300	6							X	X	X													
GRG	GREGG	PGE	10 m lowerlmet variables for monitoring	SRF/MET	36_53'35.00" N	119_32'38.00" W	774.8150	4082.4690	84							X	X	X													
HER	HERNDON	PGE	10 m lowerlmet variables for monitoring	SRF/MET	36_50'41.00" N	119_32'23.00" W	774.3750	4051.8930	73							X		X													
KTP	KETTLEMAN CITY	PGE	10 m lowerlmet variables for monitoring	SRF/MET	36_04'35.60" N	119_55'13.00" W	762.5500	3995.3540	8							X	X	X	X												
LBP	LOS BANOS	PGE	10 m lowerlmet variables for monitoring	SRF/MET	37_03'11.00" N	121_01'00.00" W	676.1600	4132.4300	94							X	X	X													
MAQ	MORRO BAY A-Q	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_22'39.00" N	120_50'23.00" W	690.1500	3915.6700	43							X	X	X													
MBY	MORRO BAY POWER PLANT	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_22'27.00" N	120_51'13.00" W	690.9300	3916.4700	9							X	X	X													
MCA	MCCALL	PGE	10 m lowerlmet variables for monitoring	SRF/MET	36_36'39.00" N	118_53'12.00" W	908.4270	4056.8210	91							X	X	X													
MID	MIDWAY	PGE	10 m lowerlmet variables for monitoring	SRF/MET	35_28'04.00" N	118_27'09.00" W	922.0450	3923.2900	84							X	X	X													
MRP	MORCOM	PGE	Temp & RH in Urban Area	SRF/MET	37_17'47.00" N	120_21'40.00" W	723.9100	4130.8400	64									X	X												
PAR	PASO ROBLES	PGE	Temp & RH in Urban Area	SRF/MET	35_38'28.00" N	120_41'09.00" W	709.4900	3939.0900	236									X	X												
STK	STOCKDALE	PGE	10 m lowerlmet variables for monitoring	SRF/MET	35_19'03.00" N	119_03'00.00" W	838.5670	3913.2100	94							X	X	X	X												
SLC	LOS OSOS CEMETERY	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_18'28.00" N	120_49'05.00" W	696.9000	3909.0000	37							X	X	X													
SLD	DAVIS PEAK	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_17'37.00" N	120_47'01.00" W	701.1000	3900.3100	349							X	X	X													
SLF	FOOTHILL ROAD	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_16'34.00" N	120_45'34.00" W	708.3200	3905.9000	43							X	X	X													
SLS	SERVICE CENTER	PGE	10 m lowerlmet variab near Power Plant	SRF/MET	35_14'32.00" N	120_40'38.00" W	713.3700	3901.5800	33							X	X	X													
SMA	SANTA MARIA	PGE	Temp & RH in Urban Area	SRF/MET	34_55'04.00" N	120_27'17.00" W	732.3130	3866.7200	67									X	X												
TEM	TEMPLETON	PGE	10 m lowerlmet variables for monitoring	SRF/MET	35_34'29.00" N	120_41'49.00" W	708.6900	3939.0500	226							X	X	X													

Table 3-3 (continued)
Supplemental Measurements in Place during Fall and Winter Studies

* Key:	
Site	3-letter site abbreviation
Site name	Sponsor-designated site name
Net code	Site sponsor
Site type	SRF/AQ — surface air quality measurements
	SRF/AQ/MET — surface air quality and meteorological measurements
	SRF/MET — surface meteorological measurements
Latitude	Latitude in degrees, min, sec
Longitude	Longitude in degrees, min, sec
UTME	Coordinates in UTM Easting
UTMN	Coordinates in UTM Northing
EV_MSL (m)	Elevation in meters (m) above sea level
Purpose	Sponsor's purpose for the site
O3	Ozone (O_3)
NX	Oxides of nitrogen (NO/NO_X and NO_2 by difference)
CO	Carbon monoxide
SO	Sulfur dioxide (SO_2)
H.C.	Continuous hydrocarbon measurements: THC, NMOC
C4	Methane (CH^4)
WD	Wind direction/wind speed
ST	Sigma theta
TP	Temperature
RH	Relative humidity
SR	Solar radiation
PR	Surface barometric pressure
WE	Current weather conditions
CH	Coefficient of haze
VS	Visibility by nephelometer (light scatter)
MA	Aerosol mass (PM_{10})
S4	Sulfate (PM_{10})
N3	Nitrate (PM_{10})
CL	Chloride (PM_{10})
N4	Ammonium (PM_{10})
TC	Total carbon (PM_{10})
DI	Size-fractionated ($PM_{2.5}$) aerosol mass and XRF elements

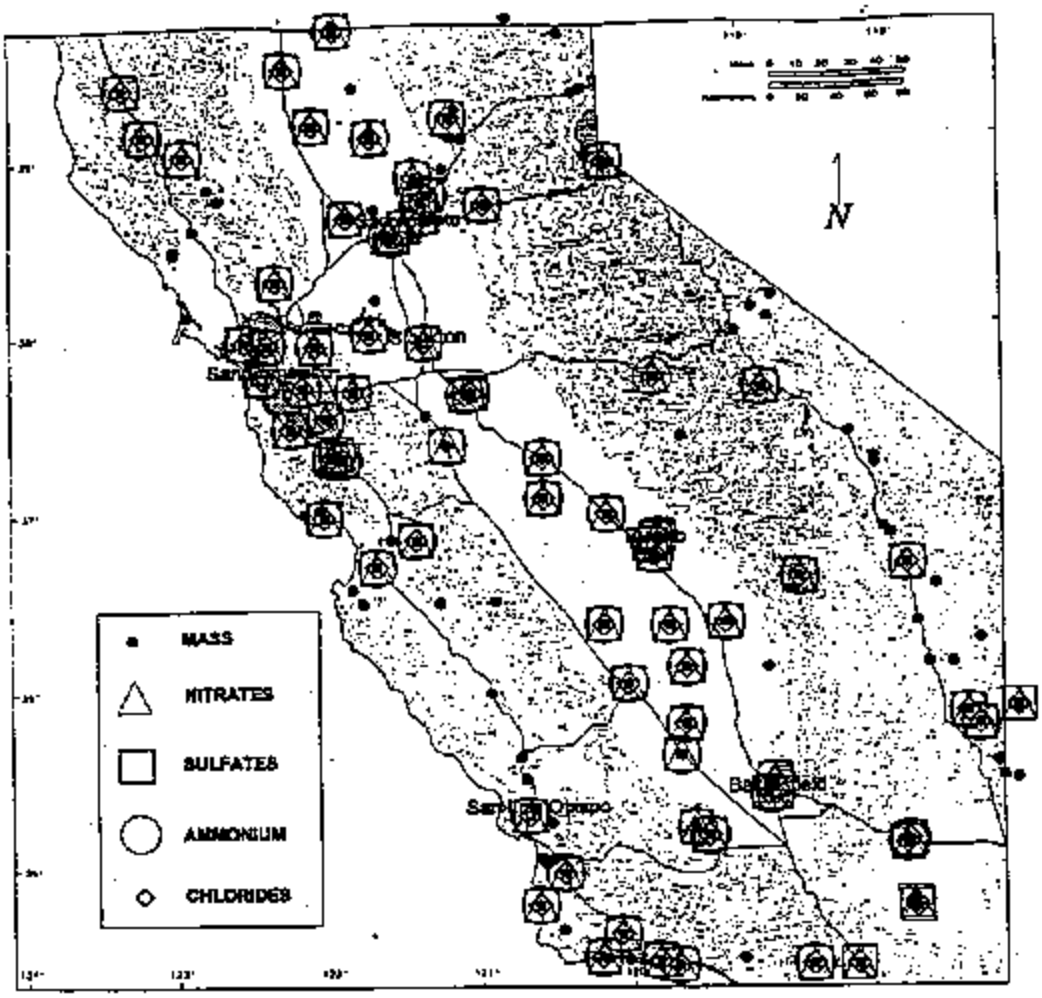


Figure 3-7. ARB PM_{10} (SSI) monitoring sites, showing chemical composition measured at each site.

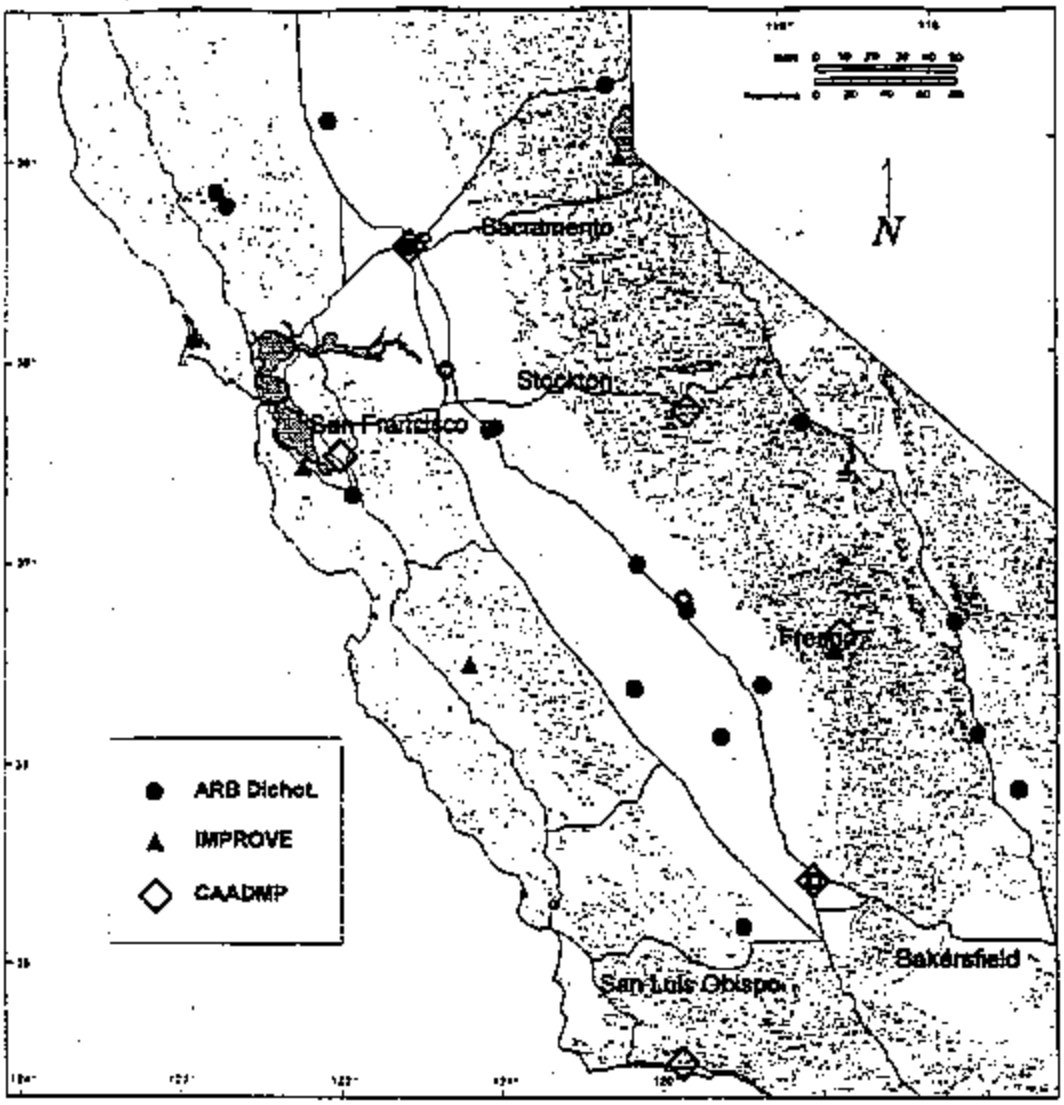


Figure 3-8. Size-fractionated PM monitoring networks, by sponsor.

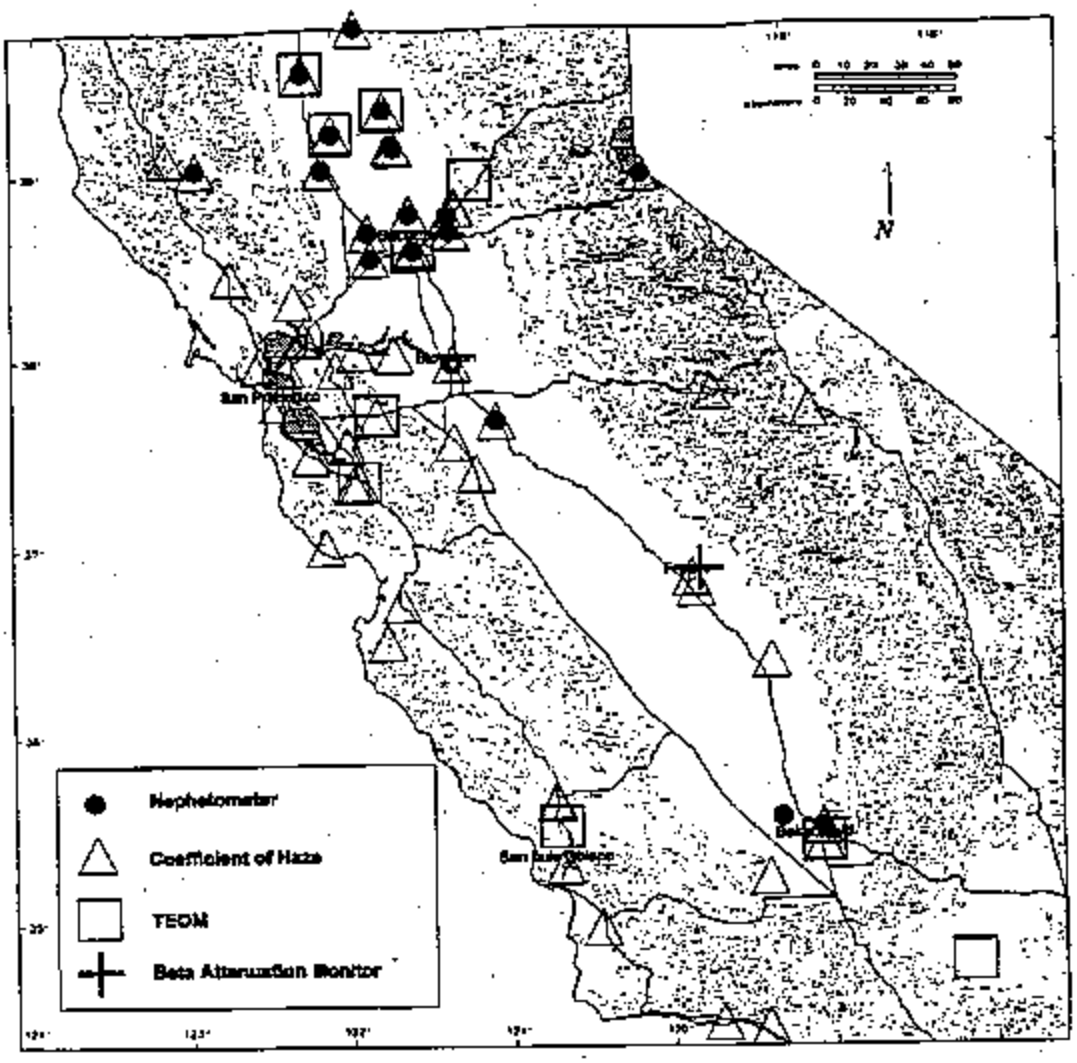


Figure 3-9. Visibility monitoring networks, by measurement method.

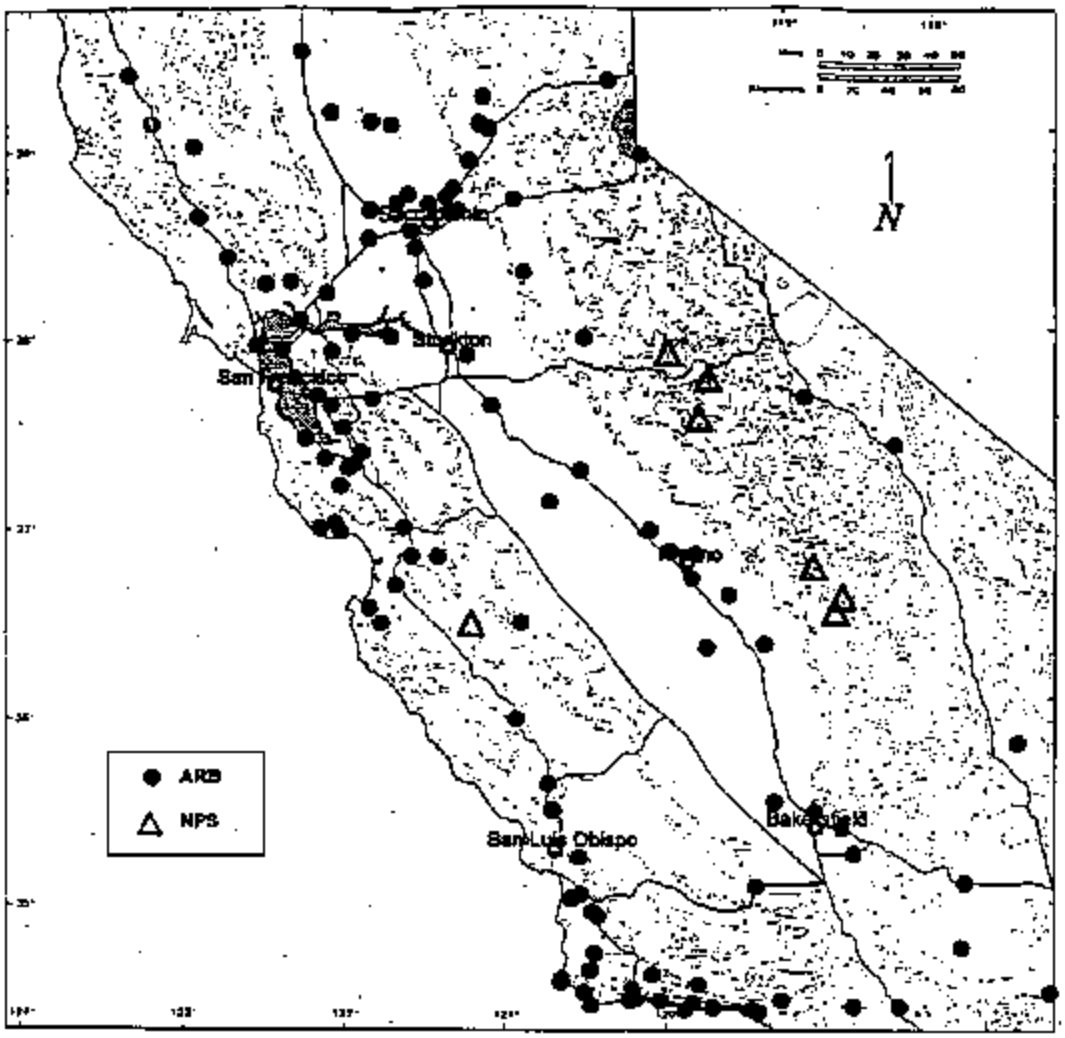


Figure 3-10. O_3 monitoring networks, by sponsor.

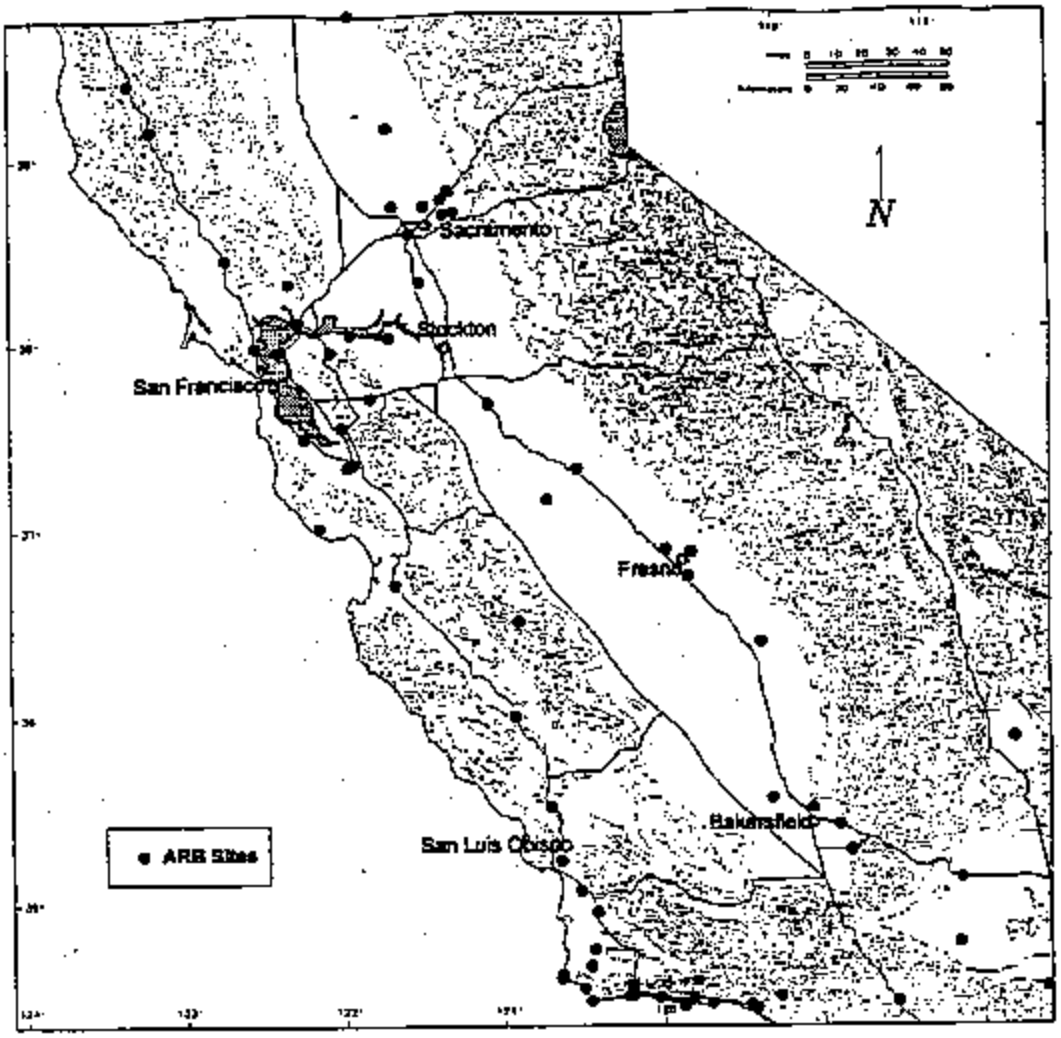


Figure 3-11. NO, NO_2, and NO_x monitoring sites, by sponsor.

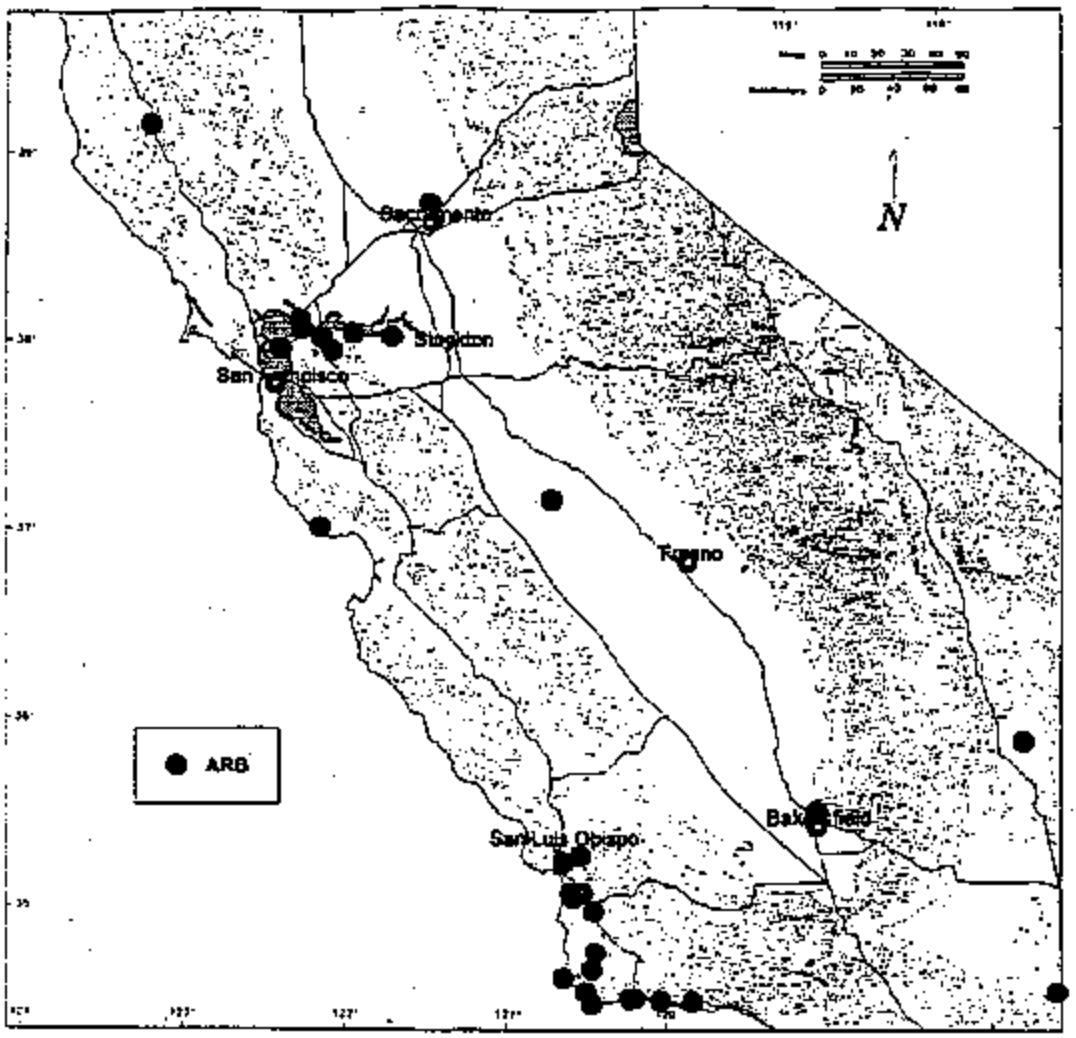


Figure 3-12. SO_2 monitoring sites, by sponsor.

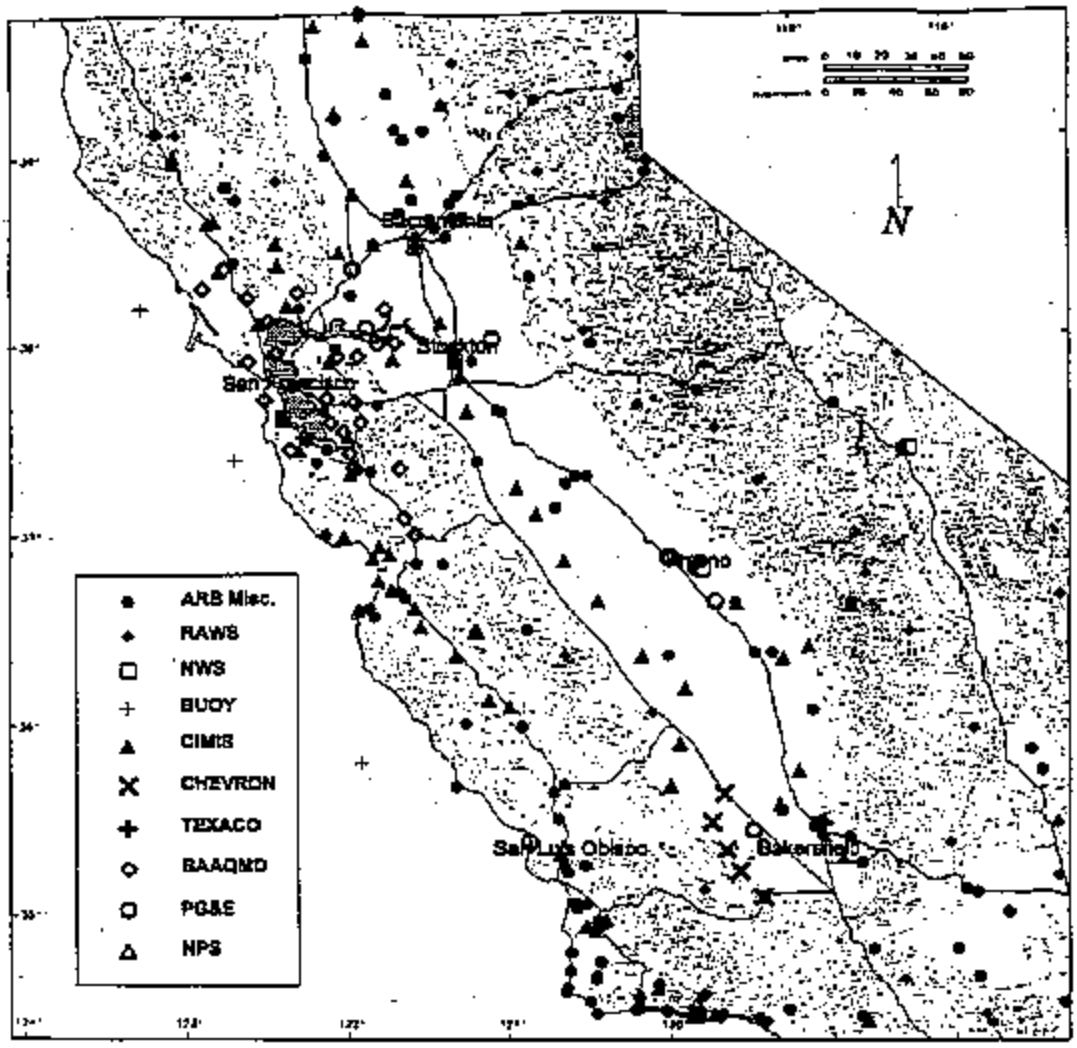


Figure 3-13. Wind speed and wind direction monitoring sites, by sponsor.

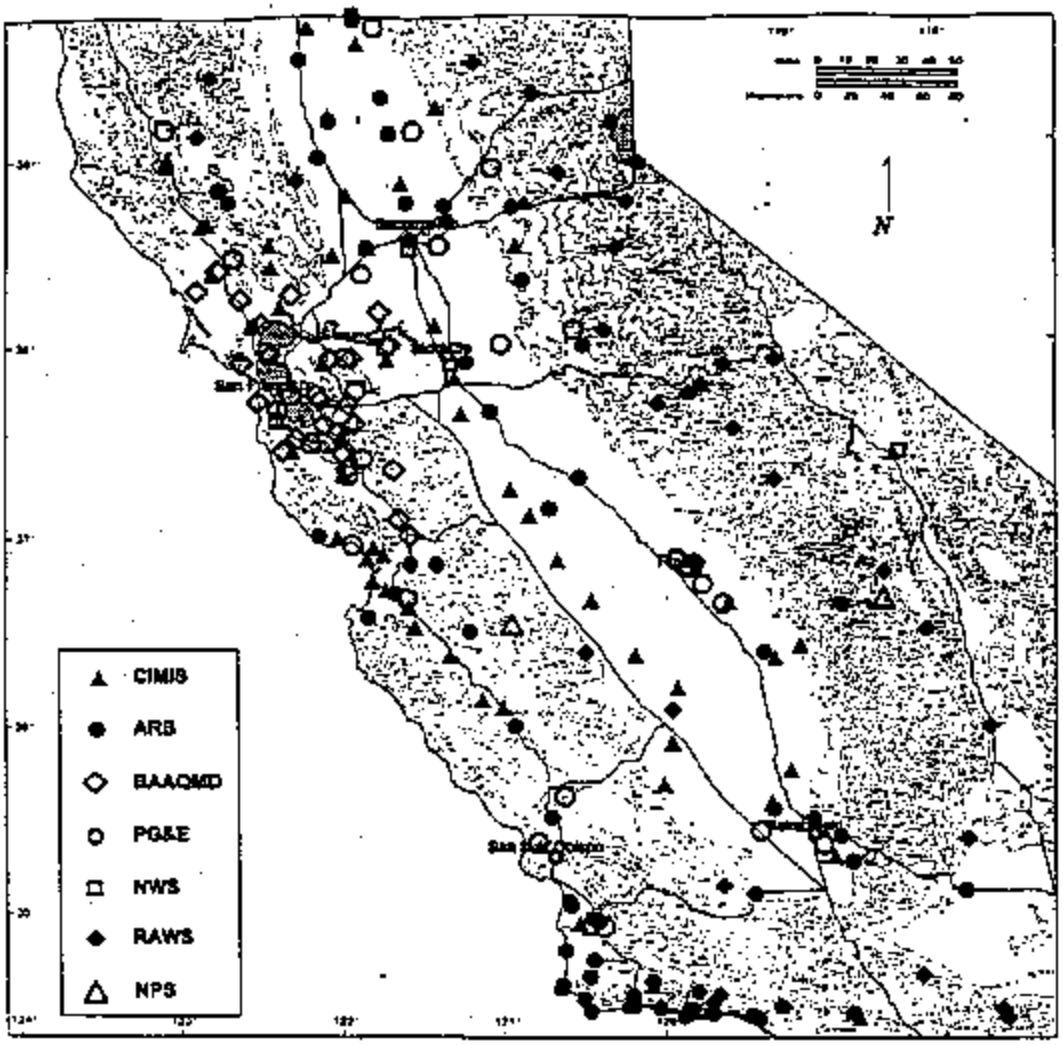


Figure 3-14. Temperature monitoring sites, by sponsor.

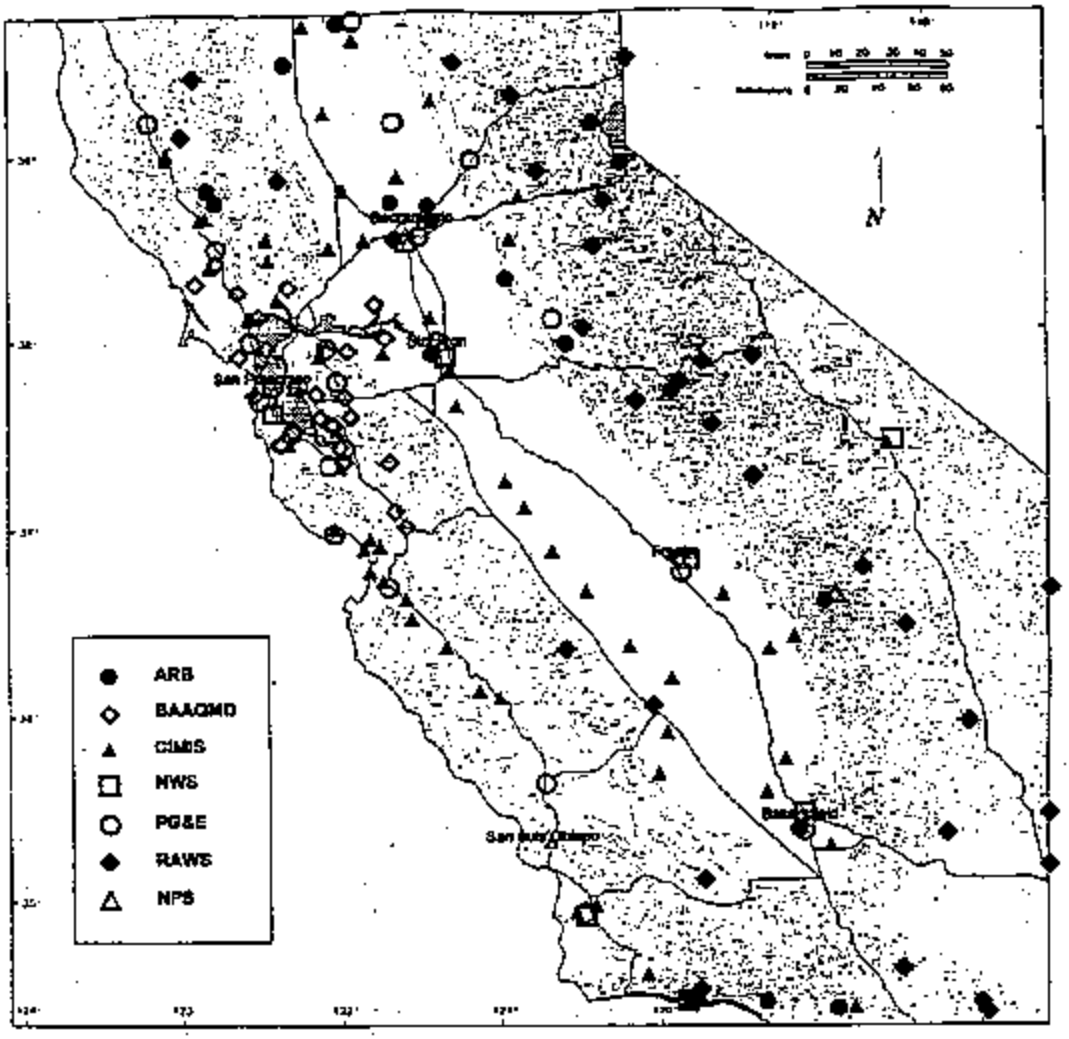


Figure 3-15. RH monitoring sites, by sponsor.

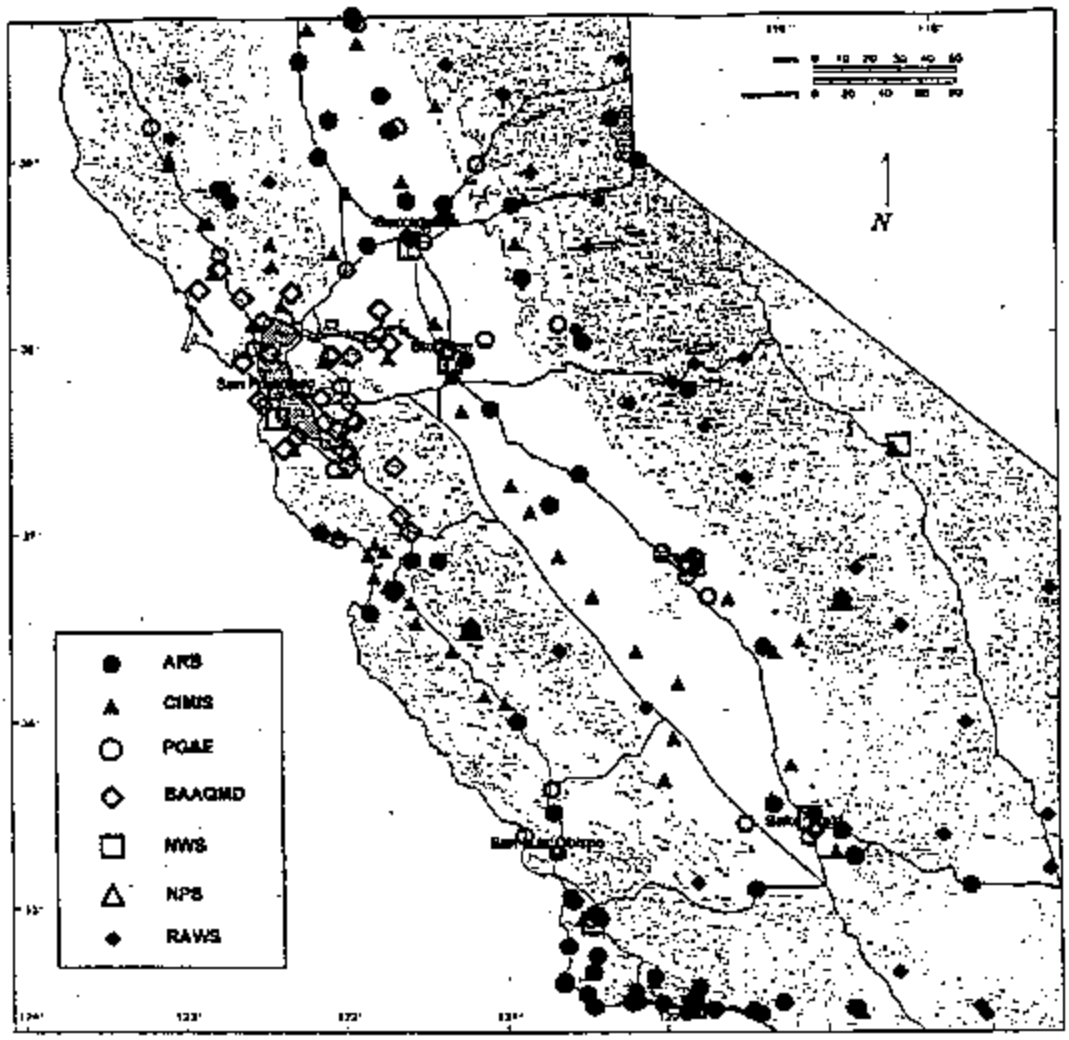


Figure 3-16. Solar radiation monitoring sites, by sponsor.

Table 3-4

General Description and Purpose of Fall and Winter Air Quality Sites

Site Code	Site Name	Site Type	Site Rationale and Characteristics*																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
COP	Van Dorsten	Core	2				1																				
01C	Irwin	Saturation					1																				
02C	Nevada	Saturation		2																				1			
03C	Tulare Lake	Saturation										2									1						
04C	Van Dorsten	Saturation	2				1																				2
05C	Pickrell	Saturation			2							2		1													
06C	Yoder	Saturation			1							2															
07C	Newark	Saturation																			2				1		
08C	Josephine	Saturation					1							2													
09C	Canal	Saturation					2														2				1		
10C	Jepsen	Saturation					1																		2		
11C	Paris	Saturation																				1					
12C	King	Saturation					2					2		1											2		
13C	Lansing	Saturation																			2	1					
14C	Zacky Farms	Saturation																					1				
15C	Pueblo	Saturation										2	1														
16C	Bainum	Saturation					2					2		1											2		
17C	Miller	Saturation				2	1																		2		
18C	Kent	Saturation																			1						
19C	Wastewater	Saturation										2			1						2						
20C	Creighton I	Saturation		2																				1			
21C	Redding	Saturation																			1						
22C	Creighton II	Saturation																			2	1					

Table 3-4 (continued)

General Description and Purpose of Fall and Winter Air Quality Sites

Site Code	Site Name	Site Type	Site Rationale and Characteristics[a]																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
Core Air Quality Monitoring Sites																											
BFK	Bakersfield	Core	1				2		2		2		2														
FEI	Fresno	Core	1				2	2		2	2																
KWR	Kern Wildlife Refuge	Core		1																				2			
Boundary and Flux Plane Sites																											
SWC	SW Chowchilla	Boundary A				2								2				1			2						
CHO	Cholame	Boundary B															1							2			
COA	Coalinga	Boundary B					2						2							1				2			
ERL	Earlimart	Boundary B		2		2							2							1							
LOO	Lookout Point	Boundary B																						2		1	
SPR	Springville	Boundary B						2											1					2			
THE	Tehachapi	Boundary B															1							2			
DEV	Devils Den	Boundary B		2															1					2			
FRI	Friant	Boundary C		2														1						2			
MKR	Mouth of the Kings River	Boundary C																		1	2						
LBS	Los Banos	Boundary C				2												1	2					2			
REY	Reyes Station	Boundary C		2													1							2			
FEL	Fellows	Boundary D			2								1								2						
KRN	Kernridge	Boundary D			2								1								2						

Table 3-4 (continued)

General Description and Purpose of Fall and Winter Air Quality Sites

Site Code	Site Name	Site Type	Site Rationale and Characteristics*																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
Bakersfield Saturation Network																											
01B	Collocated with core site	Saturation																									1
02B	Chester	Saturation	2				2		2		2																
03B	El Rio	Saturation					1	2		2																	
04B	Stockdale	Saturation	2								1																
05B	China Grade	Saturation			2								1														
06B	Santa Fe	Saturation				2															1			2	2		
07B	Truxtun	Saturation	2		2				2				1														
08B	Edison	Saturation				2															1						
09B	Mohawk	Saturation				1															2			2			
10B	Warren	Saturation					2			2			2												1		
11B	Fairway	Saturation					2	1																			
12B	Collocated with 01B	Saturation																									1
Kern Wildlife Refuge Saturation																											
13K	Gun Club	Saturation		1															2					2			
14K	Core Site	Saturation		2															2					2			1
15K	Kern National Wildlife Refuge	Saturation		1															2					2			
16K	Garces	Saturation		1															2					2			
17K	Rowlee	Saturation		1															2					2			

Table 3-4 (continued)

General Description and Purpose of Fall and Winter Air Quality Sites

Site Code	Site Name	Site Type	Site Rationale and Characteristics*																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
Fresno Saturation Network																											
18F	Cornelia	Saturation				2										1					2						
19F	Nielson	Saturation					2			1																	
20F	Swift	Saturation					1	2		2																	
21F	Core Site	Saturation																									1
22F	Hyde	Saturation					2														2				1		
23F	Fresno Air	Saturation			2				1		2																
24F	Meridien	Saturation					2	1		2						2											
25F	Library	Saturation					2		1		2																
26F	Coventry	Saturation					1			2																	
27F	Hwy. 41	Saturation					2				1																
28F	Fresno	Saturation							1		2																
29F	Browning	Saturation					2	1		2																	
30F	Shields	Saturation	2									1															
31F	Kings Canyon	Saturation	2						1		2																
32F	Illinois	Saturation					2	1		2																	
33F	Barstow	Saturation				1	2		2	2												2					
34F	Floral	Saturation				2																2					
35F	Jensen	Saturation																				1					
36F	Grantland	Saturation																			1						
37F	Site Deleted	Saturation	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
38F	Shaw	Saturation					2		2		1																
39F	Palm	Saturation												1													
40F	Malaga	Saturation																			2						
41F	Weldon	Saturation					2	1		2																	
42F	Jensen	Saturation				2																1					
43F	Barton	Saturation				2				2						1											

Table 3-4 (continued)

General Description and Purpose of Fall and Winter Air Quality Sites

* Key:	
A	Urban-general/mixed residential, commercial (shopping, office buildings)
B	Rural/regional-general
C	Industrial-general
D	Agricultural-general/mixed crop and animal farms, native vegetation
E	Residential neighborhood-general
F	Residential neighborhood-wood smoke
G	Urban commercial-restaurants (charbroiling), shopping center, offices
H	Transportation-residential neighborhood traffic
I	Transportation-commercial/residential traffic
J	Transportation-railroad/commercial traffic/agricultural
K	Industrial-oil processing and refining
L	Industrial-agricultural related (grain silos, cotton ginning, storage areas)
M	Industrial-wastewater treatment plants
N	Industrial-construction
O	Transport-through pass into or out of SJV
P	Transport-northern flux plane
Q	Transport-central flux plane
R	East or west side boundary but within valley
S	Agricultural-cotton/alfalfa/corn, citrus, nuts, vineyards, other crops
T	Agricultural-dairy
U	Agricultural-poultry
V	Agricultural-native vegetation
W	Interstitial site between core site and outlying sites; may be only during periods of inactivity at location of site
X	Clean air boundary
Y	Collocated at core site for comparison of portable results to SFS results; description is the same as the core site.
1	Primary purpose of site
2	General sources surrounding site

KWR was approximately 9 km east of the wildlife refuge. The area surrounding KWR consists of native vegetation, primarily prairie grass, with no major sources (the closest major sources are Delano and Highway 99, about 10 km to the east).

3.2.2 Boundary and Flux Plane Sites

There were no boundary or flux plane sites during the Fall study.

During the Winter study, boundary sites were located (1) in major valley passes, to evaluate transport into and out of the valley; and (2) on the perimeter of the valley floor outside the saturation network regions, to obtain a better spatial coverage of the edges of the valley. Flux plane sites were located along two east-west lines (Figure 3-2), one at the northern edge of the study domain and the other in the center of the study domain. Table 3-4 shows the purpose or rationale for each site, along with the sources in the general area that might influence PM concentrations at each site.

The boundary site Cholame (CHO) was located in the Coastal Range at the Cottonwood Summit at an elevation of about 640 m msl, to determine whether pollutants were transported between the coastal areas and the SJV. This site also acted as the western edge of an east-west flux plane along the center of the valley. The Coalinga (COA) site and MKR site were located at the western and eastern edges of the valley floor, respectively, to determine, along with other valley sites, the regional nature of pollutant buildup. The "lake" theory assumes that pollutants build up in the valley uniformly over time, whereas the "ice cream cone" theory assumes that pollutants are concentrated at a given location (e.g., an urban center) and then disperse throughout the valley over time. Reyes Station (REY) at 914 m msl and Tehachapi (TEH) at 949 m msl were located in passes in the Tehachapi Mountains, to examine the potential for transport of PM in or out of the valley during winter PM episodes. Lookout Point (LOO) at 1,174 m msl was in the Sierra Nevada at an elevation that is typically above the inversion height observed during winter PM episodes. The elevations of LOO, TEH, REY, and CHO are above the typical boundary layer, so data from these sites should also make it possible to estimate pollutant levels aloft as well as evaluate the homogeneity of pollutant concentrations above the boundary layer.

The flux plane along the northern boundary consisted of three sites—two 24-hour sampling sites using portable samplers (Los Banos [LBS] and Friant [FRI]) and the high-frequency measurement boundary site collecting the 3-hour samples (SWC). The second flux plane ran along the center of the valley located about halfway between Fresno and Bakersfield and extended from CHO in the Coastal Range on the west side of the valley to Springville (SPR) in the Sierra Nevada on the east side of the valley. The

KWR core site was also part of this flux plane. The purpose of this flux plane was to examine the potential for pollutant transport between Fresno and Bakersfield.

3.2.3 Saturation Samplers

For the Fall and Winter studies, the two general objectives of the saturation network were to obtain a better understanding of the spatial influence of individual sources or source types and to obtain a better understanding of the impact of those sources at the core sites, both averaged over a 24-hour period.

3.2.3.1 Rationale

Two general source categories were established for the Fall and Winter studies: continuous sources and intermittent sources. Continuous sources were defined as sources that operate throughout the duration of the study, although not necessarily for 24 hours each day. Examples of continuous sources include animal ranches (such as dairies and poultry farms), roads, wastewater treatment plants, and native vegetation. Intermittent sources were defined as sources that might cause one or several events during the sampling period but would be inactive most of the time. Examples of intermittent sources include harvesting operations, short-term construction, and certain kinds of industrial operations.

For continuous sources, saturation samplers were placed just outside the source and in a path between the source and the core site. In general, saturation sites were placed between the source and respective core site, but independent of the general wind flow during the study period, because of the need to understand the potential impact of the source at the core site. Thus, wind directions away from the core site provided information on only one of the study's two objectives—that is, information on the spatial influence of sources—and not on the potential impact of the source at the core site.

For intermittent sources, saturation samplers were placed within the source area, if possible, to obtain the full impact of that source when activity occurred. During nonactive periods, intermittent source samplers acted as interstitial monitors between the core site and other potential sites at a distance further from the core site. Data from these sites might also lead to a better understanding of potential sources that might be upwind of the intermittent site, yet not in the path between the core site and the upwind site. Thus, the spatial influence of sources might be evaluated during periods when other wind directions dominate.

3.2.3.2 Location

Before project personnel entered the field, they examined Department of Water Resources (DWR) land use maps, U.S. Geological Survey (USGS) topographical maps, and county and city street maps to obtain a general idea of potential sources within the Fall and Winter study domains. General source types that were of interest included residential neighborhoods; areas with fireplaces or wood-burning inserts versus areas without; commercial areas with shopping centers and/or office buildings; agricultural activities, such as tillage and harvesting (alfalfa, corn, or cotton), dairy farms, and poultry farms; native vegetation; industrial sites, such as wastewater treatment plants, industrial parks, cotton ginning, grain transport and storage areas, and construction; and sites influenced by motor vehicle traffic.

With the street and topographical maps as a guide, preliminary field surveys of the areas were conducted to determine the exact locations of the sites, including the specifics of the power pole or street light where a sampler would be placed. The surveys were conducted only about six weeks before the beginning of the study, in the hope that activity at certain source types (such as harvesting) would still be viable during the study period. Two to three days were required for every 20 sites, given the geographic distances covered in this study. Each potential site and its general surrounding area were videotaped and photographed. Backup sites were also noted; for example, if an intermittent source chosen in the initial survey was no longer viable, then another similar source could be used. Several days before the study began, a final site review was conducted with site operators to finalize the site locations and to familiarize the operators with those locations.

3.2.4 Upper Air and Surface Meteorological Sites

Routine upper air meteorological measurement data within the valley do not exist. However, historically these data have been obtained from two rawinsondings per day at the Oakland and Vandenberg airports, which are along the coast. On the other hand, a reasonably dense network of surface stations exists within the valley (Solomon et al. 1997, Thuillier 1995).

3.2.4.1 Upper Air Meteorological Sites

Upper air meteorological measurements were not performed during the Fall study, because of its more limited domain and the more limited modeling that was expected to be performed.

For the Winter study, the objectives in placing the measurement sites were as follows:

- Characterize surface and aloft transport patterns and other atmospheric parameters that affect the formation, mixing, and transport of PM and associated chemical species in the central and

southern SJV during the winter (e.g., drainage flows from the Kings River Canyon into the SJV, the strength and depth of inversions, and the formation and dissipation of fog layers).

- Document the meteorological conditions during aerosol and related chemical sampling at the core sites and other sampling locations.
- Optimize performance of the RWPs, RASSs, and surface meteorological instruments, or ensure that a site was suitable for rawinsonde balloon launch operations.
- Collect data for diagnostic meteorological modeling of the study domain and for possible prognostic meteorological modeling.

To fulfill the above objectives, meteorological and fog modelers and data analysts were asked to recommend locations for four RWPs with RASSs, two rawinsondes, one DAS, and one sodar. The RWP measures wind speed and wind direction in layers up to about 4,000 m agl, and the RASS measures temperature in layers up to about 3,500 m agl. Rawinsondes measure wind speed, wind direction, temperature, and RH at discrete points in space and time up to about 5,000 m. The DAS measures wind speed and wind direction in layers up to about 600 m, whereas the sodar simply measures the top of the inversion up to about 600 m. Three of the RWPs with RASSs were aligned along the central axis of the valley—one at the northern flux plane, one in the central region, and one in the southern portion of the valley. A fourth RWP with a RASS was sited east of Fresno at MKR, because historically the flow drainage from this basin appears to be one of the stronger slope flows in the winter and seems to influence the greater Fresno area, especially along the east side (Smith and Lehrman 1996).

The DAS and sodar were placed along the west of the central valley axis at KWR to evaluate any flow divergence between the east and west sides of the valley. The sodar was previously at the FEL WSO site to measure the influence of drainage flows between the coast and the valley that follow Route 58 and Route 166.

3.2.4.2 Surface Meteorological Sites

One standard surface meteorological measurement site was operated during the Fall study just north of site C09 at the southern, central edge of Corcoran (Figure 3-1).

During the Winter study, two types of surface meteorological systems were employed. One system used standard anemometers atop a 10-m tower to measure wind speed, wind direction, temperature, RH, and solar radiation (Figure 3-6). The other system used sonic anemometers (sonics) (items 1–5 in Figure 3-6) at a height of 2 m. The standard anemometers are typically mounted on 10-m or 2-m towers (e.g., CIMIS networks are on 2-m towers) and are widely used in the routine monitoring networks to measure wind

speed, wind direction, temperature, and sometimes RH and solar radiation. The standard anemometer's wind speed sensor thresholds are typically about 0.5 to 1.0 m/s, but they may be as low as 0.2 m/s.

Because of limited resources, only 10 standard surface meteorological monitoring stations were deployed during the Winter study. One each was placed at the sites where there was an RWP with a RASS (ELN, MKR, COR, and MTL), at the core sites (SWC, FRE, and KWR), at FEL and KRN (previous WSO sites), and at CAR (to fill a gap in the surface meteorological monitoring network in the center of the valley). The locations of all surface meteorological sites were chosen on the basis of (1) a review of the historical meteorological measurement network (private communication, Lehrman 1995) and (2) the need to support upper air meteorological measurements and core site measurements with surface meteorological data.

The five sonics were placed to obtain an overview of the characteristic low wind speeds often observed in the valley during winter stagnation periods (Figure 3-6). Sonics were used because they have a low wind speed threshold (0.05 m/s). The specific purposes of these surface meteorological measurements were to evaluate how low the wind speeds are in the valley, whether well-maintained standard anemometers can be used instead of sonics, and how representative the TSS 5A study site is. On the basis of a historical analysis of wind speeds in the valley, the sonics were placed in locations where low wind speeds would be expected. Specific site location requirements included level fetch and the absence of nearby obstructions. Detailed site descriptions are in Solomon et al. (1997).

3.2.5 TSS 5A Site

Because TSS 5A focused on the mixing and dispersion of microscale processes under low wind speed stable conditions, the scale of interest was limited to an area of about 0.5 km^2 spatially and a depth of a few hundred meters.

The location for the TSS 5A site was chosen because it is isolated (i.e., situated well away from topographic influences, with minimal influence from vehicle activity, buildings, other structures, and significant plant canopies) and free of local activity. This site is in the central SJV approximately 16 km north-northeast of Corcoran on a 0.65 km^2 fallow farm field. The field's southwest corner forms the intersection of 4th Avenue and Kent Avenue (Figure 3-2), and its western edge of the field forms the dividing line between Kings County and Tulare County. The site is more than 32 km east of the Kettleman Hills and more than 16 km west of the Sierra Nevada foothills.

For TSS 5A, 12 sonic anemometers and 36 tracer samplers were located in three concentric circles around the tracer release point out to a distance of 400 m (Figure 3-17). A minisodar, video camera, and standard meteorological monitoring equipment were also used during the study. The meteorological parameters included wind speed and wind direction measured by sonic anemometers at 12 locations (3 locations for u, v, w, and T and 9 locations for u, and v) at a sampling frequency of 10 Hz; wind speed and wind direction recorded by sensors that use a conventional (bivane) wind measurement system at two levels; and solar radiation, temperature, delta temperature, RH, and three-dimensional wind field measurements up to a height of 200 m via a miniphased-array sodar. During the meteorological data collection period, SF_6 tracer experiments were performed every 3 hours, from 1500 PST on January 3 until 1700 PST on January 15. Each tracer was continuously released for 1 hour and simultaneously monitored during that hour and the next 2 hours at 15-minute averaging periods. These experiments were specifically designed to examine dispersion and mixing rates at time scales adequate to resolve "meander," which may be the dominant dispersion mechanism under low wind speed stable conditions. The results are useful for evaluation of meteorological models under near-calm conditions and for model development and evaluation.

3.2.6 TSS 11 Site

Several sample platforms were considered for measuring fog and related species in the vertical direction. the most practical was to use a tall structure like a radio or TV tower. Since there are no tall towers in the southern portion of the valley, a site was chosen in Walnut Grove about 20 mi south of Sacramento, which has several tall radio and TV towers.

Permission was obtained to use the 430-m Candelabra Tower, which is the original transmission tower built by Sacramento TV stations that broadcast to the middle of the Central Valley. This tower is operated by KCRA (Channel 3, NBC), KXTV (Channel 10, ABC), and KVOR (Channel 13, CBS). These stations now transmit from nearby 610-m towers, so the Candelabra Tower is a backup transmission facility. Space on the tower is rented, and many microwave dishes and antennas for emergency services, pager services, repeaters, and so on are mounted on it.

Three TV transmission antennas are mounted more than 30 m apart on a triangular structure at the top of the tower. A two-story building at 430 m agl near the top of the tower houses amplifier equipment for the repeater and pager antennas and is the upper terminal for the elevator. The instruments for the trace gas measurements were housed in this building, and the time-lapse videos were recorded at this level.

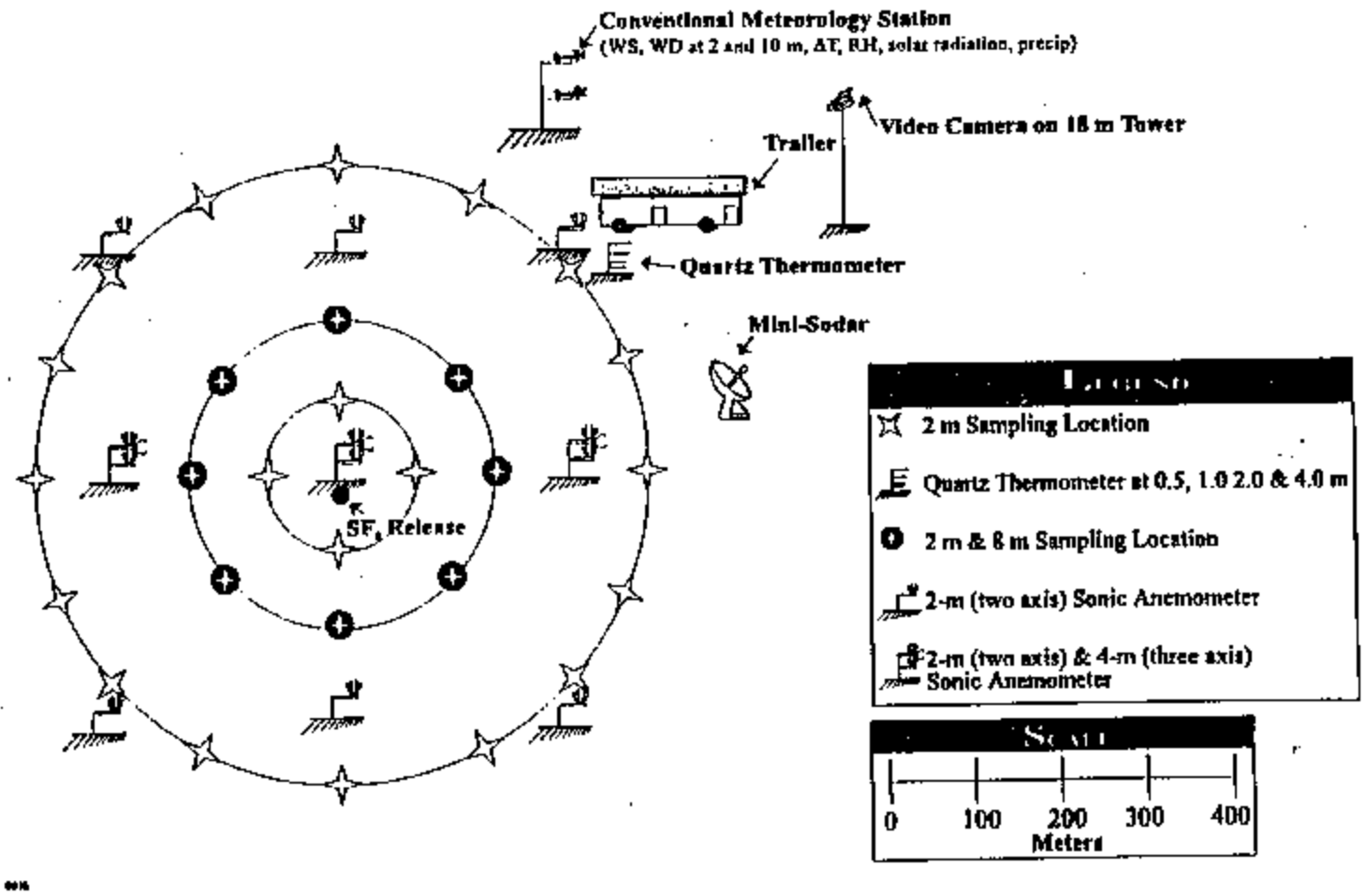


Figure 3-17. Sampling array for TSS 5A.

The license to use the Candelabra Tower for this TSS lists the location as being 38° 14' 50" north latitude and 121° 30' 03" west longitude.

The 609-m tower north of the Candelabra Tower is operated by KVIE (Channel 6, PBS) and KTXL (Channel 40, independent), the one to the east is operated by KCRA, and the one to the south is operated by KXTV and KVOR. The ARB operates temperature, wind speed, and wind direction sensors on the KCRA tower; meteorological data from its sensors supported the vertical fog measurements.

3.2.7 Air Quality and Meteorological Monitoring Site Logistics

During the Fall study, the core site was located at an existing District site in Corcoran. Logistics at that site consisted of installing some additional power (more circuit breakers) and installing the samplers. The samplers were on the roof of the building and were accessible by ladder from outside the building. Saturation sites required only installation, operation, and removal, which were performed by two dedicated technicians who had had previous experience with saturation samplers and SFSs. Details of the Fall study saturation sampler logistics are in Section 3.2.7.2.

Logistics for the Winter study program were much more complex, especially at the core sites, because several contractors performed many and varied types of measurements at each site. In addition, because of the large number of sites using portable monitors (saturation, boundary, and flux plane), the large geographical area over which these monitors were located, and the need to visit each site each day, the logistics tasks for the saturation monitoring networks—at least for operations—were also complex and required nine persons to perform. The Winter study logistics are described in more detail below.

3.2.7.1 Core and RWP Sites

Site logistics tasks include implementing the overall schedule, finding sites, handling site leases, and arranging for any licenses, installation, operation, and decommission. Specific site installation needs include utilities (power, water, and phone), refrigerators, sampling platforms, fences, miscellaneous infrastructure for monitor installation, and trailer installation and setup. These duties were split between the CRPAQS Technical Committee and contractors. In general, the Technical Committee identified site locations and made initial contacts with property owners. The committee also worked with PG&E on sites where power drops were needed from a utility pole outside the site's fence line. The siting contractor, Sonoma Technology, Inc. (STI), was responsible for specific site setup—that is, all work performed within the fence line at the core and Boundary A sites, including installation of fences, platforms, and trailers; providing power to trailers and platforms; installing phones; and providing

bathroom facilities (these were available at buildings near some sites, whereas other sites required a portable toilet). RWP sites were installed by the contractor operating the sites (a different group within STI), because they require specialized knowledge to install and operate.

Three primary tables and a number of maps were prepared before going into the field. Initially, street maps (such as American Automobile Association maps) were prepared with the specific location of each site clearly marked and labeled based on the initial in-field review of the sites. Later, sites were shown on electronic maps (via MapExpert, from DeLorme Mapping, in Freeport, Maine). Final versions of the electronic maps are in Figures 3-1 through 3-6. Coordinates for each site were obtained from the MapExpert maps. The three tables included an earlier version of Tables 3-1, 3-5, and 3-6 that specified the power and space requirements for the core and Boundary A sites. Each contractor who operated equipment at the site was surveyed for space and power requirements, and that survey became the basis for the tables. The contractor preparing the sites used these tables in determining the size of the site; the site layout, including the number of trailers and size of the platforms; and the power required at each trailer and at each platform.

Power requirements were based on the full operating surge for each instrument—that is, the amperage used when an instrument is first turned on. Then one circuit breaker was assigned to each instrument or small group of instruments to meet the surge requirements. Typically, one 15-A or 20-A breaker was assigned for each sampler, to ensure continued sampler operation if a power outage occurred and all the units turned on simultaneously. Although this was a costlier and conservative approach, it was considered far less costly than losing all the samples from a given sampling period at a site. Finally, the total power requirements for a site were determined, on the basis of the surge potential, by simply summing the individual power needs. For the core and the Boundary A sites, the total power requirements, using the assumptions above, were quite large (about 880, 580, 460, and 370 A for BFK, FEI, KWR, and SWC, respectively). Profiler sites also had large power requirements—150 A per site. At the core sites, the large power requirements required the purchase of extremely large circuit breakers as the main breaker for the site (about $4,000–$5,000 each), which was unanticipated and caused cost overruns.

Space requirements were also determined on an instrument-by-instrument basis, allowing a minimum of about 2.4 m between ambient aerosol samplers on platforms and a minimum of about 1.2 m for samplers that need bench space inside trailers. Fog samplers, especially those operating at very high flow rates,

Table 3-5
Site Power Requirements for Winter Study

Site	Item	Operator	# of Items	Power/Item	Power/Item (Operating A)	# of Breakers (size in A)	# of 110 Outlets	Total Power (110 eq.)	Platform (P)/ Trailer (T)
BAK	SES	DRI/STI	16	15	12	16 (20)	16	240	P
	Portable PM10	DRI/STI	8	Battery		—	—	0	P
	HVDVI	Caltech	1	15	8	1 (20)	1	15	P
	VAPS	EPA	1	15		2 (20)	2	15	P
	Hi-Vol PM10	DRI/STI	1	15	8	1 (20)	1	15	P
	ETH impactor	CSU	1	5	3	1 (10)	1	5	P
	CASCC2	CSU	1	5	3	1 (10)	1	5	P
	Rawinsonde (tracker)	Lindsey	1	15		1 (20)	1	15	P
	CADMP (PM2.5)	ARB-RD	1	15		1 (20)	1	15	P
	CE-CERT sampler	CE-CERT	1	15		1 (20)	1	15	P
	Misc. & outside lights	DRI/STI	1	20		2 (10)	3	20	P
	AQ and met. audits	AV	1	20		1 (20)	3	20	P
	Nephelometer	DRI/STI	1	10		1 (15)	2	10	P
	Trailers	ARB-ML/ STI	2	40@225v		2 (40@225v)	2@225v	160	T
	Cont. H_2O_2	CSU	1	5	4	1 (10)	1	5	T
	Rawinsonde (computer)	Lindsey	1	5		1 (10)	1	5	T
	TEOM	DRI/STI	2	15		2 (20)	2	30	T
	Carbonyls	DRI/STI	1	10		1 (15)	1	10	T
	VOC (TENAX)	DRI/STI	2	10		2 (15)	2	20	T
	VOC (canister)	DRI/STI	2	10		2 (15)	2	20	T
	Cont. NH3	TEI	2	10		2 (15)	2	20	T
	Aethelometer	Magee Sci.	2	10		2 (15)	2	20	T
	TEOM (computer)	DRI/STI	4	5		4 (10)	4	20	T
	Portable sampler battery	DRI/STI	25	0.5		2	5	12.5	T (with 5 multiple plug)
	MOUDI	DRI/STI	3	15		3 (20)	3	45	T
	Misc.	DRI/STI	2	20		4 (10)	4	40	T
	Data aquisition system	DRI/STI	1	5	5	1 (10)	1	5	T
	AQ and met audits	AV	1	20		1 (20)	2	20	T
	Freezer	DRI/STI	4	15		4 (20)	4	60	T
						BAKERSFIELD—GRAND TOTAL POWER (A):		882.5	
						TOTAL POWER PLATFORM:		390	
						TOTAL POWER TRAILER:		492.5	

Table 3-5 (continued)
Site Power Requirements for Winter Study

Site	Item	Operator	# of Items	Power/Item	Power/Item (Operating A)	# of Breakers (size in A)	# of 110 Outlets	Total Power (110 eq.)	Platform (P)/ Trailer (T)
FRE	SFS	DRI/STI	8	15	12	16 (20)	16	120	P
	Portable PM10	DRI/STI	4	Battery		--	—	0	P
	Surface met. station	STI	1	5		1 (10)	1	5	P
	Rawinsonde (tracker)	Lindsey	1	15		1 (20)	1	15	P
	CASCC2	CSU	1	5	3	1 (10)	1	5	P
	ETH impactor	CSU	1	5	3	1 (10)	1	5	P
	HVDVI	Caltech	1	15	8	1 (20)	1	15	P
	AQ and met. audits	AV	1	20		1 (20)	3	20	P
	Nephelometer	DRI/STI	1	10		1 (15)	2	10	p
	Misc. & outside lights	DRI/STI	1	20		2 (10)	3	20	P
	TEOM or BAM	DRI/STI	1	15		1(20)	1	15	P
	Trailers	ARB-MLD/STI	2	40@225v		2 (40@225v)	2@225v	160	T
	TEOM or BAM	DRI/STI	1	5		1 (10)	1	5	T
	HPLC H_2O_2	NCAR	1	15		1 (20)	1	15	T
	Cont. H_2O_2	CSU	1	5	4	1 (10)	1	5	T
	Carbonyls	DRI/STI	1	10		1 (15)	1	10	T
	VOC (TENAX)	DRI/STI	2	10		2 (15)	2	20	T
	VOC (canister)	DRI/STI	2	10		2 (15)	2	20	T
	Portable sampler battery	DRI/STI	40	0.5		2	5	20	T (with 5 multiple plug)
	Rawinsonde (computer)	Lindsey	1	5		1 (5)	1	5	T
	AQ and met. audits	AV	1	20		1 (20)	2	20	T
	Data aquisition system	DRI/STI	1	5	5	1 (10)	1	5	T
	Misc.	DRI/STI	1	20		2 (10)	3	20	T
	Freezer	DRI/STI	3	15		3 (20)	3	45	T
							FRESNO—GRAND TOTAL POWER:	580	
							TOTAL POWER PLATFORM:	230	
							TOTAL POWER TRAILER:	350	

Table 3-5 (continued)
Site Power Requirements for Winter Study

Site	Item	Operator	# of Items	Power/Item	Power/Item (Operating A)	# of Breakers (size in A)	# of 110 Outlets	Total Power (110 eq.)	Platform (P)/ Trailer (T)
KWR	SFS	DRI/STI	8	15	12	16 (20)	16	120	P
	HVDVI	Caltech	1	15	8	1 (20)	1	15	P
	Surface met. station	PG&E	1	5		1 (10)	1	5	P
	Portable PM10	DRI/STI	4	Battery		—	—	0	P
	PMS CSASP	CSU	1	5	2	1 (10)	1	5	P
	CASCC2	CSU	1	5	3	1 (10)	1	5	P
	SFCASCC	CSU	1	5	4	1 (10)	1	5	P
	IESL Impactor	CSU	1	15	10	1 (20)	1	15	P
	AQ and met. audits	AV	1	20		1 (20)	3	20	P
	Nephelometer	DRI/STI	1	10		1 (15)	2	10	P
	Misc. & outside lights	CSU	1	20		2 (10)	3	20	P
	TEOM (ARB)	DRI/STI	1	15		1(20)	1	15	P
	TEOM (computer)	DRI/STI	1	5		1 (10)	1	5	T
	Portable sampler battery	DRI/STI	12	0.5		2 (10)	3	6	T (with 3 multiple plug)
	Trailers	ARB-RD/STI	1	40@225v		1 (40@225v)	1@225v	80	T
	Cont. H_2O_2	CSU	2	5		2 (10)	2	10	T
	HPLC H_2O_2	NCAR	1	15		1 (20)	1	15	T
	O_3	DRI/STI	1	6	4	1 (10)	1	6	T
	NO/NOx	DRI/STI	1	6	4	1 (10)	1	6	T
	SO_2	DRI/STI	1	6	4	1 (10)	1	6	T
	CO	DRI/STI	1	6	4	1 (10)	1	6	T
	DAS	PG&E	1	20		1 (20)	2 (DAS)	20	T
	AQ and met. audits	AV	1	20		1 (20)	2	20	T
	Data aquisition system	DRI/STI	1	5	5	1 (10)	1	5	T
	Misc.	DRI/STI	1	20		2 (10)	3	20	T
	Freezer	DRI/STI	2	10		2 (15)	2	20	T
							KERN WILDLIFE REFUGE—GRAND TOTAL POWER:	460	
							TOTAL POWER PLATFORM:	235	
							TOTAL POWER TRAILER:	225	

Table 3-5 (continued)
Site Power Requirements for Winter Study

Site	Item	Operator	# of Items	Power/Item	Power/Item (Operating A)	# of Breakers (size in A)	# of 110 Outlets	Total Power (110 eq.)	Platform (P)/ Trailer (T)
SWC	SFS	DRI/STI	8	15	12	16 (20)	16	120	P
	Surface met. station	STI	1	5		1 (10)	1	5	P
	AQ and met. audits	AV	1	20		1 (20)	2	20	P
	BAM	DRI/STI	2	15		2 (20)	2	30	P
	Nephelometer	DRI/STI	1	10		1 (15)	2	10	P
	Misc. & outside lights	DRI/STI	1	20		2 (10)	3	20	P
	Trailers	ARB-RD/STI	1	40@225v		1 (40@225v)	1@225v	80	T
	AQ and met. audits	AV	1	20		1 (20)	2	20	T
	O^3	DRI/STI	1	6	4	1 (10)	1	6	T
	NO/NOx	DRI/STI	1	6	4	1 (10)	1	6	T
	SO2	DRI/STI	1	6	4	1 (10)	1	6	T
	CO	DRI/STI	1	6	4	1 (10)	1	6	T
	Data aquisition system	DRI/STI	1	5	5	1 (10)	1	5	T
	Misc.	DRI/STI	1	20		2 (10)	3	20	T
	Freezer	DRI/STI	1	10	7	1 (15)	1	10	T
							SOUTHWEST CHOWCHILLA—GRAND TOTAL POWER:	364	
							TOTAL POWER PLATFORM:	205	
							TOTAL POWER TRAILER:	159	

Table 3-5 (continued)
Site Power Requirements for Winter Study

Site	Item	Operator	# of Items	Power/Item	Power/Item (Operating A)	# of Breakers (size in A)	# of 110 Outlets	Total Power (110 eq.)	Platform (P)/ Trailer (T)
ELN	RWP	ARD/STI	1 / site	30 @ 225v		1 (30 @ 223)	1 @ 225v	60	
				20 RWP		1 (20)	1	20	
				20 computer		1 (20)	1	20	
	Surface met.	ARB/STI	1/site	10		1 (15)	1	10	
	RWP & surface met.	AV	2	20		2 (20)	3	40	
	RWP—GRAND TOTAL POWER PER SITE:							150	
CAR	Surface Met.	ARB/STI	1/site	10		1 (15)	1	10	
	Audits	AV	1	20		1 (20)	2	20	
	STAND ALONE SURFACE MET—GRAND TOTAL POWER PER SITE:							30	

Table 3-6
Site Space Requirements for Winter Study

Site	Item	Operator	# of Items	Space/Item (lin. ft)	Total Space (lin. ft)	Platform (P)/ Trailer (T)	Comments
BAK	SFS	DRI/STI	16	8	128	P	
	PM-2.5 fed. ref. method	EPA	3	8	24	P	
	Portable PM-10	DRI/STI	8	3	24	P	
	HVDVI	Caltech	1	8	8	P	
	VAPS	EPA	2	8	16	P	
	Hi-Vol PM-10	DRI/STI	1	8	8	P	
	CADMP	ARB-RD	1	8	8	P	
	CE-CERT sampler	CE-CERT	1	8	8	P	
	Nephelometer	DRI/STI	1	8	8	P*	* Requires space, but not platform
	ETH impactor	CSU	1	30	30	P*	* Requires space, but not platform
	CASCC2	CSU	1	30	30	P*	* Requires space, but not platform
	Rawinsonde (tracker)	Lindsey	1	10	10	P*	* Requires space, but not platform
	Trailers	ARB-RD/STI	2		0	T	25 x 30 ft reserved for trailer
	TEOM	DRI/STI	2	8	16	T	
	Cont. H_2O_2	CSU	1	3	3	T1	Near trailer?
	Rawinsonde (computer)	Lindsey	1	3	3	T1	
	MOUDI	DRI/STI	3	1.5	4.5	T1	
	Cont. NH_3	TEI	2	3	6	T1	Rack-mounted
	Aethelometer	Magee Sci.	2	3	6	T1	Rack-mounted
	Work space—fog & filter	DRI/STI	1	12	12	T1	
	TEOM (computer)	DRI/STI	4	2.5	10	T1	
	Data acquisition system	DRI/STI	1	2.5	2.5	T1	
	Carbonyls	DRI/STI	1	2.5	2.5	T2	
	VOC (TENAX)	DRI/STI	2	2.5	5	T2	
	VOC (canister)	DRI/STI	2	2.5	5	T2	
	Freezer	DRI/STI	4	3	12	T2	
	Portable sampler battery	DRI/STI	25	0.5	5	T2	3 5-ft shelves stacked on floor
				BAKERSFIELD—PLATFORM SPACE:	324		Requires min. 300-ft platform
				TRAILER COUNTER:	47		
				TRAILER FLOOR:	29.5		

Table 3-6 (continued)
Site Space Requirements for Winter Study

Site	Item	Operator	# of Items	Space/Item (lin. ft)	Total Space (lin. ft)	Platform (P)/ Trailer (T)	Comments
TRE	SFS	DRI/STI	8	8	64	P	
	Portable PM-10	DRI/STI	4	3	12	P	
	TEOM	DRI/STI	1	8	8	P	
	HVDVI	Caltech	1	8	8	P	
	Nephelometer	DRI/STI	1	8	8	P*	* Requires space, but not platform
	CASCC2	CSU	1	30	30	P*	* Requires space, but not platform
	ETH impactor	CSU	1	30	30	P*	* Requires space, but not platform
	Surface met.	STI	1	10	10	P*	* Requires space, but not platform
	Rawinsonde (tracker)	Lindsey	1	10	10	P*	* Requires space, but not platform
	HPLC H_2O_2	NCAR	1	3	3	T1	
	Cont. H_2O_2	CSU	1	3	3	T1	
	Work space—fog & filter	DRI/STI	1	12	12	T1	
	TEOM (computer)	DRI/STI	1	2.5	2.5	T1	
	Rawinsonde (computer)	Lindsey	1	3	3	T1	
	Data acquisition system	DRI/STI	1	3	3	T1	
	Carbonyls	DRI/STI	1	2.5	2.5	T2	
	VOC (TENAX)	DRI/STI	2	2.5	5	T2	
	VOC (canister)	DRI/STI	2	2.5	5	T2	
	Freezer	DRI/STI	3	3	9	T2	
	Portable sampler battery	DRI/STI	40	0.5	10	T2	8 5-ft shelves stacked on floor
				FRESNO—PLATFORM SPACE:	180		Requires min. 100-ft platform
				OFFICE COUNTER (T1):	26.5		
				OFFICE FLOOR (T2):	31.5		

Table 3-6 (continued)
Site Space Requirements for Winter Study

Site	Item	Operator	# of Items	Space/Item (lin. ft)	Total Space (lin. ft)	Platform (P)/ Trailer (T)	Comments
KWR	SFS	DRI/STI	8	8	64	P	
	Portable PM-10	DRI/STI	4	3	12	P	
	TEOM	DRI/STI	1	8	8	P	Not confirmed
	HVDVI	Caltech	1	8	8	P	
	Nephelometer	DRI/STI	1	8	8	P*	* Requires space, but not platform
	Surface met.	STI	1	10	10	P*	* Requires space, but not platform
	PMS CSASP	CSU	1	20	20	P*	* Requires space, but not platform
	CASCC2	CSU	1	30	30	P*	* Requires space, but not platform
	SFCASCC	CSU	1	20	20	P*	* Requires space, but not platform
	IESL impactor	CSU	1	30	30	P*	* Requires space, but not platform
	Trailers	ARB-RDSTI	1	30	30	T	
	Cont. H_2O_2	CSU	2	3	6	T1	
	HPLC H_2O_2	NCAR	1	3	3	T1	
	Data acquisition system	DRI/STI	1	3	3	T1	
	Work space—fog & filter	DRI/STI	1	16	16	T1	
	TEOM (computer)	DRI/STI	1	2.5	2.5	T1	
	O_3	DRI/STI	1	3	3	T2	On rack
	NO/NOx	DRI/STI	1	3	3	T2	On rack
	SO_2	DRI/STI	1	3	3	T2	On rack
	CO	DRI/STI	1	3	3	T2	On rack
	Freezer	DRI/STI	2	3	6	T2	
	Portable sampler battery	DRI/STI	12	0.5	6	T2	2.5-ft shelves stacked on floor
	DAS	PG&E	1	3	3	T1	
	DAS	PG&E	1	3	3	T2	
				KERN WILDLIFE REFUGE—PLATFORM SPACE:	240		Requires min. 130-ft platform
				TRAILER COUNTER:	30.5		
				TRAILER FLOOR:	15		

Table 3-6 (continued)
Site Space Requirements for Winter Study

Site	Item	Operator	# of Items	Space/Item (lin. ft)	Total Space (lin. ft)	Platform (P)/ Trailer (T)	Comments
SWC	SFS	DRI/STI	8	8	64	P	
	BAM	DRI/STI	2	8	16	P	
	Surface met.	STI	1	10	10	P*	* Requires space, but not platform
	Nephelometer	DRI/STI	1	8	8	P*	* Requires space, but not platform
	Trailers	ARB-RDSTI	1			T	
	Data acquisition system	DRI/STI	1	3	3	T1	
	Work space—filter prep.	DRI/STI	1	6	6	T1	
	Freezer	DRI/STI	1	3	3	T2	
	O_3	DRI/STI	1	3	3	T2	On rack
	NO/NOx	DRI/STI	1	3	3	T2	On rack
	SO_2	DRI/STI	1	3	3	T2	On rack
	CO	DRI/STI	1	3	3	T2	On rack
	SOUTHWEST CHOWCHILLA—PLATFORM SPACE:				90		Requires min. of 75-ft platform
	TRAILER COUNTER:				9		Small trailer suitable
	TRAILER FLOOR:				6		
ELN, COR, MKR, MET	RWP	ARB/STI	1/site	70 x 45	125 x 75	P	* Requires space, but not platform * Requires space, but not platform * Requires space, but not platform
	Surface met.	ARB/STI	1/site	12 x 12	12 x 12	P	* Requires space, but not platform
	Audits with DAS	AV		12 x 12	12 x 12	P	* Requires space, but not platform
CAR	Surface met. (Caruthers)	STI	1/site	12 x 12	12 x 12	P	* Requires space, but not platform
	Audits	AV					

required considerably more space (a maximum radius of about 5 m, depending on the sampler). Separate power and platforms were arranged for the fog samplers, because they were not on the main sampling platforms, and for the surface-based meteorological tower at the core sites. Space requirements for the profilers were obtained directly from the STI contractor who was overseeing installation and operation of the profiler sites.

3.2.7.2 Saturation Sites

Portable sampler sites (saturation, boundary, and flux plane sites) did not need the infrastructure of the larger sites, because they used battery-operated samplers that attached easily to utility poles. Well before the study, the Technical Committee located utility poles for the portable sampler sites and obtained permission to use these poles. Several days before sampling began, site operators and the Technical Committee members who had previously identified the site toured the portable saturation networks to familiarize the site operators with the site locations. Although this step was not in the initial plans, it proved beneficial to the site operators. Just before the study, site operators installed the samplers on the utility poles. When the study began, site operators maintained the operation of the portable sites, which included changing filters and batteries each day and resetting the timer once each week. Battery charging stations were maintained at each of the core sites, and portable sampler operators worked out of core sites to obtain preloaded filter packs and batteries before heading out to other sites. Each operator took spare batteries in case a battery failed to charge during the previous 24-hour period. Using centralized locations for battery and filter exchanges worked well, because each portable site operator reported to one of the core site supervisors, informing that supervisor of problems or other issues.

3.2.7.3 Filter Shipping Logistics

Approximately 1,100 filters were used each day during the field measurements. Preparing filters and filter holders and transferring them into and out of the field was a significant effort. A limiting factor was the number of filter holders, because at least four sets had to circulate at any given time—one set was being changed in the laboratory, two sets were in transit, and one set was used for sampling. Predictably, this procedure stretched available resources to the limit.

3.3 Field and Laboratory Measurements and Methods

During the Fall study, PM_{10} mass and composition, light absorption (B_{abs}), and NH_3 concentrations were sampled at 10 saturation monitoring sites and at the core site, while PM_{10} mass, B_{abs}, and NH_3 were sampled at 12 additional saturation sites. Twenty-four-hour average samples were collected daily at all Fall study sites. After collection, samples were shipped to the laboratory for chemical analysis. The core

site was collocated with the District site that operated on its normal every-sixth-day schedule. One surface meteorological measurement site was located in Corcoran 150 m north of site 09C.

The Winter study consisted of daily sampling for size-fractionated PM (PM_{10} and $PM_{2.5}$), PM composition, PM precursor gases, fog size and composition, surface and aloft meteorological variables, and emissions activity data. Various types of samplers were located at over 65 sites during the Winter study, as shown in Figures 3-2 through 3-6.

Table 3-7 lists the site measurements by general category, and Table 3-8 lists them by parameter. Although not listed, emissions activity data were obtained at every aerosol sampling location during the Fall and Winter studies. Details of the emissions activity data collection and archiving are in Section 3.3.5.1.

The following sections provide details of the measurement methods used during the Fall and Winter studies.

3.3.1 Aerosol and Related Gas Phase Species Measurements—Fall Study

3.3.1.1 Core Site Aerosol Measurements

At the Corcoran core site, a PM_{10} medium-volume SFS and a PM_{10} portable sampler were collocated on the roof of a one-story building in downtown Corcoran with three District samplers; two PM_{10} size-selective inlet (SSI) samplers, and one low-volume dichotomous virtual impactor (DVI). The District samplers operated according to the District's normal every-sixth-day sampling protocol.

The SFS used a Sierra-Andersen SA-254 medium-volume SSI inlet that sampled PM_{10} when operated at 113 l/min (Chow and Egami 1997). In Oregon, the SFS was designated as an EPA PM_{10} reference sampler when equipped with such an SSI (Federal Register 1988). During the Fall study, the SFS collected daily 24-hour-average filter samples.

The SFS' 12 sampling ports were operated by solenoid valves. Samples could thus be collected through two multistage filter holders containing filter substrates that allowed chemical analysis of the sample by various methods, as described below. A timer switch controlling the solenoid valves allowed filter changeover at midnight, unassisted by technicians; thus, two sets of filters were installed at any given time—one was sampling while the other was about to sample or needed to be changed. A vacuum pump drew air through these filters when the valves were open. During the Fall study, the flow rate was

Table 3-7

Site Measurements by Category for Fall and Winter Studies

Site Code	Site Name	Site Type	Measurements*																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
Fall Study:																											
COP	Van Dorsten	Core	1		1		2																				
01C	Irwin	Saturation			1																						
02C	Nevada	Saturation			1																						
03C	Tulare Lake	Saturation		1	1																						
04C	Van Dorsten	Saturation			1																						
05C	Pickrell	Saturation		1	1																						
06C	Yoder	Saturation		1	1																						
07C	Newark	Saturation			1																						
08C	Josephine	Saturation		1	1																						
09C	Canal	Saturation		1	1																						
10C	Jepsen	Saturation			1																						
11C	Paris	Saturation		1	1																						
12C	King	Saturation			1																						
13C	Lansing	Saturation		1	1																						
14C	Zacky Farms	Saturation			1																						
15C	Pueblo	Saturation		1	1																						
16C	Bainum	Saturation			1																						
17C	Miller	Saturation			1																						
18C	Kent	Saturation			1																						
19C	Wastewater	Saturation		1	1																						
20C	Creighton 1	Saturation		1	1																						
21C	Redding	Saturation			1																						
22C	Creighton 2	Saturation			1																						
CRM	Corcoran	Surface meteorology								2																	

Table 3-7 (continued)

Site Measurements by Category for Fall and Winter Studies

Site Code	Site Name	Site Type	Measurements*																									
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
WinterStudy																												
Core Air Quality Monitoring Sites																												
BFK	Bakersfield	Core	1	1	1		2	1	1	2		1					1	1	1									
FEI	Fresno	Core	1	1	1		2	1	1	1		1					1											
KWR	Kern Wildlife Refuge	Core	1	1	1		1	1	1	1				1			1											
Boundary and Flux Plane Sites																												
SWC	SW Chowchilla	Boundary A	1	1			1			1								1										
CHO	Cholame	Boundary B		1	1	1																						
COA	Coalinga	Boundary B		1	1	1																						
ERL	Earlimart	Boundary B		1	1	1																						
LOO	Lookout Point	Boundary B		1	1	1	2			2																		
SPR	Springville	Boundary B		1	1	1																						
THE	Tehachapi	Boundary B			1																							
DEV	Devils Den	Boundary B			1																							
FRI	Friant	Boundary C			1																							
MKR	Mouth of Kings River	Boundary C			1																							
LBS	Los Banos	Boundary C			1																							
REY	Reyes Station	Boundary C			1																							
FEL	Fellows	Boundary D		$SO_4^=$	1		1			1					1													
KRN	Kernridge	Boundary D		$SO_4^=$	1		1			1																		
Winter Study:																												
Bakersfield Saturation Network																												
01B	Collocated with core site	Saturation		1	1																							
02B	Chester	Saturation			1																							

Table 3-7 (continued)

Site Measurements by Category for Fall and Winter Studies

Site Code	Site Name	Site Type	Measurements*																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
03B	El Rio	Saturation			1																						
04B	Stockdale	Saturation		1	1																						
05B	China Grade	Saturation		1	1																						
06B	Santa Fe	Saturation			1																						
07B	Truxtun	Saturation		1	1																						
08B	Edison	Saturation			1																						
09B	Mohawk	Saturation		1	1																						
10B	Warren	Saturation		1	1																						
11B	Fairway	Saturation			1																						
12B	Collocated with 01B	Saturation		1	1																						
Kern Wildlife Refuge Saturation																											
13K	Gun Club	Saturation			1																						
14K	Core Site	Saturation			1																						
15K	Kern National Wildlife Refuge	Saturation		1	1																						
16K	Garces	Saturation			1																						
17K	Rowlee	Saturation			1																						
Winter Study:																											
Fresno Saturation Network																											
18F	Cornelia	Saturation			1																						
19F	Nielson	Saturation			1																						
20F	Swift	Saturation			1																						
21F	Core site	Saturation			1																						
22F	Hyde	Saturation			1																						
23F	Fresno Air	Saturation			1																						
24F	Meridien	Saturation		1	1																						
25F	Library	Saturation			1																						

Table 3-7 (continued)

Site Measurements by Category for Fall and Winter Studies

Site Code	Site Name	Site Type	Measurements*																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
26F	Coventry	Saturation			1																						
27F	Hwy. 41	Saturation		1	1																						
28F	Fresno	Saturation		1	1																						
29F	Browning	Saturation		1	1																						
30F	Shields	Saturation		1	1																						
31F	Kings Canyon	Saturation		1	1																						
32F	Illinois	Saturation		1	1																						
33F	Barstow	Saturation		1	1																						
34F	Floral	Saturation			1																						
35F	Jensen	Saturation		1	1																						
36F	Grantland	Saturation			1																						
37F	Site deleted	Saturation	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
38F	Shaw	Saturation		1	1																						
39F	Palm	Saturation		1	1																						
40F	Malaga	Saturation		1	1																						
41F	Weldon	Saturation		1	1																						
42F	Jensen	Saturation			1																						
43F	Barton	Saturation			1																						
Winter Study:																											
Meteorological Measurement Network																											
ELN	El Nido	Upper air								1			1														
MKR	Mouth of Kings River	Upper air								1			1														
COR	Corcoran	Upper air								1			1														
MTL	Mettler	Upper air								1			1														
CRT	Caruthers	Surface								1																	
TS5	TSS 5A special study site	Surface								1	1			1		1											

Table 3-7 (continued)

Site Measurements by Category for Fall and Winter Studies

Site Code	Site Name	Site Type	Measurements*																								
			A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
NMD	North of Madera	Surface									1																
PAN	Panoche Water District	Surface									1																
PVA	Porterville Airport	Surface									1																
PWR	Pixley Wildlife Refuge	Surface									1																
LHA	Lost Hills Airport	Surface									1																

Table 3-7 (continued)

Site Measurements by Category for Fall and Winter Studies

* Key:

A	PM-10/PM-2.5 mass: Fall study SFS PM-10 sampler operated on a 24-hr sampling frequency; Winter study PM-10/PM-2.5 SFS's and SGS's on a 3-hr sampling frequency 8 times per day; also includes continuous PM-10 or PM-2.5 mass using BAMs or TEOMs
B	PM-10 chemistry (PM) (SGS and portables); PM-2.5 chemistry (SFS only); chemistry (PM) = ions ($SO_4^{=}$, NO_3^-, NH_4^+, F, Cl, K, Na), OC, EC, elements by XRF, HNO_3, NH_3
C	PM-10 mass and NH3: saturation site portable samplers operated on a 24-hr sampling frequency
D	PM-10/PM-2.5 mass: boundary site portable samplers operated on a 24-hr sampling frequency
E	Criteria gases: SO_2, O_3, NO/NO_2/NOX, CO
F	Fog (size and chemistry): chemistry (fog) = chemistry (PM) + formaldehyde, S(IV), TOC, organic acids, H_2O_2aq, HMSA, DMA
G	VOC (C_2–C_{20}), carbonyls, aerosol organic species: C_2–C_{10} using canisters/GC-MS; C_{10}–C_{20} using TENAX cartridges/GC-MS; carbonyls using DNPH cartridges/LC; aerosol organic species using IIVDVI/GC-MS
H	Surface meteorology — standard: surface wind speed, wind direction, T, RH, and solar radiation using standard anemometers
I	Surface meteorology — sonic: surface wind speed, and direction using sonic anemometers
J	Rawinsondes (4/day): T, RH, wind speed, and wind direction in the vertical direction; launches at 0400 and 1600 PST to coincide with NWS launches at Vandenberg and Oakland; other launches at 1000 and 2200 PST
K	RWP with RASS: wind speed, wind direction, and T in the vertical direction continuously
L	DAS: wind speed and wind direction in the vertical direction continuously
M	Acoustic sounder: mixing height continuously
N	TSS 5A: special site for studying mixing and dispersion at low wind speeds
O	Visibility: light absorption from absorption measurements on Teflon filters, light scattering from nephelometers, COH; also includes MOUDIs
P	Mass and PM chemistry at BFK site only
Q	Collocated measurements: at BFK core site only
1	Installed for IMS95
2	Existing at nearby site

Table 3-8

Measurements Made during Winter Study

Measurement	Contractor	Temporal Scale	Core & Related Saturation Sites			Boundary Sites					Surface & Upper Air Meteorological Sites						Walnut Grove	
			FEL or Nearby FRE[1]	BFK or Nearby BAK[1]	KWR	Boundary A (SWC)[1]	Boundary B[1]	Boundary C[1]	FEL[1]	KRN[1]	CRT	Santa Ana	ELN	COR	MKR	MET	Tower	Base
			(Number of Samplers or Sites (Saturation Samplers); x=1)								(Number of Samplers or Sites (Saturation Samplers))							
PM-10																		
Dichot PM_{10} Mass	ARB	24 hour	FRE	BAK														
Dichot PM_{10} Elements	ARB	24 hour	FRE	BAK														
HiVol SSI PM_{10} Mass	ARB	24 hour	FRE	BAK														
HiVol SSI PM_{10} Ammonium	ARB	24 hour	FRE	BAK														
HiVol SSI PM_{10} Sulfate	ARB	24 hour	FRE	BAK														
HiVol SSI PM_{10} Nitrate	ARB	24 hour	FRE	BAK														
HiVol SSI PM_{10} Total Carbon (TC)	ARB	24 hour	FRE	BAK														
HiVol SSI PM_{10} Mass	ARB	24 hour		x														
HiVol SSI PM_{10} Nitrate	ARB	24 hour		x														
HiVol SSI PM_{10} Sulfate	ARB	24 hour		x														
HiVol SSI PM_{10} Ammonium	ARB	24 hour		x														
HiVol SSI PM_{10} TC	ARB	24 hour		x														
HiVol SSI PM_{10} Mass	WSO	24 hour							x	x								
HiVol SSI PM_{10} Sulfate	WSO	24 hour							x	x								
HiVol Total Suspended PM	ARB	24 hour	x	x														
HiVol Total Suspended PM	WSO	24 hour							x									
Portabe PM_{10} Mass @ Saturation Sites	DRI/STI	24 hour	x (25)	x (12)	x (5)		x (5)	x (5)										
Portabe PM_{10} Elements	DRI/STI	24 hour	x (13)	x (7)	x (1)		x (5)											
Portabe PM_{10} OC/EC	DRI/STI	24 hour	x (13)	x (7)	x (1)		x (5)											
Portabe PM_{10} Anions (SO_4, NO_3, Cl)	DRI/STI	24 hour	x (13)	x (7)	x (1)		x (5)											
Portabe PM_{10} Ammonium	DRI/STI	24 hour	x (13)	x (7)	x (1)		x (5)											
Portabe PM_{10} H_2O Soluble K	DRI/STI	24 hour	x (13)	x (7)	x (1)		x (5)											
Portabe PM_{10} B_{abs}	DRI/STI	24 hour	x (25)	x (12)	x (5)		x (5)	x (5)										
SFS PM_{10} Mass	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM_{10} Elements	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM_{10} OC/EC	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM_{10} Anions (SO_4, NO_3, Cl)	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM_{10} Ammonium	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM_{10} H_2O Soluble K	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM_{10} Volatilized Nitrate	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM_{10} B_{abs}	DRI/STI	24 hour	x	x (2)	x													
BAM PM_{10} Mass	DRI/STI	1 hour				x												
TEOM PM_{10} Mass	ARB	1 hour	x		x													
PM-2.5																		
Dichot $PM_{2.5}$ Mass	ARB	24 hour	FRE	BAK														
Dichot $PM_{2.5}$ Elements	ARB	24 hour	FRE	BAK														
SFS $PM_{2.5}$ Mass	DRI/STI	3 hour	x	x (2)	x	x												
SFS $PM_{2.5}$ Elements	DRI/STI	3 hour	x	x (2)	x	x												
SFS $PM_{2.5}$ OC/EC	DRI/STI	3 hour	x	x (2)	x	x												
SFS $PM_{2.5}$ Anions (SO_4, NO_3, Cl)	DRI/STI	3 hour	x	x (2)	x	x												
SFS $PM_{2.5}$ Ammonium	DRI/STI	3 hour	x	x (2)	x	x												
SFS $PM_{2.5}$ H_2O Soluble K	DRI/STI	3 hour	x	x (2)	x	x												
SFS PM2.5 B_{abs}	DRI/STI	3 hour	x	x (2)	x	x												
SFS $PM_{2.5}$ Volatilized Nitrate	DRI/STI	3 hour	x	x (2)	x	x												
SFS $PM_{2.5}$ Adsorbed OC	DRI/STI	3 hour	x	x (2)	x	x												

Table 3-8 (continued)

Measurements Made during Winter Study

Measurement	Contractor	Temporal Scale	Core & Related Saturation Sites			Boundary Sites					Surface & Upper Air Meteorological Sites						Walnut Grove	
			FEI or Nearby FRE[1]	BFK or Nearby BAK[1]	KWR	Boundary A (SWC)[1]	Boundary B[1]	Boundary C[1]	FEL[1]	KRN[1]	CRT	Sonic Sites	ELN	COR	MKR	MET	Tower	Base
			(Number of Samplers or Sites (Saturation Samplers), x=)								(Number of Samplers or Sites (Saturation Samplers)							
PM-2.5 (continued)																		
Portable $PM_{2.5}$ Mass	DRI/STI	24 hour					x (6)											
Portable $PM_{2.5}$ Elements	DRI/STI	25 hour					x (6)											
Portable $PM_{2.5}$ B_{abs}	DRI/STI	24 hour					x (6)											
RAM $PM_{2.5}$ Mass	DRI/STI	1 hour				x												
TEOM $PM_{2.5}$ Mass	DRI/STI	1 hour		No Data														
Special Studies for PM and Visibility																		
CADMP PM_{10} Mass	ARB	24 hour		x														
CADMP PM_{10} Ca, Mg, Na, K	ARB	24 hour		x														
CADMP PM_{10} NH_4	ARB	24 hour		x														
CADMP PM_{10} SO_4, NO_3, Cl	ARB	24 hour		x														
CADMP PM_{10} HNO_3	ARB	24 hour		x														
CADMP PM_{10} HNO_2	ARB	24 hour		x														
CADMP PM_{10} NH_3	ARB	24 hour		x														
CADMP PM_{10} SO_2	ARB	24 hour		x														
CADMP $PM_{2.5}$ Mass	ARB	24 hour		x														
CADMP $PM_{2.5}$ Ca, Mg, Na, K	ARB	24 hour		x														
CADMP $PM_{2.5}$ NH_4	ARB	24 hour		x														
CADMP $PM_{2.5}$ SO_4, NO_3, Cl	ARB	24 hour		x														
CADMP $PM_{2.5}$ HNO_3	ARB	24 hour		x														
CADMP $PM_{2.5}$ HNO_2	ARB	24 hour		x														
CADMP $PM_{2.5}$ NH_3	ARB	24 hour		x														
CADMP $PM_{2.5}$ SO_2	ARB	24 hour		x														
CE-CERT $PM_{2.5}$ Acid Deposition Sampler (ADS)	ARB	24 hour		x														
CE-CERT ADS $PM_{2.5}$ Mass	ARB	24 hour		x														
CE-CERT ADS NO_3, NO_2, SO_4	ARB	24 hour		x														
CE-CERT ADS NH_4+	ARB	24 hour		x														
CE-CERT ADS HNO_3	ARB	24 hour		x														
CE-CERT ADS HNO_2	ARB	24 hour		x														
CE-CERT ADS NH_3	ARB	24 hour		x														
HVOVI for Organic Aerosol Species	Caltech	24 hour	x	x	x													
MOVUI and Chemistry (Event-Based)	DRI/STI	6 hour		x														
VAPS	ARB/EPA	24 hour		x														
VAPS PM_{10} Mass	ARB/EPA	24 hour		x														
VAPS PM_{10} Sulfate	ARB/EPA	24 hour		x														
VAPS PM_{10} Nitrate	ARB/EPA	24 hour		x														
VAPS PM_{10} Elements	ARB/EPA	24 hour		x														
Nephelometer (B_{scat})	ARB	1 hour	FRE	BAK														
Nephelometer (B_{scat})	DRI/STI	1 hour	x	x	x	x												
COH	ARB	2 hour	FRE	BAK														
Filter-Based Gaseous																		
SFS Ammonia	DRI/STI	3 hour	x	x (2)	x	x												
SFS Nitric Acid	DRI/STI	3 hour	x	x (2)	x	x												
Portable Ammonia	DRI/STI	24 hour	x (25)	x (12)	x (5)		x (5)	x (5)										
Portable Nitric Acid	DRI/STI	24 hour	x (12)	x (7)	x (1)		x (5)											

Table 3-8 (continued)

Measurements Made during Winter Study

Measurement	Contractor	Temporal Scale	Core & Related Saturation Sites			Boundary Sites					Surface & Upper Air Meteorological Sites						Walnut Grove	
			FEI or Nearby FRE[1]	BFK or Nearby BAK[1]	KWR	Boundary A (SWC)[1]	Boundary B[1]	Boundary C[1]	FEL[1]	KRN[1]	CRT	Sonic Sites	ELN	COR	MKR	MET	Tower	Base
			(Number of Samplers or Sites (Saturation Samplers); x=1								(Number of Samplers or Sites (Saturation Samplers)							
Continuous Gaseous																		
CO	ARB	1 hour	FRE	BAK														
CO	DRI/STI	1 hour			x	x												
CO	WSO								x	x								
$NO/NO_2/NO_x$	ARB	1 hour	FRE	BAK														
$NO/NO_2/NO_x$	DRI/STI	1 hour			x	x											x	x
$NO/NO_2/NO_x$	WSO								x	x								
O_3	ARB	1 hour	FRE	BAK														
O_3	DRI/STI	1 hour			x	x												
O_3	WSO								x	x								
SO_2	ARB	1 hour	FRE	BAK													x	x
SO_2	DRI/STI	1 hour			x	x											x	x
SO_2	WSO								x	x								
Hydrocarbons (canisters C2—C12)	OGI/STI	3 hour	2/day	2/day														
Hydrocarbons (cartridges C10—C20)	OGI/STI	3 hour	2/day	2/day														
Hydrocarbons (canisters C2—C12)	OGI/STI	24 hour	x															
Hydrocarbons (cartridges (C10—C20)	OGI/STI	24 hour	x															
Carbonyls (cartridges C2—C7)	Atm/AA/STI	3 hour	2/day	2/day														
Carbonyls (cartridges C2—C7)	Atm/AA/STI	24 hour	x															
Total Hydrocarbons	ARB	1 hour	FRE	BAK														
Toxic Compounds (Xontech 910)	ARB	1 hour	FRE	BAK														
Ammonia (NH_3)/$NO/NO_2/NO_x$	STI/TEI	1 hour		x														
Fog (Event-Based)																		
CASCC2/CHRCC Water Content (Bulk Fog Sampler)	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC pH	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Nitrate	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Sulfate	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Ammonium	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Cl	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Na, K, Ca, Mg	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Fe, Mn	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Total Organic Carbon (TOC)	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Dissolved Organic Carbon (DOC)	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Organic Acids	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Hydroperoxides (H_2O_2 & Organics)	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Total S(IV)	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC HMS	CSU	20 min	x	x	x												x	x
CASCC2/CHRCC Formaldehyde	CSU	20 min	x	x	x												x	x
Collocated CASCC2 and Chemistry as above	CSU	20 min																x
CSASF Fog Drop Size Distribution	CSU	1 min			x													x
Entrainment — Differential Mobility Analyzer	CSU	continuous															x	
Size Fractionating CASCC Water Content	CSU	20 min			x													x
Size-Fractionating CASCC pH	CSU	20 min			x													x
Size-Fractionating CASCC Nitrate	CSU	20 min			x													x
Size-Fractionating CASCC Sulfate	CSU	20 min			x													x
Size-Fractionating CASCC Cl	CSU	20 min			x													x
Size-Fractionating CASCC Ammonium	CSU	20 min			x													x
Size-Fractionating CASCC Na, K, Ca, Mg	CSU	20 min			x													x

Table 3-8 (continued)

Measurements Made during Winter Study

Measurement	Contractor	Temporal Scale	Core & Related Saturation Sites			Boundary Sites					Surface & Upper Air Meteorological Sites						Walnut Grove	
			FEI or Nearby FRE[1]	BFK or Nearby BAK[1]	KWR	Boundary A (SWC)[2]	Boundary B[2]	Boundary C[1]	FEL[1]	KRV[1]	CRT	Sonic Sites	ELN	COR	MKR	MET	Tower	Base
			(Number of Samplers or Sites (Saturation Samplers); x=1								(Number of Samplers or Sites [Saturation Samplers]							
Fog (Event-Based) (continued)																		
Size-Fractionating CASCC Fe & Mn	CSU	20 min			x													x
Size-Fractionating CASCC Organic Acids	CSU	20 min			x													x
Size-Fractionating CASCC TOC	CSU	20 min			x													x
Size-Fractionating CASCC Hydroperoxides	CSU	20 min			x													x
Size-Fractionating CASCC Total S(IV)	CSU	20 min			x													x
Size-Fractionating CASCC HMS	CSU	20 min			x													x
Size-Fractionating CASCC Formaldehyde	CSU	20 min			x													x
IESL Cloud Impactor Water Content	CSU	1 hour			x													x
IESL Cloud Impactor pH	CSU	1 hour			x													x
IESL Cloud Impactor Nitrate	CSU	1 hour			x													x
IESL Cloud Impactor Sulfate	CSU	1 hour			x													x
IESL Cloud Impactor Ammonium	CSU	1 hour			x													x
IESL Cloud Impactor Cl	CSU	1 hour			x													x
IESL Cloud Impactor Na, K, Ca, Mg	CSU	1 hour			x													x
IESL Cloud Impactor Fe, Mn	CSU	1 hour			x													x
IESL Cloud Impactor TOC	CSU	1 hour			x													x
IESL Cloud Impactor Organic Acids	CSU	1 hour			x													x
IESL Cloud Impactor Hydroperoxides	CSU	1 hour			x													x
IESL Cloud Impactor Total S(IV)	CSU	1 hour			x													x
IESL Cloud Impactor HMS	CSU	1 hour			x													x
IESL Cloud Impactor Formaldehyde	CSU	1 hour			x													x
ETH Cloud Impactor Water Content	CSU	1 hour	x	x														
ETH Cloud Impactor pH	CSU	1 hour	x	x														
ETH Cloud Impactor Ammonia	CSU	1 hour	x	x														x
ETH Cloud Impactor Nitric Acid	CSU	1 hour	x	x														x
ETH Cloud Impactor Major Ions	CSU	1 hour	x	x														
Berner Aerosol Impactor and Major Ions	CSU	1 hour																x
Hydrogen Peroxide (gas phase, continuous)	NCAR/CSU	10 min		x	x													x
Organic Hydroperoxides (gas phase, continuous)	NCAR/CSU	10 min			x													
CSASP - Drop Size Distribution (optical method)	CSU	5 min			x													
Annular Denuder NH_3, HNO_3, SO_2	CSU	1 hour																x
Surface and Upper Air Meteorology																		
RWP/RASS (WS/WD, T)	ARB	continuous											x	x				
RWP/RASS (WS/WD, T)	STI	continuous													x	x		
OAS (WS/WD)	PG&E	continuous			x													
Sodar (Mixing Height)	WSO	continuous							x									
Rawinsonde (WS, WD, T, RH, P)	STI	15—20 min	4/day	4/day														
WS/WD (Standard Anemometer) (Surface)	ARB	1 hour	FRE	BAK														
WS/WD (Standard Anemometer) (Surface)	STI	1 hour			x	x		x			x						x	
WS/WD (Standard Anemometer) (Surface)	WSO	1 hour							x	x								
WS/WD (Sonic Anemometer) (Surface)	SAWV	1 hour																
Temperature (Surface)	ARB	1 hour	FRE	BAK														
Temperature (Surface)	STI	1 hour			x	x		x									x	
RH (Surface)	ARB	1 hour		BAK														
RH (Surface)	STI	1 hour			x	x		x									x	
Pressure (Surface)	ARB	1 hour															x	
Solar Radiation	ARB	1 hour		BAK														

Measurements Made during Winter Study

[1] FRE & BAK samplers were designed as an integral part of the study. Other samplers at those sites were supplemental.

[2] Boundary A [refers to SWC with high time resolution (3-hr) PM_{18} and $PM_{2.5}$ mass and chemistry, criteria pollutants, surface meteorology and other related measurements -- fog was not measured at this site.

[3] Boundary B [refers to boundary sites where chemical measurements were obtained].

[4] Boundary C [refers to boundary sites where only PM-10 mass, NH_3, and B_{ab}, measurements were obtained].

[5] West side operator sites reactivated for the study.

[6] WS/WD refers to wind speed/wind direction.

controlled through each filter pack, two per sampling period, at 20 l/min by maintaining a constant pressure across a valve with a differential pressure regulator. The remaining flow rate (73 l/min) needed by the inlet to obtain a 10-µm cutpoint was created by drawing the sample through a bypass port.

Two sets of filters, schematically shown as Unit 0 in Figure 3-18, were employed during each sampling period. One set used a Teflon front filter for PM_{10}, XRF for elements, B_{abs}, and a prefired quartz fiber backup filter for artifact OC. The second set used a prefired quartz fiber front filter for analyzing OC, EC, and ions and used an NaCl-impregnated cellulose backup filter for collecting HNO_3. The removable 47-mm-diameter Nuclepore filter holders were connected to the sampler via a quick-disconnect attachment for easy removal and installation, which took about 15 minutes, including the checking of flow rates.

During transport and storage in the field, all filters were stored in plastic resealable bags onsite in refrigerators at reduced temperatures. Prepackaged filters were transported between the laboratory and field via overnight shipping in coolers containing blue ice. In the laboratory, all filters were stored in a freezer until they were chemically analyzed.

3.3.1.2 Saturation Site Aerosol Measurements

Saturation sites employed battery-powered portable samplers (the Minivol Portable Survey Sampler from Airmetrics, in Springfield, Oregon) (Chow and Egami 1997) that were placed at 3 m agl, usually on utility poles. These samplers consisted of a pump, timer, tubing and fittings, removable filter holder, flow meter, impactor inlet ($PM_{2.5}$ or PM_{10}), and battery pack. All parts were packaged in a plastic cylindrical enclosure 18 cm in diameter and 46 cm long. A carrying handle allowed the sampler to be suspended from a hook or hanging bracket. The sampler weighed 8 kg, most of which was the weight of the battery. The sampler was placed at and removed from elevated locations with a grappling pole.

Removable 47-mm-diameter Nuclepore filter holders were connected to the sampler via a quick-disconnect attachment. Single or multiple filter holders were used. The filter substrate depended on the species of interest and the chemical analysis method. Two removable battery packs accompanied each sampler so that one was charging while the other was sampling. Every time a filter was changed, the spent battery was replaced by a fresh battery.

PM_{10} was collected by the saturation sampler through an inlet that has a real impactor with a 50% collection efficiency at 10 µm aerodynamic diameter. A small amount of vacuum grease was used on the impaction plate to trap the larger particles. The sampler's nominal flow rate was 5 l/min. At this flow

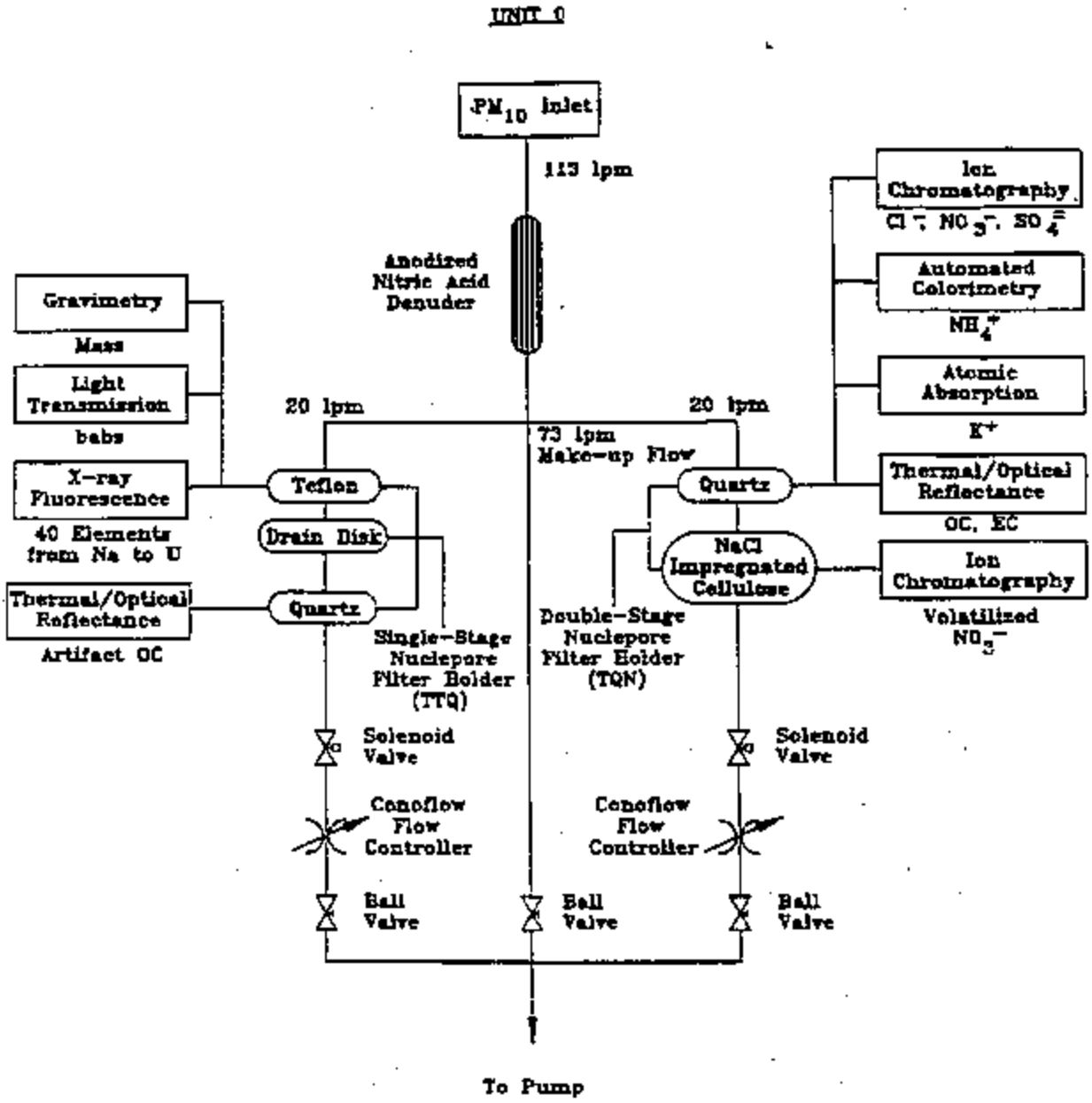


Figure 3-18. SFS configuration for PM_{10} mass and chemistry during the Fall study.

rate, the pump can operate for over 24 hours with a fully charged battery pack. Flow rates were determined by an external calibrated rotameter (0–10 l/min scale) and verified by an inline rotameter. A programmable 7-day, 24-hour internal timer kept clock time and turned the sampler on and off at prearranged times. Two samplers were deployed at each site for each set of measurements, as shown schematically in Figures 3-19 and 3-20. One set (Figure 3-19, Unit A) used a Teflon filter for PM_{10} mass and B_{abs} and a backup citric-acid-impregnated cellulose filter for NH_3. The second set was used at sites where chemical composition was to be determined. This set (Figure 3-20, Unit B) included a prefired quartz-fiber front filter for carbon analysis and ions and an NaCl-impregnated cellulose filter for collecting HNO_3. If the site had been designated for chemical analysis, then the front Teflon filter in the first set was also analyzed for elements by XRF. With two sets of samplers, filters for one set could be installed the day before sampling and removed the day after sampling while the other set was collecting samples. During transport and storage in the field, all filters were stored in plastic resealable bags onsite in refrigerators at reduced temperatures. Prepackaged filters were transported between the laboratory and field via overnight shipping in coolers containing blue ice. In the field, before and after sampling, filters were stored in an airtight cooler. In the laboratory, all filters were stored in a freezer until they were chemically analyzed.

3.3.2 Aerosol and Gas Phase Species Measurements—Winter Study

3.3.2.1 Core Sites and SWC

Air quality measurements were carried out at the three core monitoring sites (BFK, FEI, and KWR) and the Boundary A site at SWC (Figure 3-2). Several types of samplers were employed and operated on different sampling schedules, including samplers operated over 3-hour and 24-hour sampling periods, continuous samplers, and samplers operated on an event basis. Table 3-7 lists the general site measurements, and Table 3-8 lists site measurements by species.

Core site aerosol and related gas phase measurements included (1) PM_{10} and $PM_{2.5}$ mass and chemical composition and PM precursor species (HNO_3, SO_2, and NH_3) collected on filters with a 3-hour sampling frequency throughout the course of the study; (2) continuous PM_{10} or $PM_{2.5}$ collected via inertial or beta attenuation and continuous particle scattering by nephelometers; (3) speciated hydrocarbons (C_2–C_{20}) and carbonyl species two or three times per day and speciated organic aerosols once per day; and (4) a series of special measurements, including micro-orifice uniform deposit impactor (MOUDI) measurements, continuous $NO/NO_X/NH_3$, and continuous EC. These measurements and methods are described in more detail below.

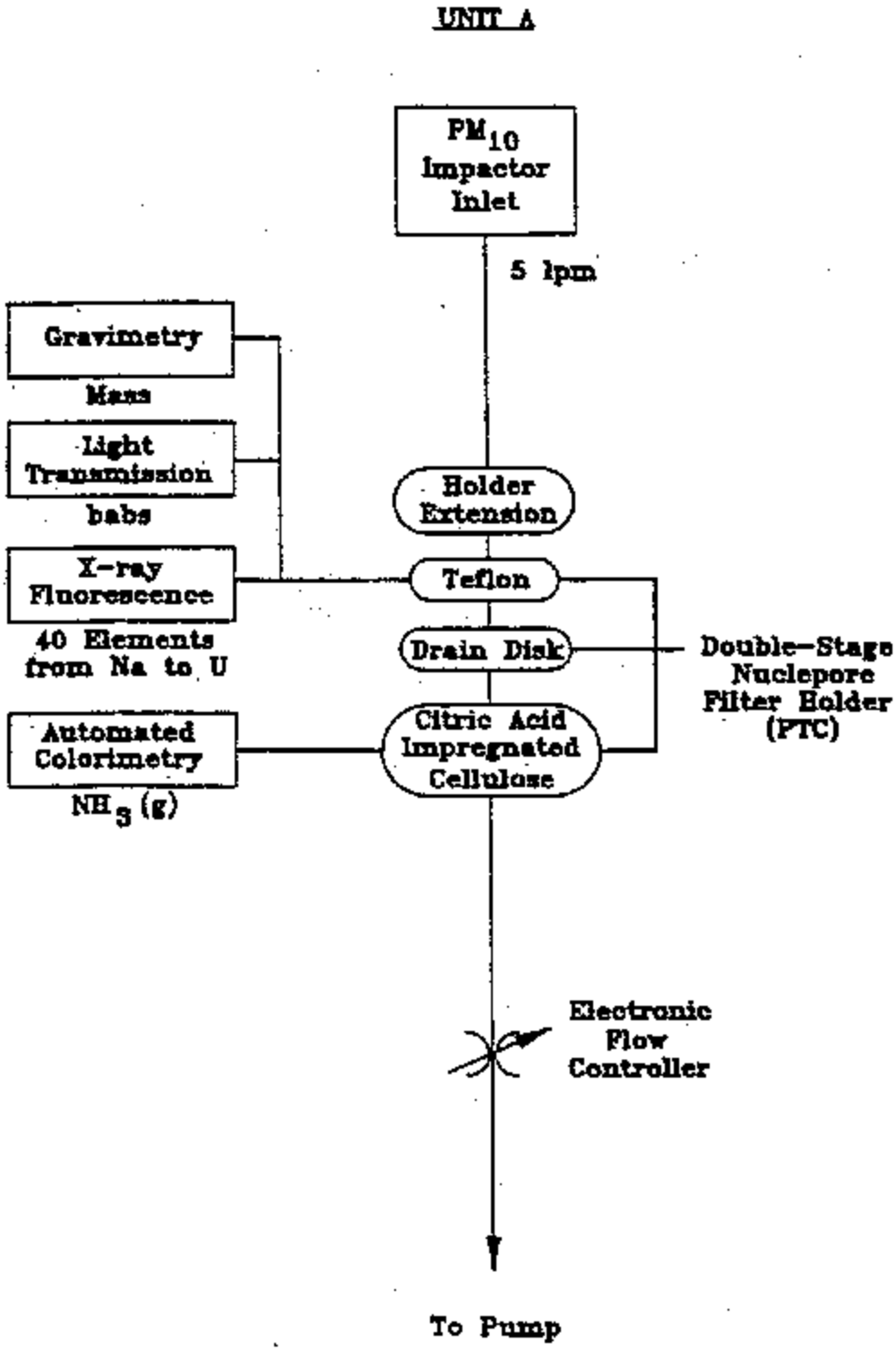


Figure 3-19. Portable filter sampler (SFS) configuration for PM_{10} mass, B_{abs}, elements, and NH_3 during the Fall and Winter studies.

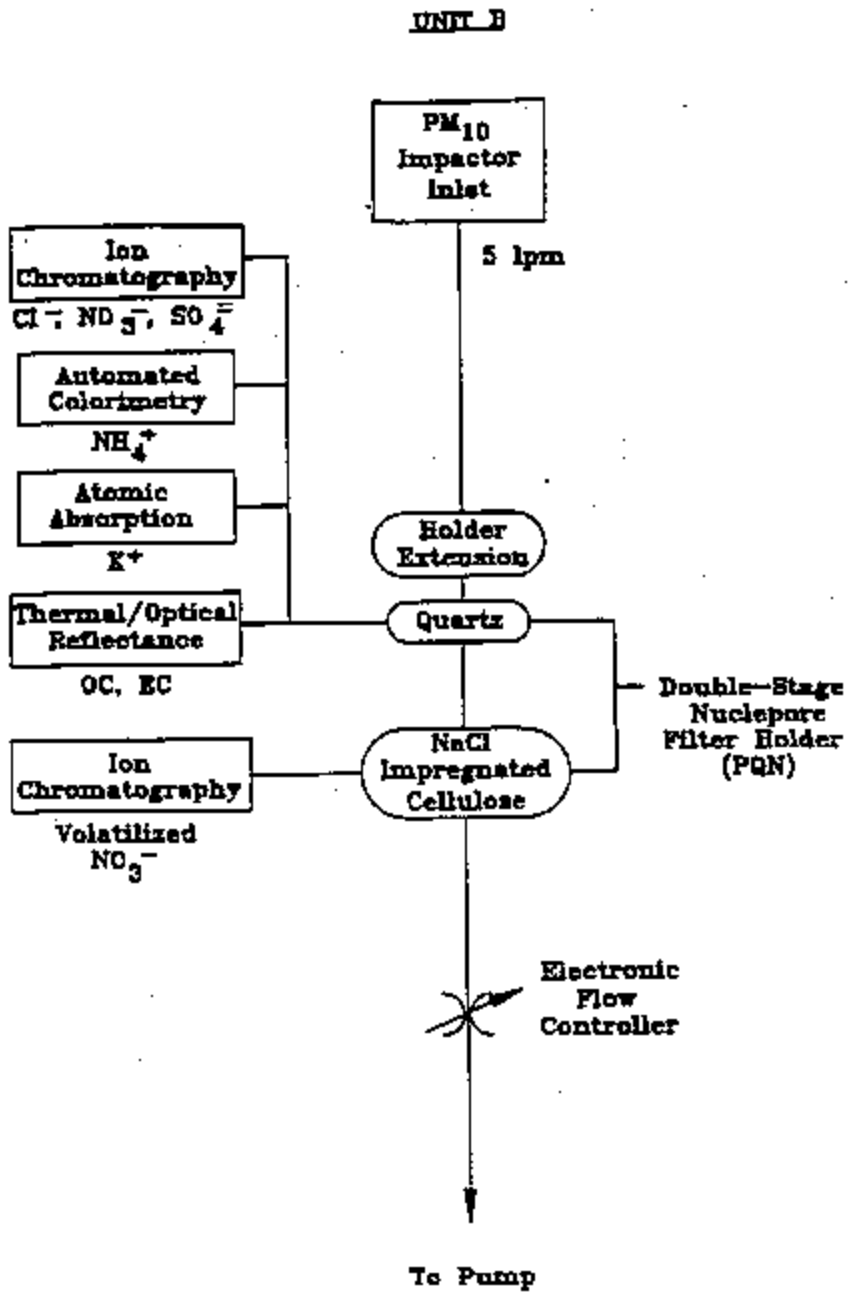


Figure 3-20. Portable filter sampler (SFS) configuration for PM_{10} chemistry during the Fall and Winter studies.

3.3.2.1.1 3-Hour Average Aerosol Sampling

Eight medium-volume sequential sampling systems were employed at each site where 3-hour aerosol measurements were to be obtained (BFK, FEI, KWR, and SWC) to determine the diurnal variations and optimal averaging times for $PM_{2.5}$, PM_{10}, and PM precursor gas samples. Table 3-9 lists the sampling times, measurement methods, and analytical methods for the short-duration 3-hour samplers. Two types of modified sequential sampling systems were used: the SFSs that collected aerosols on filters and the SGSs that collected gas phase species on reactive filters. Denuders were used in the SFSs to remove reactive gases, thus allowing particles to pass through to the filter, while Teflon coatings or open-face filter sampling were used for SGSs, thus allowing gases and particles to pass through to filters. Each sampler was targeted for a specific set of species, because of the high sampling frequency that required high flow rates. The filter-pack sampling systems included the following components:

- Two PM_{10} SFSs with aluminum-oxide-coated nitric acid denuders (Figure 3-21).
- Two $PM_{2.5}$ SFSs with aluminum-oxide-coated nitric acid denuders (Figure 3-22).
- Two SGSs, each with a PFA Teflon-coated $PM_{2.5}$ inlet—one with a citric-acid-coated denuder and one without; both used citric-acid-impregnated filters to efficiently collect NH_3 and NH_4^+ (Figure 3-23).
- Two open-faced SGSs, one with an anodized aluminum denuder and one without; both used NaCl-impregnated cellulose filters for efficient collection of HNO_3 and nitrate (Figure 3-24).

The SFS operated by drawing air through an SSI, through a denuder, and then through the filter media. The SGS operated by drawing air either directly through the filters (open-faced) or first through an inlet and/or denuders and then through the filters. Except for the open-faced samplers, all filters were located inside the sampler's plenum.

The SFS was designated as an EPA PM_{10} reference sampler when equipped with a Sierra-Andersen SA-254I PM_{10} SSI (Chow and Watson 1994a). The $PM_{2.5}$ SFS used a Bendix 240 cyclone. Both the $PM_{2.5}$ and PM_{10} inlets provided their specified 50% cutpoints at an inlet flow rate of 113 l/min. Flow rates were set with a calibrated rotameter and were monitored with the same rotameter at each sample changeout. Because of the sequential sampler, with its 12 sequential or parallel ports, there was no need for an operator to be present at every sample changing interval. In fact, during the Winter study, only one port was operated in each sampler during any given sampling period, because the maximum flow rate through the inlets (113 l/min) was adequate for the short 3-hour sampling period and still provided a sufficient sample for chemical analysis. Thus, filters were changed only once per day in the afternoon, when PM levels were usually at their lowest.

Table 3-9

Core Site Aerosol Sampling Schedule and Measurement and Analytical Methods—Winter Study

Measurement	Site	Sampling Times	Measurement Method	Analytical Method
PM_{10}	BFK FEI KWR SWC	0000–0300 PST 0300–0600 PST 0600–0900 PST 0900–1200 PST 1200–1500 PST 1500–1800 PST 1800–2100 PST 2100–2400 PST	DRI modified SFS with SA-2541 PM_{10} inlet and aluminum oxide nitric acid denuders	Mass: gravimetric analysis on Teflon membrane filters Elements: XRF analysis on Teflon membrane filters Ions: ion chromatographic analysis on quartz fiber filter extracts Na and K: atomic absorption spectrophotometry on quartz fiber filters EC/OC: thermal/optical reflectance carbon analysis on quartz fiber filters
$PM_{2.5}$	BFK FEI KWR SWC	0000–0300 PST 0300–0600 PST 0600–0900 PST 0900–1200 PST 1200–1500 PST 1500–1800 PST 1800–2100 PST 2100–2400 PST	DRI SFS with Bendix 240 Cyclone and aluminum oxide nitric acid denuders	Mass: gravimetric analysis on Teflon membrane filters Elements: XRF analysis on Teflon membrane filters Ions: ion chromatographic analysis on quartz fiber filter extracts Na and K: atomic absorption spectrophotometry on quartz fiber filters EC/OC: thermal/optical reflectance carbon analysis on quartz fiber filters
$PM_{2.5}$ ammonia and ammonium	BFK FEI KWR SWC	0000–0300 PST 0300–0600 PST 0600–0900 PST 0900–1200 PST 1200–1500 PST 1500–1800 PST 1800–2100 PST 2100–2400 PST	DRI SFS with PFA-coated Bendix 240 Cyclone inlet and plenum using the denuder difference method and impregnated filters	NH_3 and NH_4^+: Technicon automatic colorimetry on quartz fiber filter extracts

Table 3-9 (continued)

Core Site Aerosol Sampling Schedule and Measurement and Analytical Methods—Winter Study

Measurement	Site	Sampling Times	Measurement Method	Analytical Method
Nitric acid and hydrochloric acid	BFK FEI KWR SWC	0000–0300 PST 0300–0600 PST 0600-0900 PST 0900–1200 PST 1200–1500 PST 1500–1800 PST 1800–2100 PST 2100–2400 PST	DRI sequential filter pack sampler with anodized nitric and hydrochloric acid annular denuder	
PM_{10}	BFK	Continuous	TEOM	
$PM_{2.5}$	BFK	Continuous	TEOM	
PM_{10}	FEI	Continuous	TEOM	
PM_{10}	KWR	Continuous	TEOM	
PM_{10}	SWC	Continuous	BAM	
$PM_{2.5}$	SWC	Continuous	BAM	
Particle light scattering	BFK	Continuous	Open-air integrating nephelometer	

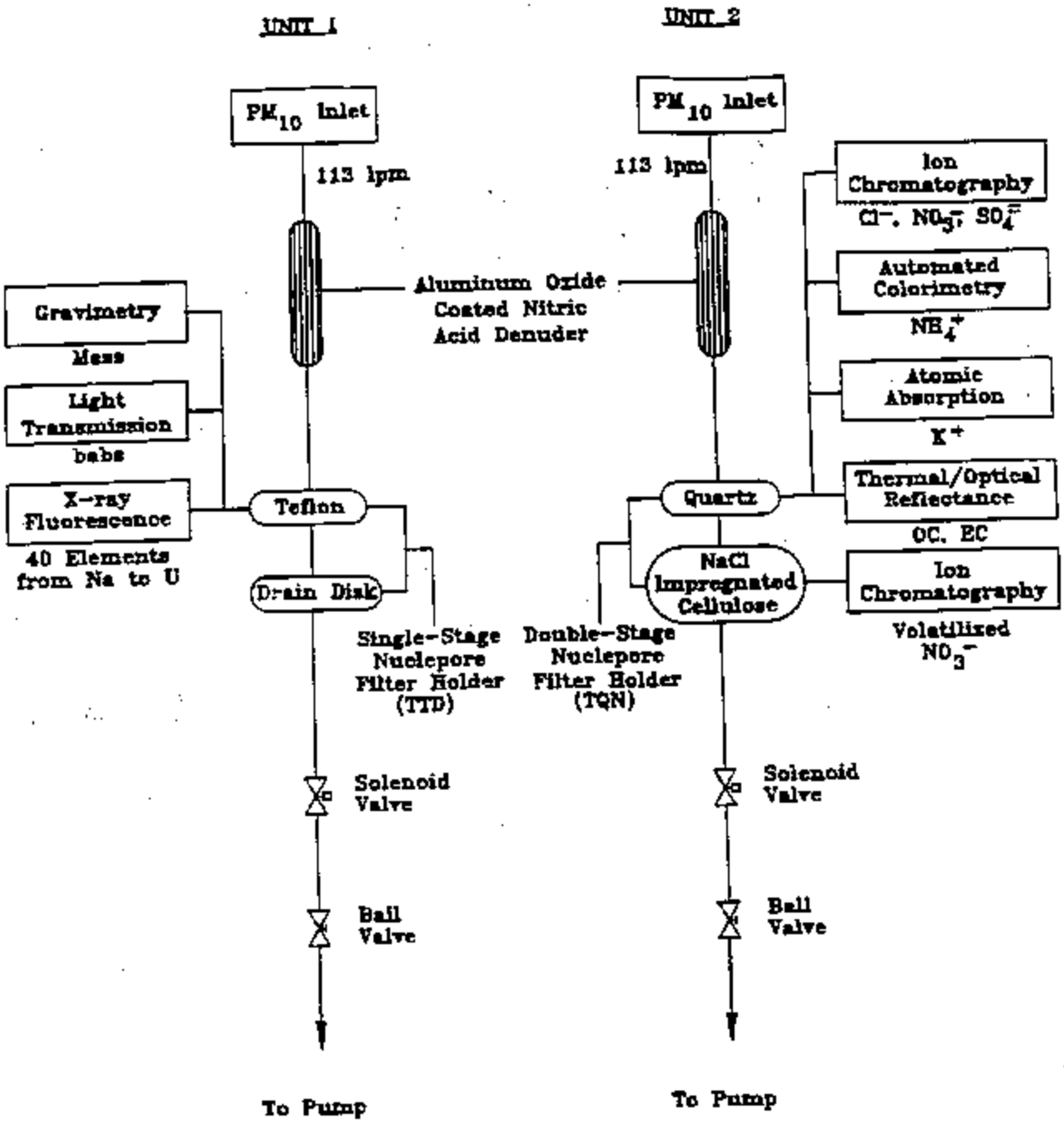


Figure 3-21. SFS configuration for PM_{10} mass and chemistry during the Winter study—Units 1 and 2, with HNO_3 denuders.

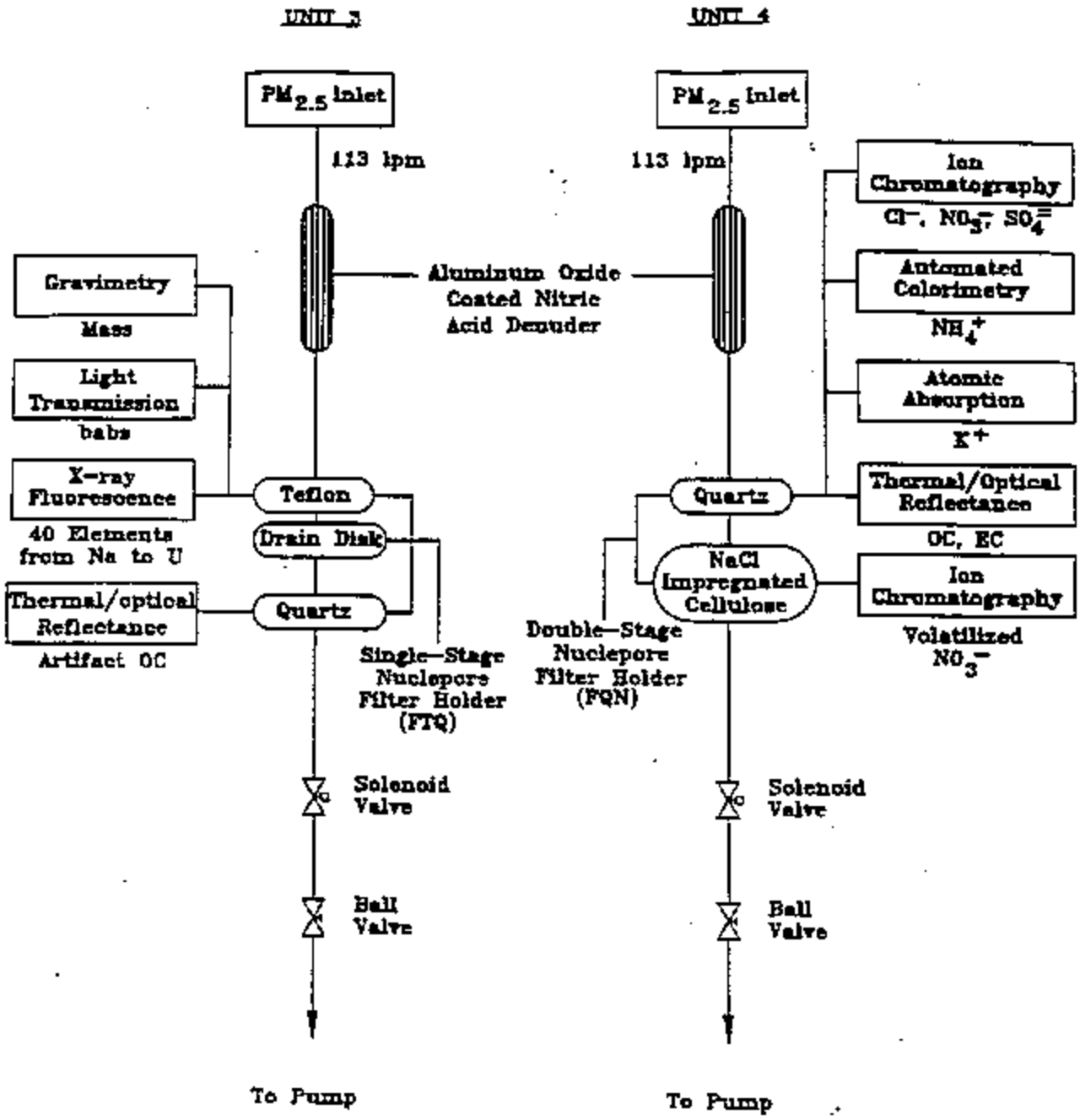


Figure 3-22. SFS configuration for PM_{10} mass and chemistry during the Winter study—Units 3 and 4, with HNO_3 denuders.

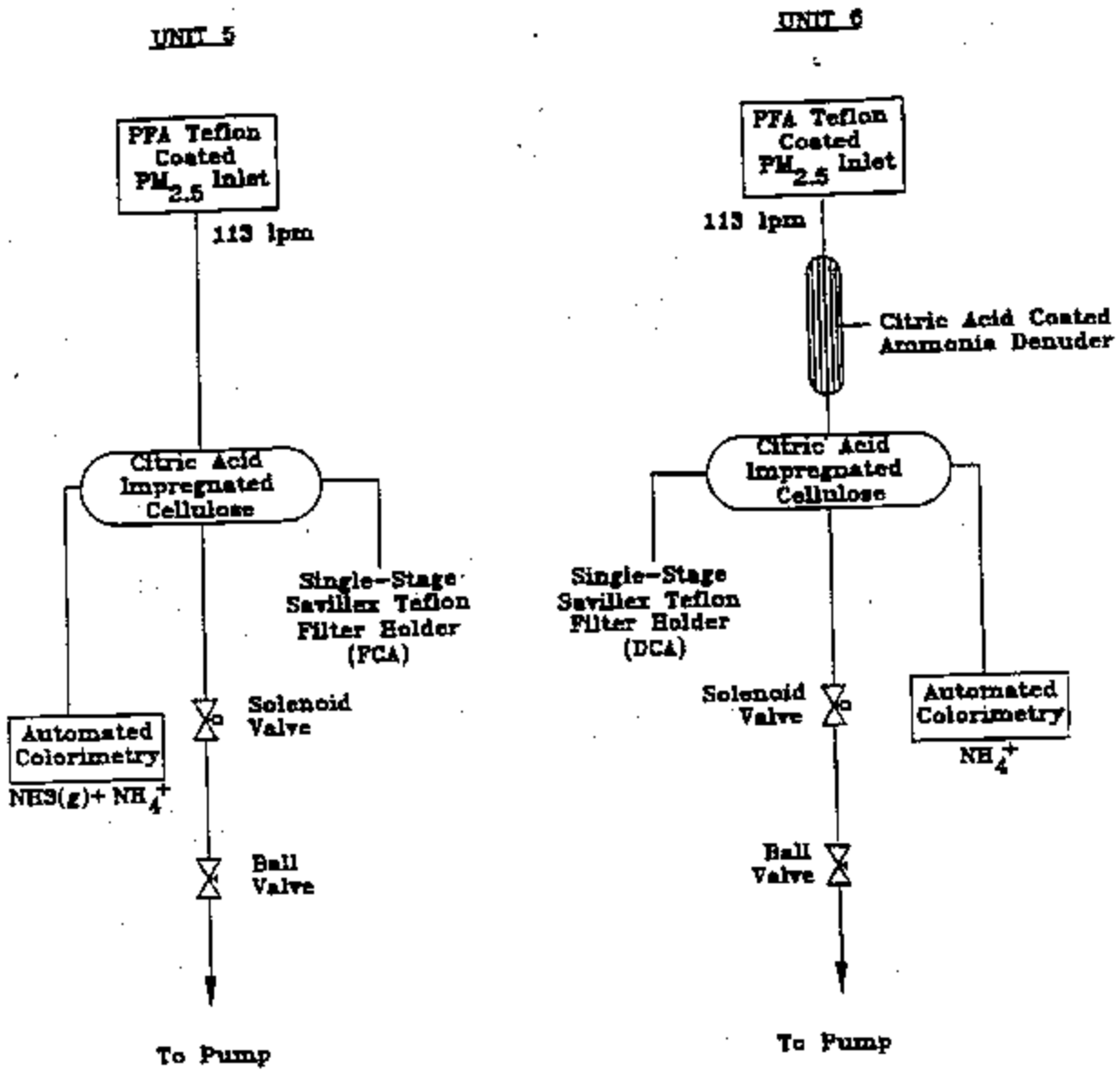


Figure 3-23. SGS configuration for ammonia and $PM_{2.5}$ ammonium during the Winter study—Units 5 and 6, sampling ammonia by the denuder difference method.

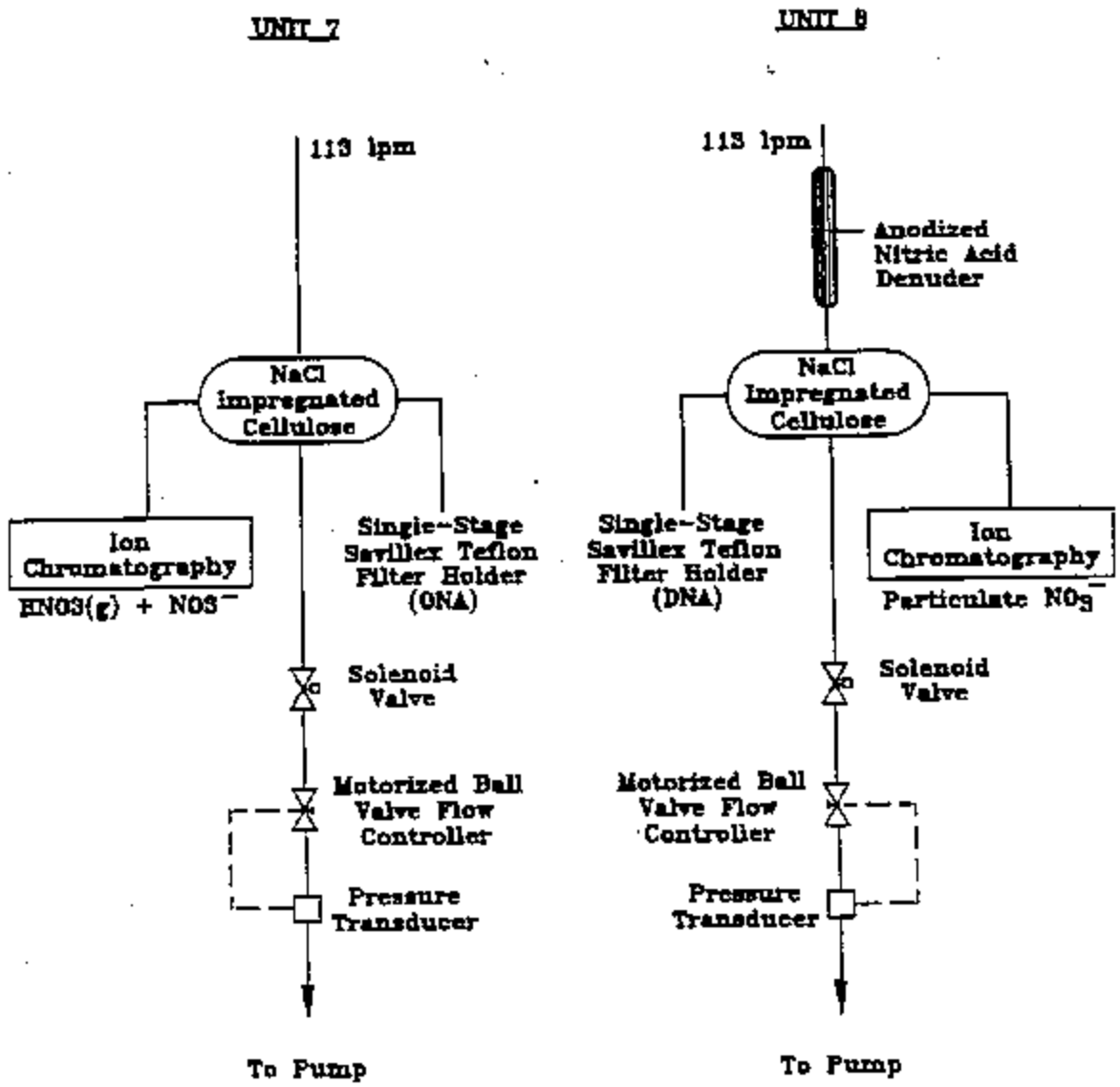


Figure 3-24. SGS configuration for nitric acid and total particulate nitrate during the Winter study—Units 7 and 8, sampling ammonia by the denuder difference method.

Figures 3-21 through 3-24 schematically show the SFS and SGS sampling configurations and list the species collected on each filter and the chemical analysis method that determined the amount of the species on the filter. Several different filter media were used either individually or in series with a second and different filter medium to optimize the choice of a chemical analysis method and, in some cases (Units 2–4 in Figures 3-21 and 3-22), to account for possible interferences or artifacts that can occur with filter-based methods.

Interferences can occur when filter-based sampling collects OC and ammonium nitrate (NH_4NO_3). The sampling systems were designed to eliminate the artifacts or to help estimate their magnitude (Chow and Egami 1997). For accurate collection of NH_4NO_3, a reactive filter (NaCl-impregnated cellulose fiber) was placed behind a quartz fiber filter, which was behind a denuder (Figures 3-20 through 3-22). The denuder removes HNO_3, the quartz filter collects the aerosol NH_4NO_3, and the reactive filter (NaCl) collects volatilized nitrate, thus providing an accurate estimate of the nitrate lost from the Teflon filters where aerosol mass was determined. However, the volatilized nitrate was not measured as part of the PM_{10} or $PM_{2.5}$ mass; and therefore, should not be added to the nitrate collected on the front quartz fiber filter (Units 0, 2, and 4) for mass balance purposes. Volatilized nitrate does provide a better estimate of total nitrate in the air if equilibrium modeling is to be performed.

In OC collection on quartz filters, there is a potential positive artifact from semivolatile or reactive organic gases that adsorb onto the quartz fiber filters or a potential negative artifact from volatilization of the collected aerosol during or after sampling (Eatough et al. 1990, McDow and Huntzicker 1990, Tang et al. 1994, Turpin et al. 1994, Chow et al. 1996). The magnitude of the positive artifact was estimated by placing a quartz fiber filter behind a Teflon filter, as shown in Figures 3-18 and 3-22 (Units 0 and 3). This estimate was complicated because, in this sampling scheme, it is not known whether volatilized OC from the Teflon filter was also being adsorbed onto the backup quartz fiber filter. Therefore, the result was an upper bound on the potential for a positive artifact, but there was no estimate of the potential negative artifact; the latter estimate probably requires a denuder system, as was used with nitrate/HNO_3.

Nitric acid was determined by the denuder difference method (Units 7 and 8, Figure 3-24), in which the difference between total nitrate (Unit 7, particulate nitrate plus gaseous nitric acid) and particulate nitrate (Unit 8) yields the nitric acid concentration. For IMS95, the HNO_3 denuder consisted of a series of anodized aluminum (aluminum-oxide-coated) tubes to remove HNO_3 (John et al. 1988). Results from the nitrogen species comparison study (Hering et al. 1988) indicated that HNO_3 concentrations obtained by the denuder difference method were not significantly different, under the conditions studied, from

those obtained by the Fourier transform infrared (FTIR) spectroscopy method, which was considered the reference method for HNO_3. For IMS95, ammonia was also determined by the denuder difference method at the core sites by using citric-acid-coated aluminum tubes. This method was not evaluated in the NSMCS.

Because of the reactivity of HNO_3 and NH_3, all components of the SGS upstream of the filters were coated with PFA Teflon, which has shown the lowest inclination to absorb nitric acid or any other reactive gaseous species. Savillex 47-mm filter holders made of injection-molded PFA Teflon were used in the SGSs. Several grids and grid rings were stacked within the holder to obtain series filtration. The Savillex support grid was replaced by a grid manufactured by ATEC, Inc. (in Calabasas, California), which was especially designed for dry deposition monitoring. This support grid's uniform porosity results in a uniform filter deposit that is more suitable for chemical analyses that do not require the entire filter. The ATEC grid also reduced the flow resistance across the filter holder.

3.3.2.1.2 Continuous Aerosol Sampling and Related Continuous Monitoring

In addition to the 3-hour PM mass samples collected by the SFS and SGS, several continuous samplers and monitors were deployed, including TEOMs, BAMs, nephelometers, and an aethelometer. These instrument methods assessed temporal variations within the 3-hour filter-based sampling. Using these instruments also made it possible to evaluate their effectiveness under SJV winter conditions for future monitoring.

3.3.2.1.2.1 TEOM Monitor

PM_{10} TEOMs were operated at FEI and KWR, and two collocated $PM_{2.5}$ TEOMs were operated at BFK. The TEOM (Patashnick and Rupprecht 1991, Rupprecht et al. 1992) has received EPA PM_{10} equivalence status for compliance monitoring. The TEOM uses a small filter mounted on the narrow end of a hollow tapered tube. The wider end of the tube is fixed, and the narrow end oscillates in response to an applied electric field. Air is drawn into a low-volume PM_{10} inlet, then through a filter and tapered tube leading to a flow controller. The oscillation frequency changes as the mass loading on the filter increases. PM_{10} concentrations are then calculated by comparing the measured frequency with standards.

Normal operating conditions for the TEOM are 3 l/min and 50° C for the inlet line temperature. However, under these conditions, negative artifacts have been noted for aerosol OC and ammonium nitrate. This type of artifact is due to volatilization of these species from the aerosol, either before collection while in the inlet tube, or after aerosol collection on the filter. Since aerosol nitrate and OC

were expected to be a significant fraction of the Winter study aerosols, the TEOMs were operated at conditions that would minimize loss of the semivolatile species (1 l/min and 30° C). Unexpectedly, however, the high humidity and occurrence of fog under these milder temperature and flow rate conditions caused significant moisture effects—negative numbers were observed as the filters dried out during the morning, when the humidity was lower, and higher mass concentrations were probably observed as humidity increased during the late afternoon and evening. Therefore, the TEOM data at FEI and KWR have been flagged as invalid, and the TEOM data at BFK have been removed from the final database archive. R&P, which had provided the BKF TEOMs at no cost, requested this removal of BFK data. Even though the FEI and KWR sites operated under the same conditions, their TEOM data remain in the final data archive, because the units at those sites were provided by ARB, and there were no specific requests to remove the data. However, similar humidity effects were observed with the FEI and KWR TEOMs.

3.3.2.1.2.2 BAM

Two collocated BAMs were operated at SWC during the Winter study; one collected PM_{10}, and the other collected $PM_{2.5}$. The BAM (from Graseby-Andersen) has received EPA PM_{10} equivalence status when an approved inlet is used, and it can make continuous measurements over averaging times as short as half an hour. In the BAM (Husar 1974, Macias and Husar 1976), beta rays (moderately-high-energy electrons) emitted by a radioactive source are directed through particles deposited on a filter, resulting in beta ray absorption or attenuation by the particles. Relevant theory and standards are then applied to relate the attenuation to the particle mass collected on the filter. In the BAM, a filter tape is pulled across the path between the beta ray emitter and a detector to measure blank attenuation, then across a sampling area where particles are collected on the tape, and finally through the detector area to measure the attenuation of the filter and the deposit.

3.3.2.1.2.3 Nephelometer

Four Optec NGN-2 open-air integrating nephelometers were operated at the three core sites (BFK, FEI, and KWR) and the Boundary A site (SWC) where 3-hour average aerosol measurements were obtained. Integrating nephelometers estimate the aerosol light scattering coefficient (B_{scat}) by directly measuring the light scattered by aerosols and gases in a sampled air volume. Scattered radiation from an illumination source is integrated over a large range of scattering angles in a defined band of visible wavelengths. The total light scattered out of the path is the same as the reduction of light along the path caused by scattering, thus enabling the integrating nephelometer to provide a direct estimate of B_{scat}.

Several versions of integrating nephelometers have been used in routine monitoring networks or visibility studies. The Optec NGN-2 unit provides continuous measurement of ambient B_{scat} measured at 550 nm. This unit can be programmed to provide three primary options for sampling and calibration: (1) continuous 2-minute integration, (2) single 10-minute integrations starting at the beginning of each hour, or (3) 2-minute integration followed by a 3-minute, low-power vent mode. The nephelometer calibration procedure is typically a clean-air zero calibration at 6-hour or 24-hour intervals, depending on aerosol levels and weekly span gas calibrations. Factory validation of the calibration is performed yearly with backscatter measurements of clean air and with a standard gas (SUVA134A) whose scattering coefficient is known.

3.3.2.1.2.4 Aethalometer

The aethalometer (from Magee Scientific in Boulder, Colorado) measures aerosol black carbon or "soot" in real time in the atmosphere with detection limits below 1 $\mu g/m^3$. The aerosol is continuously collected at flow rates of about 5 to 10 l/min on quartz fiber filters whose optical absorption has been determined. Since the absorption coefficient of soot is over 10,000 times greater than that of other aerosol species, the absorption is accurately interpreted as a mass of aerosol black carbon on the filter (Hansen et al. 1984). The rate of decrease of optical transmission is proportional to the rate of increase of the loading of optically absorbing "black" carbon or EC aerosol collected on the filter. The optical absorption measurement method on quartz fiber filters has been calibrated against a chemical determination of EC by solvent extraction pretreatment followed by thermal evolved gas analysis (Gundel et al. 1984). During the 1986 Carbonaceous Species Methods Comparison Study (CSMCS) conducted by ARB in Glendora, California (Fung and Wright 1990, Lawson et al. 1990a), the aethalometer compared well with methods that measure EC by thermal optical properties and transmission (McMurry and Zhang 1988).

During the Winter study, one aethalometer was operated at BFK in one of the instrument trailers, with the inlet line extending from the top of the trailer. Aerosol black concentrations were measured with 5-minute averaging times. Since fog was expected at the site, a screen was placed on the front of the inlet line to determine EC in the fog droplets or in the interstitial air during fogs. This was accomplished by having a two-way inlet at the front of the inlet line and allowing switching between the two. If fog droplets were present, then they were removed by the screen, thus measuring EC aerosols in the interstitial air between fog droplets. The inlet line without the screen measured EC in both the fog droplets and the air between droplets. The difference between the two represents EC aerosols within fog droplets. Previous measurements of EC in this manner have determined a significant portion of the EC in the fog droplets (Hansen 1995, private communication).

3.3.2.1.3 Daily or Event-Based Aerosol Measurements

Daily and event-based aerosol measurements included the collection of (1) 24-hour average size-fractionated samples for organic aerosol species via a high-volume dichotomous virtual impactor (HVDVI); (2) 24-hour average samples for mass and elemental analysis via a Versatile Air Pollution Sampler (VAPS); (3) 24-hour average samples for mass, elemental analysis, inorganic ions, HNO_3, and NH_3 via a CE-CERT denuder sampler and a California acid deposition sampler; and (4) highly size-resolved aerosols via Multiple Oriface Uniform Deposit Impactor (MOUDI) samplers.

3.3.2.1.3.1 HVDVI Samples for Organic Aerosol Species

Total and fine aerosol samples were collected daily from noon to noon at the three core sites via an High Volume Dichotomous Virtual Impactor (HVDVI) (Solomon et al. 1983) and analyzed for size-resolved organic aerosol species. The HVDVI was operated at a flow rate of 350 l/min, to collect aerosols in two size fractions—less than about 3 μm aerodynamic diameter (AD) and greater than about 3 μm AD. Samples were collected on 110-mm prefired quartz fiber filters that were baked at 600° C for at least two hours and then sealed in baked aluminum foil and baked glass jars. During storage, transport, and before and after sampling, filters were kept at low temperatures (<0° C) to reduce contamination and minimize loss of the semivolatile species after collection.

In the laboratory, samples were extracted in organic solvents, derivatized, and analyzed by high-resolution gas chromatography (HRGC) and gas chromatography-mass spectrometry (GC-MS) (Rogge et al. 1993a-f, Rogge 1993). This chemical analysis method, which is described further in Section 3.3.4.1.2, has identified approximately 100 individual organic species in ambient samples (Table 3-10) (Schauer et al. 1996). Schauer et al. (1996) were able to perform chemical mass balance (CMB) receptor modeling based on the organic compounds identified in Los Angeles aerosols and previously obtained source profiles. The results identified and quantified source-receptor impacts from nearly a dozen sources that are usually too similar to identify via standard CMB input data.

3.3.2.1.3.2 MOUDI Samples for Chemical Analysis of Major Components

The MOUDI sampler, which was operated only at BFK, collected samples on an event basis for 56 sampling periods. Sampling periods were 6 hours long and overlapped two of the 3-hour SFS/SGS sampling periods. The objectives of this schedule were to sample relatively dry periods between fog occurrences (1200–1800 PST), relatively wet periods (RH > 70%–80%) between fogs and after secondary reactions (0600–1200 PST), periods when wood smoke might be most prevalent (1800–2400 PST), and periods when fresh motor vehicle emissions might be most prevalent (0300–0900 PST).

Table 3-10

Compounds Available for Possible Use in Receptor Modeling Studies*

Compound	Range of Average Ambient Fine Particulate Concentration (ng/m³)	Used In Receptor Model
n-Alkanes		
n-Tricosane	3.2-6.7	Yes
n-Tetracosane	3.9-5.0	Yes
n-Pentacosane	6.7-11.2	Yes
n-Hexacosane	4.3-8.2	Yes
n-Heptacosane	5.2-6.7	Yes
n-Octacosane	2.1-3.1	Yes
n-Nonacosane	4.7-7.1	Yes
n-Triacontane	2.4-2.7	Yes
n-Hentriacontane	9.3-12.6	Yes
n-Dotriacontane	1.0-1.5	Yes
n-Tritriacontane	1.5-2.3	Yes
n-Tetratriacontane	0.36-0.68	Yes
iso- and anteiso-Alkanes		
anteiso-Triacontane	<0.03-0.23	Yes
iso-Hentriacontane	0.73-1.50	Yes
anteiso-Hentriacontane	<0.03-0.12	Yes
iso-Dotriacontane	<0.03-0.13	Yes
anteiso-Dotriacontane	0.89-1.31	Yes
iso-Tritriacontane	0.30-0.33	Yes
Hopanes and Steranes		
20S&R-5α(H),14beta(H),17β(H)-Cholestanes	0.34-1.18	Yes
20R-5α(H),14α(H),17α(H)-Cholestane	0.34-1.23	Yes
20S&R-5α(H),14β(H),17β(H)-Ergostanes	0.51-1.75	Yes
20S&R-5α(H),14β(H),17β(H)-Sitostanes	0.52-1.67	Yes
22,29,30-Trisnorneohopane	0.32-0.93	Yes
17α(H),21β(H)-29-Norhopane	0.66-2.42	Yes
17α(H),21β(H)-Hopane	1.32-4.02	Yes
22S-17α(H),21β(H)-30-Homohopane	0.52-1.42	Yes
22R-17α(H),21β(H)-30-Homohopane	0.36-1.06	Yes
22S-17α(H),21β(H)-30-Bishomohopane	0.33-0.84	Yes
22R-17α(H),21β(H)-30-Bishomohopane	0.20-0.58	Yes
n-Alkenoic acids		
cis-9-n-Octadecenoic acid	17.3-26.0	Yes
Aldehydes		
Nonanal	5.7-9.5	Yes
n-Alkanoic acids		
n-Nonanoic acid	3.3-9.9	No[a]
n-Decanoic acid	1.3-3.1	No[a]
n-Undecanoic acid	2.8-6.0	No[a]
n-Dodecanoic acid	3.7-7.0	No[a]
n-Tridecanoic acid	3.3-4.9	No[a]
n-Tetradecanoic acid	14.4-22.8	No[a]
n-Pentadecanoic acid	4.3-6.1	No[a]

Table 3-10 (continued)

Compounds Available for Possible Use in Receptor Modeling Studies

Compound	Range of Average Ambient Fine Particulate Concentration (ng/m³)	Used in Receptor Model
n-Alkanoic acids (continued)		
n-Hexadecanoic acid	118-141	No[a]
n-Heptadecanoic acid	3.4-5.2	No[a]
n-Octadecanoic acid	41.1-59.2	No[a]
n-Nonadecanoic acid	0.79-1.1	No[a]
n-Eicosanoic acid	3.1-6.1	No[a]
n-Heneicosanoic acid	1.4-2.3	No[a]
n-Docosanoic acid	5.7-9.9	No[a]
n-Tricosanoic acid	1.5-2.5	No[a]
n-Tetracosanoic acid	9.2-6.5	No[a]
n-Pentacosanoic acid	1.1-1.6	No[a]
n-Hexacosanoic acid	5.3-9.3	No[a]
n-Heptacosanoic acid	0.47-0.81	No[a]
n-Octacosanoic acid	2.7-4.9	No[a]
n-Nonacosanoic acid	0.33-0.57	No[a]
n-Triacontanoic acid	1.0-2.2	No[a]
Dicarboxylic acids		
Propanedioic acid	28.0-51.0	No[b]
2-Butenedioic acid	0.58-1.3	No[b]
Butanedioic acid	51.2-84.1	No[b]
Methylbutanedioic acid	11.6-20.3	No[b]
Pentanedioic acid	28.3-38.7	No[b]
Methylpentanedioic acid	15.5-23.7	No[b]
Hydroxybutanedioic acid	7.8-22.1	No[b]
Hexanedioic acid	14.1-24.3	No[b]
Octanedioic acid	2.5-4.1	No[b]
Nonanedioic acid	22.8-44.7	No[b]
Aromatic carboxylic acids		
1,2-Benzenedicarboxylic acid	53.5-60.6	No[b]
1,3-Benzenedicarboxylic acid	2.1-3.4	No[b]
1,4-Benzenedicarboxylic acid	0.88-2.8	No[b]
4-Methyl-1,2-benzenedicarboxylic acid	15.2-28.8	No[b]
1,2,4-Benzenetricarboxylic acid	0.45-0.84	No[b]
1,3,5-Benzenetricarboxylic acid	11.3-22.6	No[b]
1,2,4,5-Benzenetetracarboxylic acid	0.40-0.80	No[b]
Wood smoke markers		
Dehydroabietic acid	10.2-23.6	No[b]
13-Isopropyl-5\α-podocarpa-6,8,11,13-intetraen-16-oic acid	0.30-1.2	No[b]
8,15-Pimaradien-18-oic acid	0.07-1.1	Yes
Pimaric acid	0.94-4.8	Yes
Isopimaric acid	0.71-2.3	Yes
7-Oxodehydroabietic acid	1.9-4.1	No[b]
Sandaracopimaric acid	0.60-2.2	No[b]
Retene	0.01-0.10	Yes

Table 3-10 (continued)
Compounds Available for Possible Use in Receptor Modeling Studies

Compound	Range of Average Ambient Fine Particulate Concentration (ng/m³)	Used in Receptor Model
Polycyclic aromatic hydrocarbons		
Fluoranthene	0.07-0.15	No[b]
Pyrene	0.12-0.26	No[b]
Benz[a]anthracene	0.09-0.29	No[b]
Cyclopenta[cd]pyrene	0.04-0.41	No[b]
Benzo[ghi]fluoranthene	0.11-0.39	No[b]
Chrysene/triphenylene	0.23-0.61	No[b]
Benzo[k]fluoranthene	0.33-1.20	Yes
Benzo[b]fluoranthene	0.68-1.23	Yes
Benzo[e]pyrene	0.38-0.97	Yes
Benzo[a]pyrene	0.18-0.44	No[b]
Indeno[1,2,3-cd]pyrene	0.07-0.43	Yes
Indeno[1,2,3-cd]fluoranthene	0.26-1.09	Yes
Benzo[ghi]perylene	1.12-4.47	Yes
Coronene	2.41[c]	Yes
PAH ketones and quinones		
7H-Benz[de]anthracen-7-one	0.25-0.84	Yes
Benz[a]anthracene-7,12-dione	0.12-0.25	Yes
Benzo[cd]pyren-6-one	0.02-1.24	Yes
Steroids		
Cholesterol	1.9-2.7	No[c]
N-containing compounds		
3-Methoxypyridine	0.46-1.4	No[b]
Isoquinoline	0.61-1.1	No[b]
1-Methylisoquinoline	0.24-1.1	No[b]
1,2-Dimethoxy-4-nitrobenzene	0.22-3.9	No[b]
Inorganic elements		
EC	3,030-4,870	Yes
Particulate aluminum	249-330	Yes
Particulate silicon	336-600	Yes

[a] Samples were collected in Los Angeles, California in 1982 (Gray et al. 1986) and analyzed by Schauer et al. (1996).

Footnotes

[a] Not used because significant source not in model.

[b] Not used because species failed check for apparent conservation in the atmosphere (it behaves as if it is formed or depleted).

[c] Not used because data from some monitoring sites were missing.

These types of samples were collected to find out how different chemical mechanisms and emissions affect the particle sizes and the chemistry within those sizes. These data are also vital for the understanding and modeling of visibility in the study domain.

The MOUDI acquires size-resolved particle deposits on substrates amenable to mass and chemical speculation (Marple et al. 1981). The MOUDI is a multistage impactor that collects particles in up to 10 size ranges, depending on how it is configured; for the Winter study, 9 size fractions below 15 μm were collected. Each stage of the MOUDI consists of an acceleration plate, with holes that allow particles to pass through and gain inertia, and a collection plate, where particles with sufficient inertia are collected by impaction. Particles below a stage's cutpoint follow the airstream and go to the next stage. Each stage collects progressively smaller particles. The acceleration nozzles were manufactured by computerized mechanical microdrilling in thin metal plates with up to 2,000 closely spaced microscopic

acceleration nozzles at the lower size ranges. Impaction plates were removed for placement of the collection substrate. During the Winter study, the MOUDIs collected particles in these size ranges:

- < 0.054 μm
- 0.054 to 0.105 μm
- 0.105 to 0.148 μm
- 0.148 to 0.37 μm
- 0.37 to 0.54 μm
- 0.54 to 1.0 μm
- 1.0 to 1.78 μm
- 1.8 to 3.16 μm
- 3.1 to 15 μm

Three Model 100 MOUDIs with rotating acceleration plates were operated side-by-side at BFK. One MOUDI used prefired aluminum foils as collection substrates and a prefired quartz-fiber afterfilter. Samples collected by this MOUDI were analyzed for OC and EC. The other two MOUDIs used FEP (fluorocarbon) Teflon sheets as collection substrates and a Teflon-membrane afterfilter. Samples collected by these MOUDIs were analyzed for mass, chloride, nitrate, sulfate, ammonium, soluble potassium, and elements by XRF. The MOUDI substrates were 47 mm in diameter and were not greased before sampling, because the grease could interfere with chemical analysis. However, particle bounce could cause positive artifacts for subsequent stages. The magnitude of this positive interference can

sometimes be determined by the chemical composition of the samples and by making certain assumptions (for example, that crustal material is predominantly found in the size range above 1 μm).

MOUDIs were in one of the instrumented BFK trailers with copper inlet lines running from the samplers to above the trailer roof. The sample flow rate for each MOUDI (30 l/min) was controlled by the impactor stages, which acted as critical orifices. The flow rate was verified by a calibrated rotameter before and after sampling. Impactor jets were cleaned in an ultrasonic bath after every other sample, to prevent clogging by large particles. Filter substrates were loaded onto and unloaded from the impaction plates in the Desert Research Institute (DRI) laboratory and shipped in sealed ziplocked bags under refrigeration to minimize contamination and loss of volatile species. After collection, samples were stored in sealed ziplocked bags and refrigerated until they were shipped back to the laboratory for chemical analysis.

3.3.2.1.3.3 VAPS for Mass and Elemental Analysis

Fine (< 2.5 μm) and coarse (2.5 to 10 μm) particles were collected by a versatile Air Pollution Sampler (VAS) in Bakersfield from December 12, 1995 through January 6, 1996. Samples were collected daily but on a schedule based on forecasting pollution events and on the availability of personnel to change the filters. The VAPS was included in the study for QA purposes, since it is a well-established method for collecting gas phase acids and NH_3. However, because of resource limitations, gas phase species were not collected by annular denuders during IMS95; only mass and elemental composition by XRF were determined.

The VAPS (from University Research Glassware in Carrboro, North Carolina) consists of a PM_{10} inlet to remove particles greater than 10μm AD, followed by a virtual impactor to collect fine and coarse samples (Figure 3-25). The sampler is Teflon-coated to permit the transport of reactive gases (HNO_3, SO_2, and NH_3) and particles to downstream annular denuders and filters. The fine particles are separated into two fractions—instead of one fraction, as in the conventional Dichotomous Virtual Impactor (DVI) sampler. The coarse particles flow directly through the accelerator jet to the receiver assembly opening and then to the coarse-particle filter pack assembly. The fine- and coarse-particle fractions were collected on 2-μm-pore Teflon (from Gelman Inc.); however, annular denuders and PUF traps were not incorporated into the sampling arrangement for IMS95. During IMS95, the flow rate into the sampler was maintained at 35 l/min.

Versatile Air Pollutant Sampler

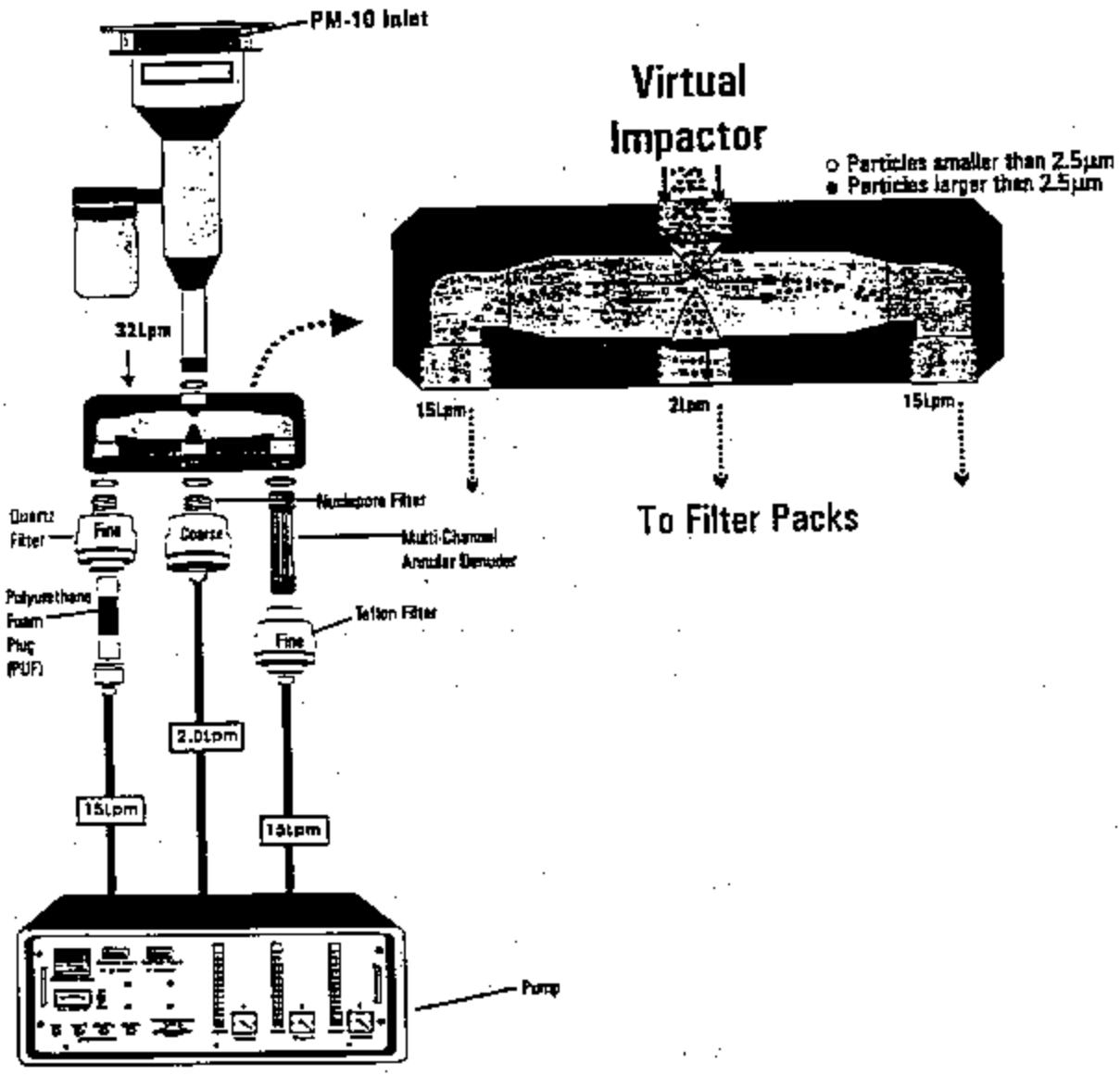


Figure 3-25. VAPS—schematic diagram

The flow rate to each fine-particle filter pack was maintained at 16 l/min; the coarse-particle flow was maintained at 3 l/min.

The filters were weighed with a Mettler M30 microbalance after equilibrating at 23° C and 40% humidity for 24 hours. After the samples were returned to the EPA at Research Triangle Park in North Carolina, they were reweighed and analyzed for elemental composition by a Kevex energy-dispersive XRF analyzer. Forty-five elements, from sodium to lead, were determined on the collected filters. Calibration of the Kevex analyzer is described by Dzubay et al. (1988) and Stevens et al. (1985).

3.3.2.1.3.4 CADMP Sampler

The California Acid Deposition Monitoring Program (CADMP) sampler has two components, one for collecting PM species in two size fractions, and one for collecting acidic gases. The PM_{10} unit collected particles below 10 µm AD on a Teflon filter and used impregnated backup filters to collect ammonia and SO_2. The Teflon filter was analyzed for sulfate, nitrate, chloride, ammonium, sodium, magnesium, calcium, and potassium ions. The $PM_{2.5}$ unit collected two samples of particles below 2.5 µm AD, one on a Teflon-nylon filter pack without a nitric acid denuder, and the other on a nitric acid denuder (consisting of anodized aluminum tubes) followed by a nylon filter. Figures 3-26 and 3-27 show the $PM_{2.5}$ and PM_{10} units used during the Winter study. The $PM_{2.5}$ Teflon filter was analyzed for the same species as the PM_{10} Teflon filter, whereas the nylon back-up filters were analyzed for nitrate ions. The difference between the total nitrate measured by the filter pack and that measured by the nylon filter below the denuder was a measure of gaseous nitric acid by the denuder difference approach. The nitrate on the nylon filter without the denuder was a measure of nitric acid by the filter-pack approach.

During IMS95, the CADMP sampler operated for 24-hour periods from midnight to midnight every other day. This sampling schedule was due to the availability of ARB personnel to change the filters, a task that had to be performed during normal ARB working hours. Flow rates through the CADMP (PM_{10} and $PM_{2.5}$) were 113 l/min, with a rate of 20 l/min through each arm of the $PM_{2.5}$ sampler and rates of 20 l/min and 2 l/min through the two arms of the PM_{10} unit, as shown in Figures 3-26 and 3-27.

An evaluation of data from the dry deposition network through September 1989 showed nothing unusual (Ashbaugh et al. 1991). Data from collocated samplers in Sacramento compared well; regression coefficients above 0.92 were found for gravimetric mass, sulfate, nitrate, SO_2, NO_2, and NH_3. The denuder difference nitric acid concentration had a regression coefficient of 0.78. However, a more recent analysis indicated a decrease in the denuder difference nitric acid concentrations at Azusa and Los Angeles (Blanchard 1994). In contrast, no similar trend was observed in the nitrate data collected by the

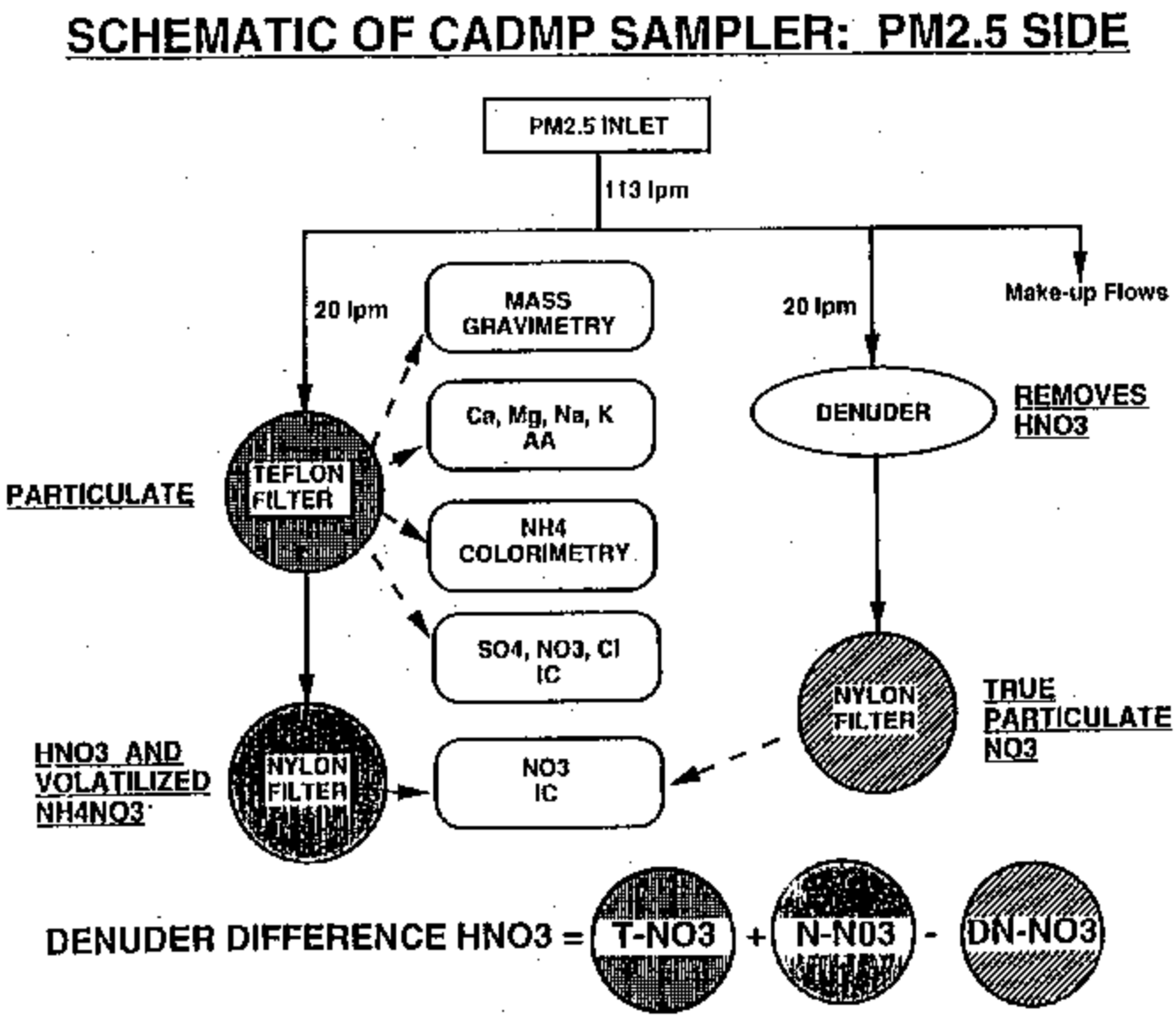


Figure 3-26. CADMP sampler $PM_{2.5}$ component—schematic diagram.

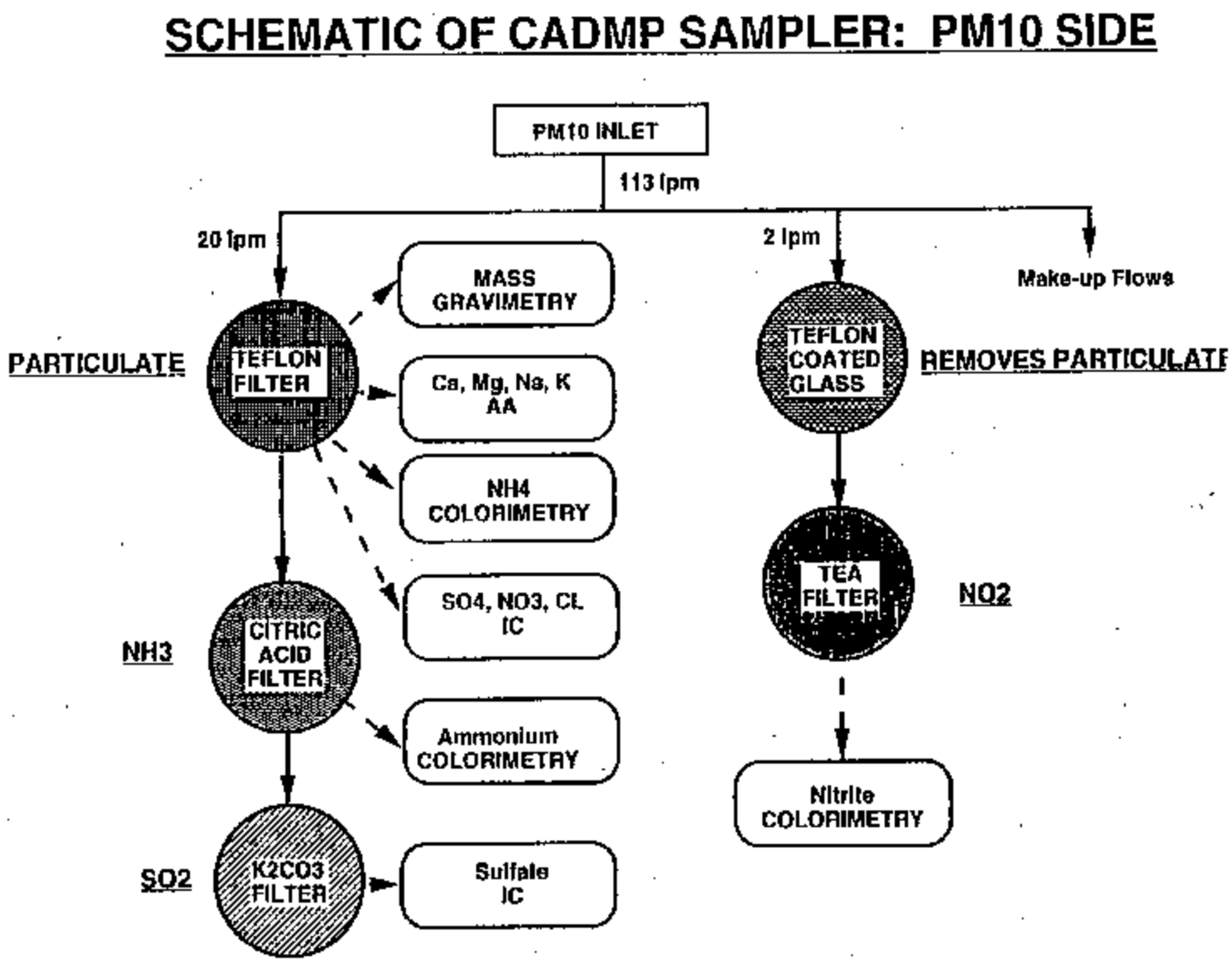


Figure 3-27. CADMP sampler PM_{10} component—schematic diagram.

filter-pack method. It is expected that the denuder difference and filter-pack measurements should track each other for nitric acid, with a positive bias in the filter-pack nitrate values because of volatilization of ammonium nitrate from the Teflon front filter. At the other sites, the filter-pack nitrate and denuder difference nitric acid curves were essentially parallel, thus suggesting that the denuders may have become ineffective at the Azusa and Los Angeles sites. For this and other reasons, ARB decided to develop a new acid deposition sampler. The development work is being performed by CE-CERT at the University of California at Riverside. The CE-CERT sampler prototype was also operated and collocated with the CADMP sampler at BFK during the Winter study.

3.3.2.1.3.5 CE-CERT Sampler for Inorganic Ions

As mentioned in Section 3.3.2.1.3.4, the ARB Research Division is replacing its current CADMP acid deposition monitor with the CE-CERT sampler. During IMS95, the two samplers were collocated on the BFK platform with the other aerosol samplers. The CE-CERT sampler uses new diffusion denuder technology that was being tested under SJV winter conditions.

The CE-CERT sampler used a of diffusion denuder that was based on flow directed around a coated surface such as a thread, instead of the inside of a coated tube and is known as a screen denuder. This principle is well known for removing particles to determine particle size distributions, mass and composition if the collected aerosol is weighed or chemically analyzed. Denuders originally consisted of long tubes, but through a progression of improvements these were replaced by bundles of long tubes, then by metal disks with fine holes, then by honeycomb structures, and finally by wire screens. The collection efficiency for gases was theoretically calculated by applying the particle diffusion theory to screens and modifying the equation slightly to apply to gases; the main difference is with the "slip correction factor," which becomes more important as the particle size decreases in relation to the mean free path of the supporting gas. The basic idea was therefore extremely simple: a very poor particle filter (such as a fine screen or cloth) would work quite well to remove reactive gases while allowing particles to pass, if the filter were coated with an appropriate reactive sorbent. Any fibrous substrate could be used, as long as the gibe density was not so great that a significant number of particles would be removed.

The screen denuder was developed to sample separately the gases derived from semivolatile PM and the PM species, such as ammonia, nitric acid, and ammonium nitrate. This would allow the particles to be quantitatively trapped on adsorbent backup filters without collection artifacts. The denuder is low-cost, compact, easily coated, and mountable in filter holders. The IMS95 denuders were 47-mm-diameter

substrates. Since blank variability is similar to that of filters, so are detection limits (approximately 1 μg per filter or, for a 24-hour sample at 5 l/min, the atmospheric detection limit is approximately 0.1 μg/m^3).

The sampling configuration is shown in Figure 3-28. Both the acid and base samplers used an uncoated front denuder to determine the amount of particulate species retained by the denuder. In the acid sampler, an NaCl-coated denuder was used to trap nitric acid, followed by two sodium-carbonate-coated denuders to trap nitrous acid. An NaCl-impregnated quartz fiber backup filter was used to quantitatively retain particulate nitrate, nitrite, and sulfate. The sampler to collect basic gases (i.e., NH_3), used a citric-acid-impregnated denuder to trap ammonia, while a similarly impregnated quartz fiber filter was used to quantitatively retain particulate ammonium.

The last component was the fine-particle sampler that used the standard CADMP cyclone and plenum as the inlet to obtain a 2.5-um size cut. The denuders removed gas phase nitric acid and ammonia, a Teflon filter removed particles and was weighed and analyzed for ions, and the impregnated quartz fiber filters trapped volatilized nitrate on an NaCl-impregnated filter and ammonium on a citric-acid-impregnated filter. The nitric acid and ammonium measurements provided an estimate of losses and gains through the CADMP inlet system.

Each component sampled for 24 hours at 5 l/min, starting at midnight. A fourth component functioned as a rotating collocated sampler. Each sampling period therefore contained one collocated set of samples.

3.3.2.1.4 Continuous and Intermittent Gas Phase Sampling

One-hour average data were obtained continuously throughout the study from continuous monitors, and several 3-hour averages were obtained from the intermittent samplers several times per day and at the same time each day. Both types of measurements are described below:

3.3.2.1.4.1 Continuous Gas Phase Species

Gas phase criteria pollutants were measured continuously at or near the three core sites and at SWC. These measurements provided hourly average data on aerosol precursor and oxidant concentrations. Ozone, NO/NO_y, CO, and SO_2 were measured at SWC and KWR by study contractors, while O_3, NO/NO_X, CO, and SO_2 were measured at ARB sites located near BFK and FEL.

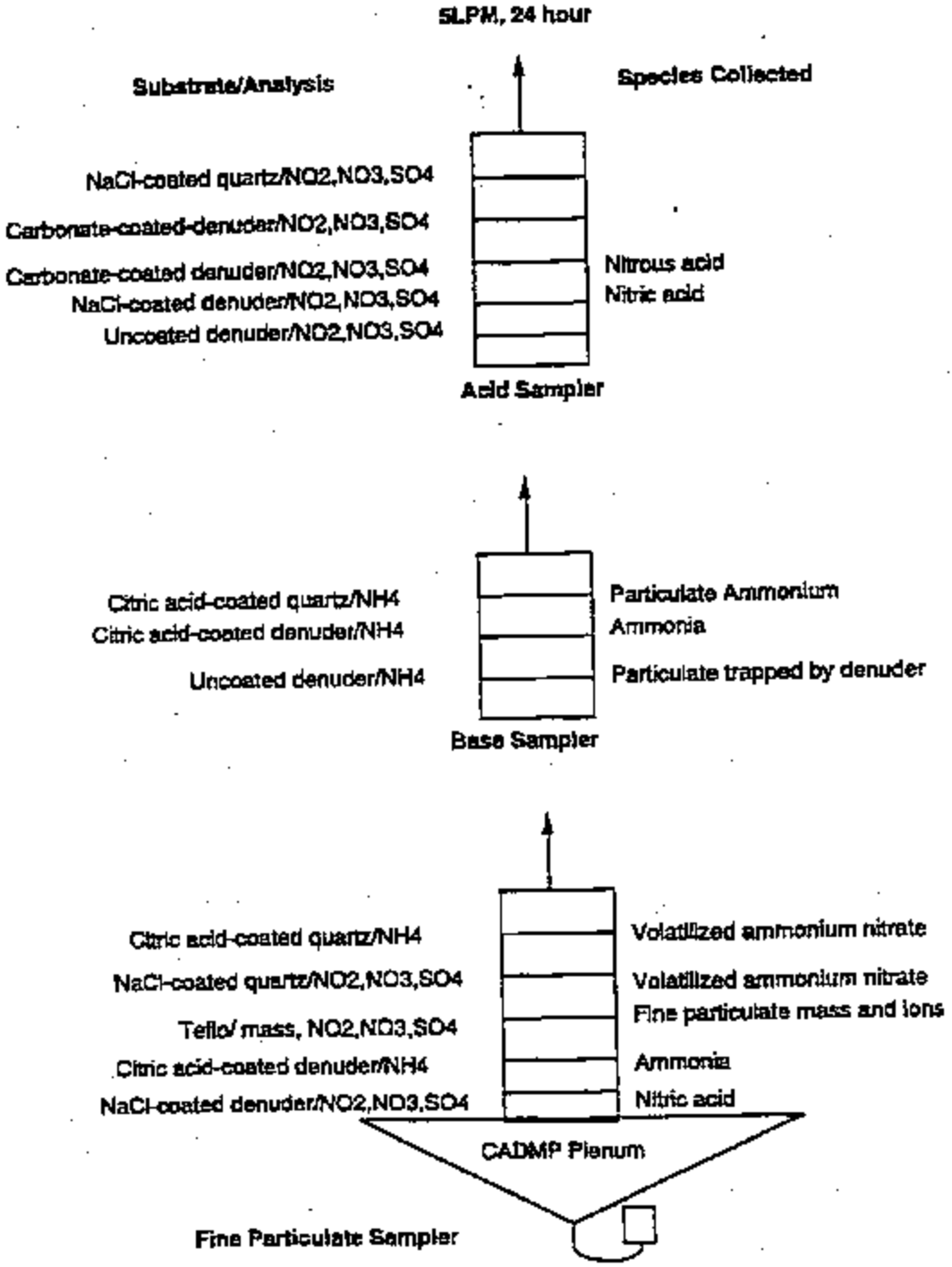


Figure 3-28. CE/CERT sampler PM_{10} component—schematic diagram.

At SWC and KWR, O_3 was measured via the Monitor Labs O_3/ethylene chemiluminescence analyzer (Model 8410E), CO was measured via the Thermo Environmental Instruments, Inc. (TEI) gas filter correlation CO analyzer (Model 48S), SO_2 was measured via the TEI pulsed fluorescence SO_2 analyzer (Model 43S), and $NO/NO_2/NO_y$ were measured via a modified TEI chemiluminescence $NO/NO_2/NO_X$ analyzer (Model 42S). The 42S was modified to measure NO_y rather than NO_X by moving the reduction chamber, where NO_2 and other NO_X are reduced to NO, to the front of the inlet line. This modification eliminates the loss of fast-reacting or sticky species that may not proceed through the inlet line to the internal reduction chamber. A summary of NO_X measurement methods is in Solomon (1994). The effectiveness of O_3 and NO/NO_X measurement methods as employed during the SJVAQS 1990 O_3 study is summarized in Solomon and Thuillier (1995).

Ammonia was measured continuously at BFK via a modified TEI Model 42 NO/NO_X analyzer (Model 17). This continuous sampler has a proprietary converter that allows the measurement of NO, NO_X, and NH_3 separately by switching among three channels rather than two, in contrast with the standard NO/NO_X monitor. This is a relatively new instrument and had not been tested before in the SJV. The SJV test was particularly challenging, because RH was high and temperatures were relatively low. The monitor was calibrated at TEI and again in the field by TEI personnel. However, the inlet line was not in place at the time of the field calibration by TEI, so this calibration was only preliminary. Personnel from the Bakersfield ARB monitoring site tried to calibrate the instrument after it was fully operational; however, the needed low concentrations (< 0.5 ppb) were difficult to generate with the available calibration equipment. The system was calibrated by both a permeation tube device and a gas cylinder containing a high ppm level of NH_3. In both cases, standard gases were diluted by a factor of 10,000 or more, which probably created considerable uncertainty in the calibration results. A larger problem was that the system had not been set up to allow for a daily zero check on a daily span during the study. A review of the data after the study showed a constant negative drift, and, without zero and span checks, no baseline could be established for the measurements. Unfortunately, no party assumed real ownership of this instrument while it was in the field, so the data from this monitor are deemed suspect.

Criteria gaseous pollutants were measured continuously at ARB sites—BAK (near BFK) and FRE (near FEI)—via the following methods, as described in the ARB "Blue Sky Reports" (ARB 1995a). O_3 was measured by the ultraviolet (UV) absorption photometric method, oxides of nitrogen (NO/NO_X and NO_2 by difference) by the NO_2-O_3 chemiluminescence method, CO by either nondispersive infrared radiation (NDIR) or the gas filter correlation absorption method, SO_2 by either flame photometric or fluorescent

methods, and methane and hydrocarbons by a gas chromatograph with a hydrogen flame ionization detector (FID).

3.3.2.1.4.2 Intermittent Gas Phase Species

Total nonmethane organic carbon (TNMOC), CO, CH_4, CO_2, speciated volatile organic compounds (VOCs) in the C_2–C_{20} carbon range, and carbonyl species in the C_2–C_7 carbon range were measured twice daily at FEI and BFK during 0600–0900 PST and 1500–1800 PST. A 24-hour integrated sample was also collected at FEI from noon to noon, to coincide with the 24-hour average speciated organic aerosol samples described earlier. The samples analyzed coincided with the last two episodes, December 24–28, 1995 and January 4–6, 1996.

Carbonyl sampling was performed by using C18 Sep-Pak cartridges (from Waters Associates in Milford, Massachusetts) that had been impregnated with purified 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid. In this method, ambient air was drawn through the cartridge, and carbonyl compounds in the air sample were captured by reacting with DNPH to form hydrazones, which were then separated and quantified by using an HPLC in the laboratory (Fung and Grosjean 1981). This method was compared and validated with long-path FTIR, differential optical absorption spectroscopy (DOAS), and a tunable diode laser spectrometer in the 1986 Carbon Species Methods Comparison Study (CSMCS).

Carbonyl compounds were sampled by an automated sampler with four active channels for collecting samples sequentially on an event basis. There was also a separate channel for taking either a duplicate sample concurrently with one of the active channels or taking a field blank. Since cartridges will naturally absorb carbonyl compounds from the surrounding air if left open, the sampler has been designed so that cartridges loaded into it are isolated from the environment and from each other by check valves upstream and solenoid valves downstream of the cartridge. Programmable timers with memory protection controlled the operation of the pump and the solenoid valves according to the prescribed schedule. Duplicate samples were collected on collocated cartridges by activating a parallel channel simultaneously. A mode selection switch deactivated the parallel channel to collect field blanks. Sampling flow rates were controlled at a nominal flow rate of about 0.85 l/min by a differential flow controller with a typical precision of ± 5% or less. Flow rates were maintained despite changes in flow resistance from cartridge to cartridge.

TNMOC, CO, CH_4, CO_2, and speciated VOCs in the C_2-C_{20} carbon range were collected by two samplers, one for gas phase hydrocarbons in the C_2-C_{10} carbon range and the other for gas phase hydrocarbons in the C_{11}-C_{20} carbon range.

Hydrocarbons in the C_2-C_{10} range were collected in 6-l SUMMA® polished stainless steel canisters provided by Biospherics Research Corporation and were sampled according to the schedule described above. Table 3-11 lists the species determined. An additional canister sampler collected collocated and blank samples and was switched among the three sites during the Winter study.

The stainless steel canisters were cleaned before each use, via a modification of the protocol in EPA Method TO-14 (Rasmussen 1989). The canisters were cleaned by heating them in an oven at 120 C through several mass transfer fill-evacuation cycles using moisturized zero air. The final cycle pumped the cans down to a vacuum of 10 microns. A cold trap prevented contamination of the canisters by the vacuum pump. All containers were helium leak-tested to 10^{-9} scc/s before use and certified as being clean by EPA Method TO-12.

The integrated ambient air samplers provided by Oregon Graduate Institute (OGI) used a 12-V DC diaphragm pump constructed of stainless steel and Teflon, which minimizes possible sample contamination by the pump. Each pump was tested to verify that it was free of contamination before use. The pump's maximum unloaded flow is 5 l/min. A constant rate of air flow was integrated into the canisters via a Veriflow 423 back-pressure flow controller constructed from 316 stainless steel and Teflon. The sampling system was controlled by a programmable Chrontrol® timer accurate to within ± 0.5 minute.

Hydrocarbons in the C_{10}-C_{20} range were collected by cartridges containing Tenax® chromatographic column material. Samples were collected at a flow rate of 200 ml/min, resulting in the collection of 36 l of air for a 3-hour sample and 130 l of air for a 24-hour sample. The detection limit for the combined Tenax and GC-MS method was about 15 pptv. The cartridges were collected on the same schedule as the canisters, including blanks and duplicates.

3.3.2.2 Saturation Monitoring Sites

The portable samplers used at the saturation monitoring sites were not certified for determining compliance with the current PM_{10} standards; however, their measurements have been shown to be comparable to PM_{10} compliance monitors (Chow and Egami 1997). Validation of saturation monitors with SFS and compliance monitors was incorporated into the study protocol.

Saturation monitoring networks were established in and around BFK and FEI, and around KWR. Samplers were located near the long-term monitoring sites operated by the District and ARB, near

Table 3-11
NMOC Species Determined during Winter Study

Species	Abbreviated Name	Carbon Number	Functional Group
Ethane	ethane	2	alkane
Ethene	ethene	2	alkene
Ethyne	ethyne	2	alkene
Propane	propane	3	alkane
Propene	propene	3	alkene
Isobutane	ibutane	4	alkane
Isobutene	ibutene	4	alkene
1-Butene	x1buten	4	alkene
1,3-Butadiene	x13butad	4	alkene
Butane	butane	4	alkane
trans-2-Butene	t2buten	4	alkene
2,2-Dimethylpropane	x22dpro	4	alkane
cis-2-Butene	c2buten	4	alkene
3-Methyl-1-butene	x3mbute1	5	alkene
Isopentane	ipentane	5	alkane
1-Pentene	pentene1	5	alkene
2-Methyl-1-butene	x2m1bute	5	alkene
Pentane	pentane	5	alkane
Isoprene	isoprene	5	alkene
trans-2-Pentene	t2penten	5	alkene
cis-2-Pentene	c2penten	5	alkene
2-Methyl-2-butene	x2m2bute	5	alkene
2,2-Dimethylbutane	x22mbuta	6	alkane
Cyclopentane	cypentan	5	alkane
2,3-Dimethylbutane	x23mbuta	6	alkane
cis-4-Methyl-2-pentene	c4mpnte2	6	alkene
2-Methylpentane	x2mpenta	6	alkane
3-Methylpentane	x3mpenta	6	alkane
2-Methyl-1-pentene	x2mpnte1	6	alkene
1-Hexene	x1hexene	6	alkene
Hexane	hexane	6	alkane
trans-2-Hexane	t2hexene	6	alkene
2-Methyl-2-pentene	x2m2pnte	6	alkene
cis-2-Hexene	c2hexene	6	alkene
Methylcyclopentane	mcypenta	6	alkane
2,4-Dimethylpentane	x24mpnta	7	alkane
Benzene	benzene	6	aromatic
Cyclohexane	cyhexane	6	alkane
2-Methylhexane	x2mhexan	7	alkane
2,3-Dimethylpentane	x23mpnta	7	alkane
3-Methylhexane	x3mhexan	7	alkane

Table 3-11 (continued)
NMOC Species Determined during Winter Study

Species	Abbreviated Name	Carbon Number	Species
Heptane	heptane	7	alkane
Methylcyclohexane	mcyhexan	7	alkane
4-Methyl-1-pentene	x4mpnte1	6	alkene
2,4,4-Trimethyl-2-pentene	x244t2pe	8	alkene
2,5-Dimethylhexane	x25mhexa	8	alkane
2,4-Dimethylhexane	x24mhexa	8	alkane
2,3,4-Trimethylpentane	x234mpta	8	alkane
Toluene	toluene	7	aromatic
2,3-Dimethylhexane	x23mhexa	8	alkane
2-Methylheptane	x2mhepta	8	alkane
3-Ethylhexane	x3ethexa	8	alkane
2,2-Dimethylheptane	x22mhept	9	alkane
2,2,4-Trimethylhexane	x224mhxa	9	alkane
Octane	octane	8	alkane
Ethylcyclohexane	etcyhexa	8	alkane
Ethylbenzene	etbenzen	8	aromatic
m&p-Xylene	mpxylene	8	aromatic
Styrene	styrene	9	aromatic
o-Xylene	oxylene	8	aromatic
Nonane	nonane	9	alkane
Isopropylbenzene	iprobenz	8	aromatic
n-Propylbenzene	nprobenz	8	aromatic
p-Ethyltoluene	petoluen	9	aromatic
o-Ethyltoluene	petoluen	9	aromatic
m-Ethyltoluen	metoluen	9	aromatic
1,3,5-Trimethylbenzene	x135tmbz	9	aromatic
1,2,4-Trimethylbenzene	x124tmbz	9	aromatic
Decane	decane	10	alkane
a-Pinene	apinene	10	alkene
b-Pinene	bpinene	10	alkene
Methylstyrene	mstyrene	10	aromatic
1,2,3-Trimethylbenzenze	x123tmbz	9	aromatic
1,3-Dimethylbenzene	x13dbenz	8	aromatic
1,4-dimethylbenzene	x14dbenz	8	aromatic
2,4,4-Trimethyl-1-pentene	x244t1pe	8	alkene
Formaldehyde	formalde	1	carbonyl
Acetaldehyde	acetalde	2	carbonyl
Acetone	acetone	2	carbonyl
Propanal	propanal	3	carbonyl
Methyl ethyl ketone and butanal	mekbut	4	carbonyl
Pentanal and pentanone	penpan	5	carbonyl
Cyclohexanone	cyhex	6	carbonyl
Hexanal and hexanone	hexhex	6	carbonyl
Benzaldehyde	benzalde	7	carbonyl

potential PM_{10} sources in the vicinity of these long-term sites, and between the potential emitters and the long-term monitors. The information gathered over micro (<1 km), neighborhood (1 km to 10 km), and urban (10 km to 50 km) scales in this study can be extrapolated to the long-term monitoring sites with similar surroundings throughout the SJV, to better understand which emitters have regional as well as extremely local effects. The study results can also be used to prioritize future emissions inventory projects.

Twelve monitoring sites were located in and around Bakersfield (Figure 3-4), including two sets collocated together and at the BFK core site. The site locations were based on the siting criteria defined in Section 3.2. Site types in the Bakersfield area included residential, industrial (oil field or refinery), motor vehicle, and agricultural (field crops). Four monitoring sites were located around the KWR core site, one at each compass direction, and a fifth was collocated at KWR. Three of the surrounding sites (13K, 16K, and 17K) were within about 1.5 km of KWR, and the fourth was about 9 km to the west, next to the Kern National Wildlife Refuge (KNWR) and adjacent to the historical site at KNWR. Twenty-five sites were located in and around Fresno (Figure 3-3), including one collocated at the FEI core site. The site locations in the Fresno area were based on the siting criteria defined in Section 3.2. Site types included residential, industrial (construction, airport, landfill/sewage treatment plant, railroad, and shipping), motor vehicle, residential/commercial, residential (with and without wood burning), and agricultural (livestock and field crops).

Portable battery-powered samplers that could be quickly and easily located without major infrastructure were placed on utility poles (power or street light) at the saturation site locations. The saturation sampler included the battery, pump, and timer controls in the base of the sampler (about 46 cm high and 18 cm in diameter) with a multistage Nucleopore filter holder mounted on the top of the unit. The sampler was designed to allow easy removal and replacement of the battery and filter holder and easy access to the 7-day timer, which must be accessed once a week when it operates every other day. Depending on what was to be measured at the site, either two or four portable units were mounted on each pole, with the sampler inlets at about 3 m. Sites where only PM_{10} mass and NH_3 were obtained required only two samplers, one that operated while the other was being changed. Sites where chemical measurements were obtained (Table 3-1) required four samplers, one set that operated while the other set was being changed. Table 3-7 shows the chemical measurements performed at each site by category, and Table 3-9 lists the species measured.

3.3.2.3 Boundary and Flux Plane Sites

Three types of boundary sites were established during the Winter study, as discussed earlier. Table 3-7 shows the site measurements by category, Table 3-8 shows the site measurements by species, and Table 3-4 cites the rationale for each site location. There was one Boundary A site in the center of the northern flux plane at SWC (Figure 3-2). SWC measurements were similar to those at the core sites, except for the fog and organic species measurements (VOCs, carbonyl compounds, and speciated organic aerosols). Measurements included PM_{10} and $PM_{2.5}$ mass and chemical composition, HNO_3, and NH_3 collected at a 3-hour sampling frequency via SFSs and SGSs (Chow and Egami 1997); the SGSs used denuder difference technology for HNO_3, and NH_3. Hourly averaged concentrations of O_3 and other criteria pollutants were measured continuously throughout the study period, and PM_{10} and $PM_{2.5}$ mass were monitored continuously by the BAM. Visibility-related measurements and surface meteorological variables were also obtained at SWC. Twenty-four-hour average PM samples were collected at 11 boundary and flux plane air quality sites (Figure 3-2) via the same battery-powered portable samplers described in Section 3.3.2.2. Two additional sites (FEL and KRN, the Boundary D sites) used standard PM_{10} SSI samplers to determine PM_{10} mass, sulfate, and nitrate. The 11 portable monitoring sites sampled for PM_{10} mass and NH_3, and 6 of those sites (Boundary C sites; see Table 3-7) sampled for PM_{10} chemical composition, HNO_3, and $PM_{2.5}$ mass. Samples were also collected for $PM_{2.5}$ elemental composition, but chemical analysis was not performed on these filters. Figure 3-29 illustrates the $PM_{2.5}$ portable sampler and measurements obtained at the boundary and flux plane sites where $PM_{2.5}$ was collected.

The sites where only PM_{10} mass and NH_3 were collected are the Boundary B sites (Table 3-7). Results from these sites provide information on PM levels between the core air quality sites, the nature of pollution buildup in the valley, transport across the northern boundary of the study domain and in and out of the valley through passes, and recirculation caused by slope flows associated with the Sierra Nevada and the Coastal Range.

3.3.3 Fog Measurements

Fog measurements were made at the three core sites (BFK, FEI, and KWR) in the southern SJV from December 9, 1995 through January 6, 1996. KWR was designated as the primary fog sampling site and was more heavily instrumented than the other two sites. Both bulk and size-fractionated fog chemistry and related parameters were measured at all three sites. Gas phase peroxide measurements were also obtained at all three sites during various portions of the 28-day study period. After the southern SJV

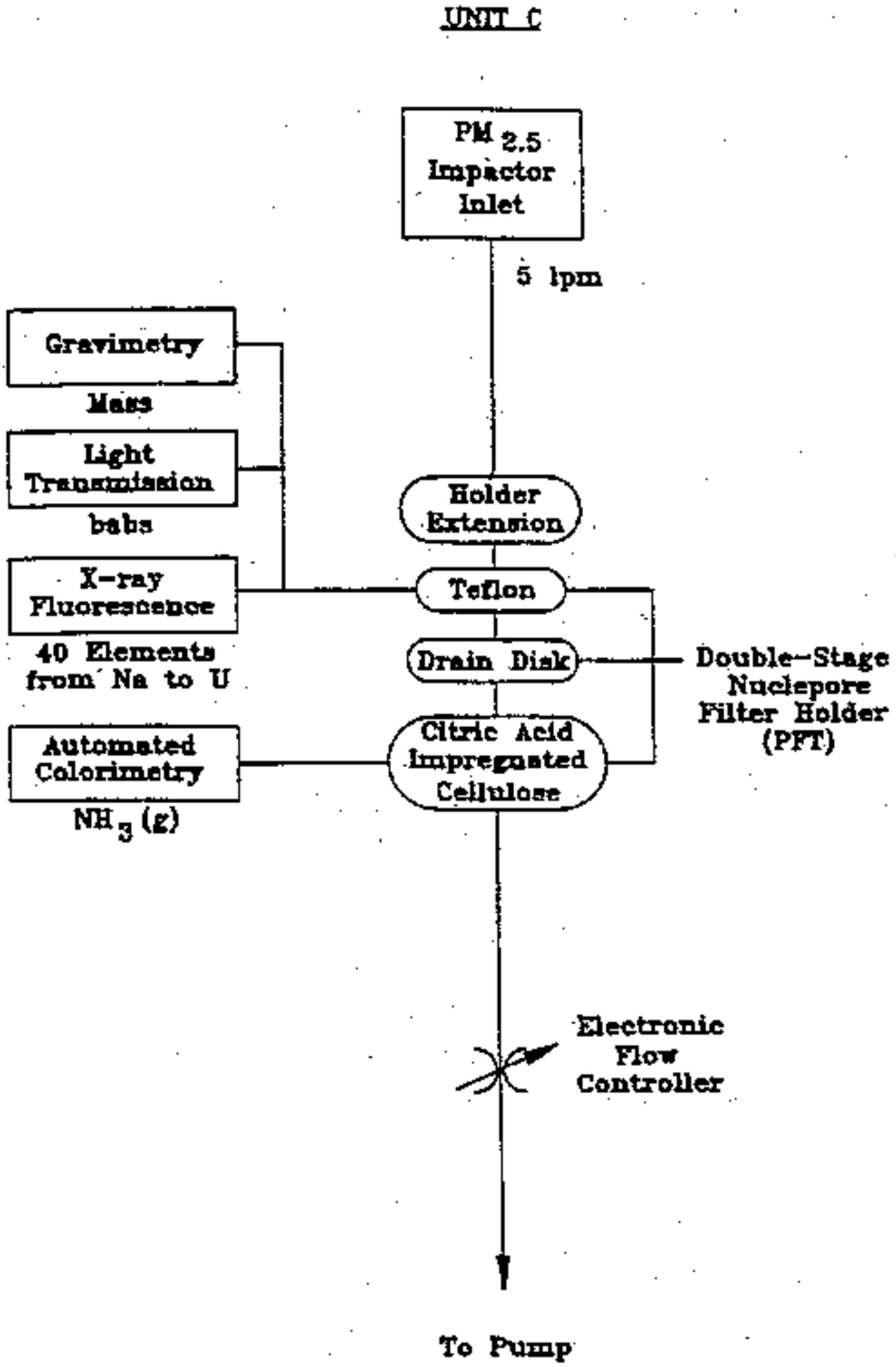


Figure 3-29. Portable filter sampler (SFS) configuration for $PM_{2.5}$ mass, B_{abs}, elements, and NH_3 during the Fall and Winter studies.

portion of the study, the fog instrumentation was moved to a TV tower in Walnut Grove to obtain vertical measurements of fog and related parameters. The instrumentation and measurements at each site are outlined below, and details are in Collett et al. (1996a, 1996b, 1997) and Richards et al. (1997).

3.3.3.1 Cloud/Fog Sampling

Four different cloud/fog sampler types were used in IMS95. One type collected "bulk" samples representative of the entire fog drop size distribution, while three other types collected multiple independent cloud drop size fractions, as described below.

3.3.3.1.1 Caltech Active Strand Cloudwater Collector Version 2

The Caltech Active Strand Cloudwater Collector Version 2 (CASCC2) (Hoffmann et al. 1989, Collett et al. 1994, Demoz et al. 1996) collected bulk fog samples at the three winter core sites and the Candelabra Tower. This instrument (Figure 3-30) collects fog droplets by inertial impaction on a bank of Teflon cylinders. The cylinders consist of a 508-μm-diameter Teflon strand, wrapped around three Teflon-coated frames, forming 6 collector rows. The frames are enclosed in a Plexiglas housing and supported above a Teflon sample trough. Air is drawn through the CASCC2 at 5.8 m^3/min by a fan at the rear of the collector. The theoretical 50% size cut for the CASCC2 corresponds to a drop diameter of 3.5 μm. As droplets impact on the Teflon collection strands, they coalesce and are pulled by gravity and aerodynamic drag down into the sample trough. Collected fog water flows from the sample trough, through a Teflon sample tube, and into a polyethylene sample bottle. During IMS95, the sample was retrieved manually at the end of each sample period.

At all sites, aliquots of CASCC2 samples were prepared for analysis of pH, major ions, S(IV), organic acids, trace metals, formaldehyde, and hydroperoxides. In some cases, not all species were analyzed, especially when there was insufficient sample volume or insufficient time, to preserve unstable species. Some samples collected at KWR and the Candelabra Tower were also analyzed for hydroxymethane sulfonate (HMS), total organic carbon (TOC), and dissolved organic carbon (DOC).

3.3.3.1.2 Size-Fractionating Caltech Active Strand Cloudwater Collector

The size-fractionating Caltech Active Strand Cloudwater Collector (SFCASCC) (Munger et al. 1989, Demoz et al. 1996) is a larger version of the CASCC2 with an additional inlet for collecting large fog drops. This collector, depicted in Figure 3-30 (top), was deployed at KWR and at the Candelabra Tower.

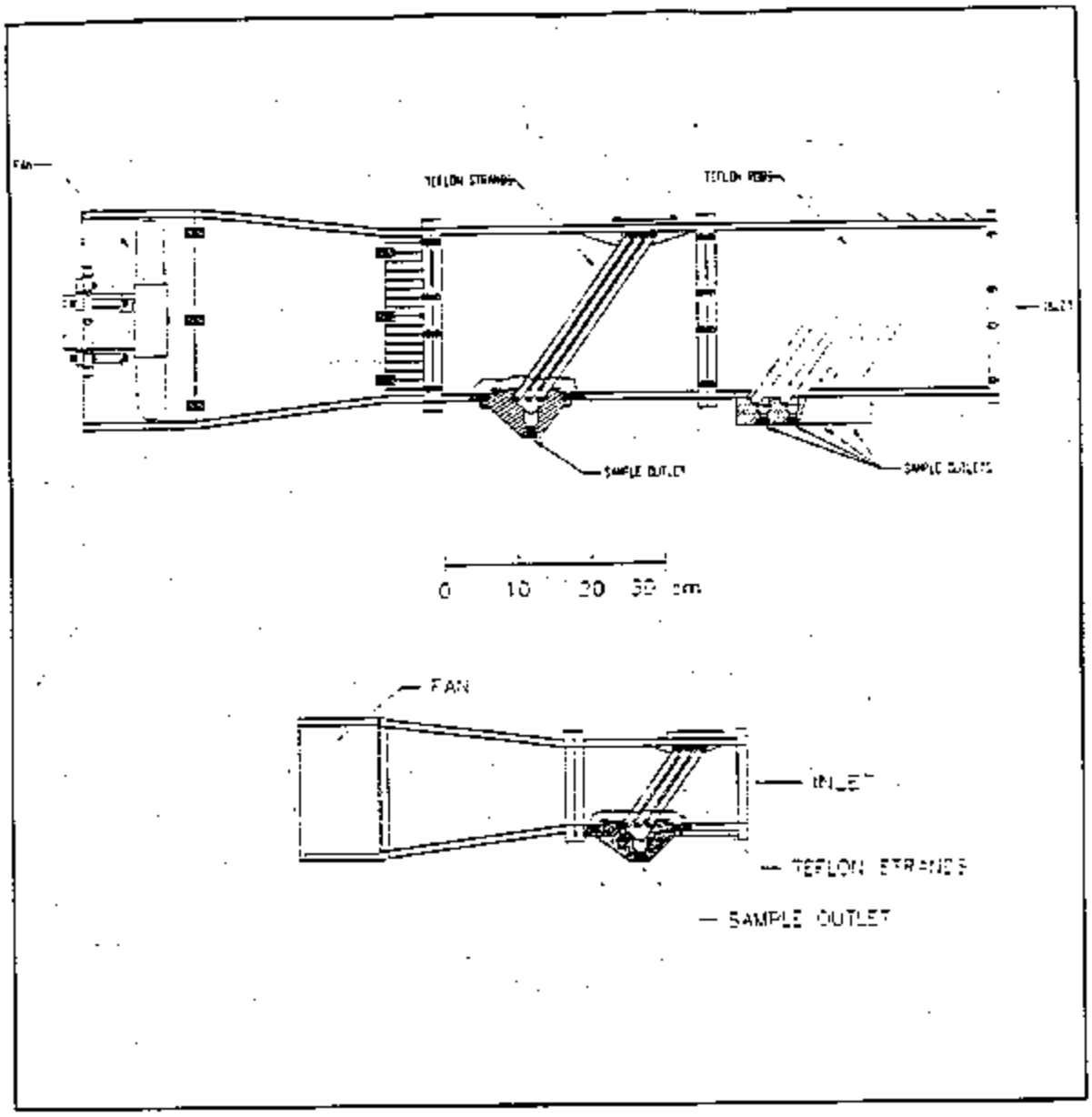


Figure 3-30. SFCASCC and CASCC2.

Air was drawn through this collector at 19 m^3/min. Its inlet contains 4 rows of 12.7-mm-diameter Teflon rods; the theoretical 50% size cut for this stage is 23 µm. The second stage contains 6 rows of a 508-µm-diameter Teflon strand and provides a 50% size cut of 4 µm. Both collector stages are contained in a Plexiglas housing. Samples from each collection stage drain through a collection trough into a polyethylene sample bottle via a Teflon sample tube. Samples were retrieved manually at the end of each sampling period.

As sample volume and time permitted, aliquots of SFCASCC samples were prepared for analysis of pH, major ions, S(IV), organic acids, trace metals, formaldehyde, HMS, hydroperoxides, and TOC. Some samples collected at KWR and the at the tower were also analyzed for DOC.

3.3.3.1.3 IESL Impactor

A three-stage fog impactor was also deployed at the KWR core site and at the Candelabra Tower. The Institute for Environmental Studies large (IESL) impactor (Figure 3-31) collected three independent size fractions of fog water. Details of the collector design are in Collett et al. (1995). The IESL impactor is a three-stage, cascade jet impactor. The impaction plates are made of Teflon, and the impactor housing and jet plates are made of Plexiglas. Each jet plate contains several cylindrical jets that accelerate air toward an impaction plate as the air moves through the jets. Drops with sufficient inertia impact and are collected by this stage. Smaller drops pass through and are available for collection in a subsequent stage downstream. The IESL impactor features 7 impaction stages (size cuts of 30, 20, 15, 12, 10, 4, and 3 µm), 3 of which can be used simultaneously. Air was drawn through the IESL impactor by a Gast regenerative blower (model R4110-2), with the flow set at 1,500 l/min controlled by a Sierra inline mass flow meter (Model 760). As the stage size cuts decreased from 30 to 3 µm, velocities increased from 137 to 1,370 cm/s, and the pressure drop increased from 0.01 to 1.1 mbar. The number of jets in each stage ranged from 21 to 213, and jet diameters ranged from 3.32 to 0.33 cm.

The IESL impactor is 0.6 m in diameter and stands as high as 1 m, depending on the size cuts chosen. Because of its size and weight, the IESL impactor was mounted on a mobile cart. The cart housed the flow system and an overhead crane that lifted impactor stages for sample retrieval. Entry of precipitation into the impactor was minimized by a precipitation shield that mounts above the impactor inlet. An impaction stage was included in the inlet to remove any precipitation-sized particles (drops larger than 100 µm) that circumvented the precipitation shield. The height of the impactor inlet, with the impactor on the cart, helped to minimize contamination from dust and debris disturbed at the ground during operation. Samples

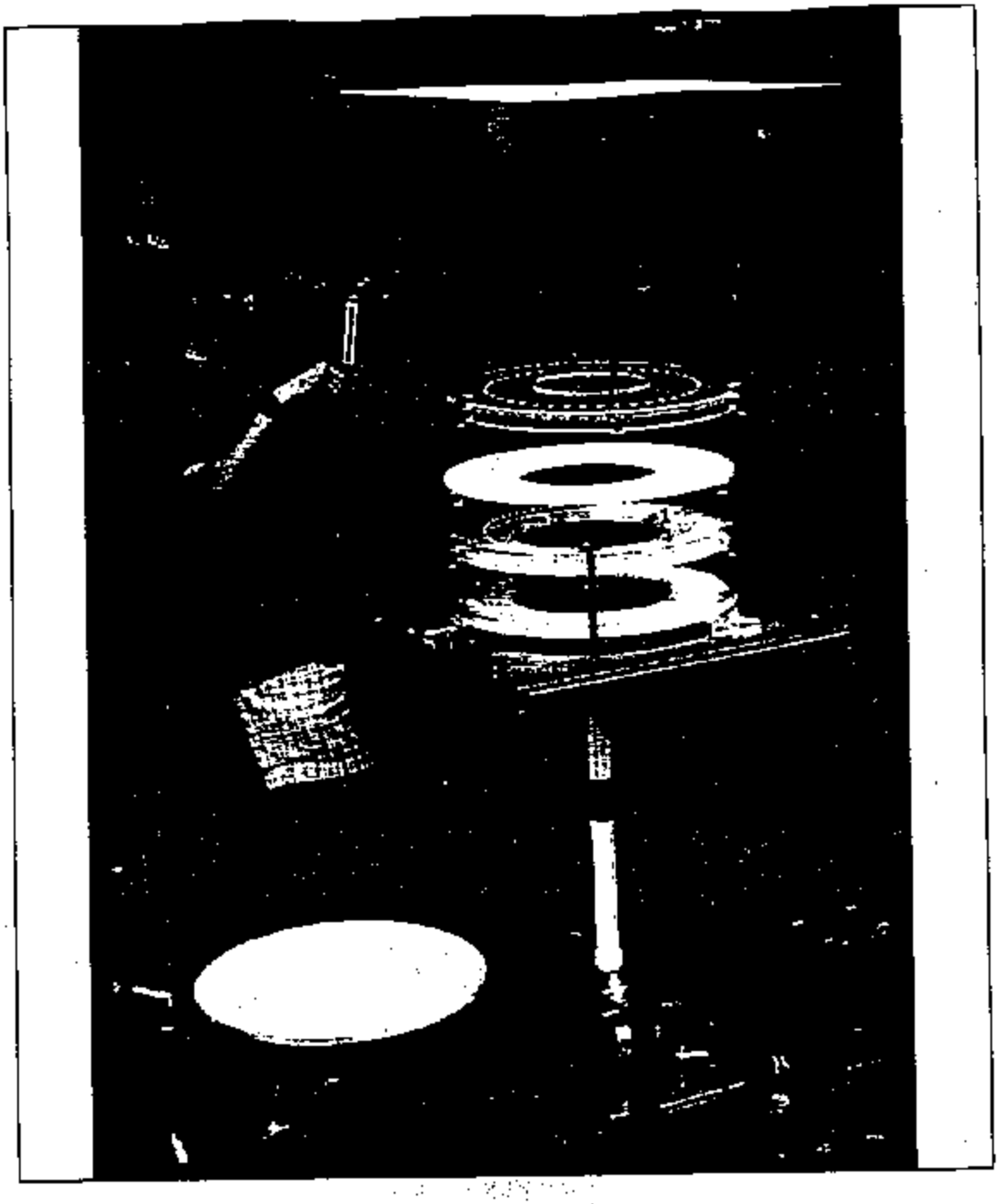


Figure 3-31. Three-stage IESL fog impactor.

were retrieved manually by pipette and transferred to polyethylene sample vials at the end of each sampling period. Because of limited ground-based fog at the Candelabra Tower, samples were collected with this sampler only at KWR. As sample volume and time permitted, aliquots of samples collected by the IESL impactor were prepared for analysis of pH, major ions, S(IV), organic acids, trace metals, formaldehyde, HMS, hydroperoxides, and TOC.

3.3.3.1.4 ETH Impactor

ETH two-stage jet impactors were used at Bakersfield and Fresno to collect separate samples of large and small fog drops. The ETH impactor (Collett et al. 1993, 1995), shown in Figure 3-32, contains two impaction stages in series. Air is drawn through the impactor by a regenerative blower. The flow rate is set by adjusting a gate valve downstream of the impactor, and the flow is checked by measuring the time to inflate a bag of known volume or by readout from an inline volumetric flow meter. The ETH impactor was typically operated at flow rates from 300 to 400 l/min. The size cut of each stage was a weak function of flow rate in this range. Drops larger than 10 μm (depending on flow rate) were collected on the first stage, while drops between diameters from 3 and 10 μm (depending on flow rate) were collected on the second stage. Each stage consists of a Plexiglas jet plate and a Teflon impaction plate. Shallow troughs in the impaction plates help to confine the collected sample to facilitate sample retrieval. Samples were manually retrieved at the end of each sampling period by disassembling the impactor and pipetting the sample collected on each stage into a polyethylene sample vial. Samples from the ETH impactors were analyzed for pH and major ions as sample volume permitted.

3.3.3.2 Fog-Related Sampling

In addition to collecting fog samples, Colorado State University (CSU) ran a Particle Measurement Systems (PMS) classical scattering aerosol spectrometer probe (CSASP) 100-HV cloud drop sizing probe during some events at KWR and the Candelabra Tower. CSU also collected aerosols and trace gases at the Candelabra Tower. These measurements are briefly described below.

3.3.3.2.1 CSASP

A PMS CSASP measured the droplet size distribution during several fog events at KWR during the study. The CSASP uses a helium-neon laser to illuminate the sampling zone where the air flow is flowing perpendicular to the laser beam. If no particles are within the sample air flow, then the laser terminates on a dump spot, and no particles are counted. Particles passing through the sampling zone scatter light

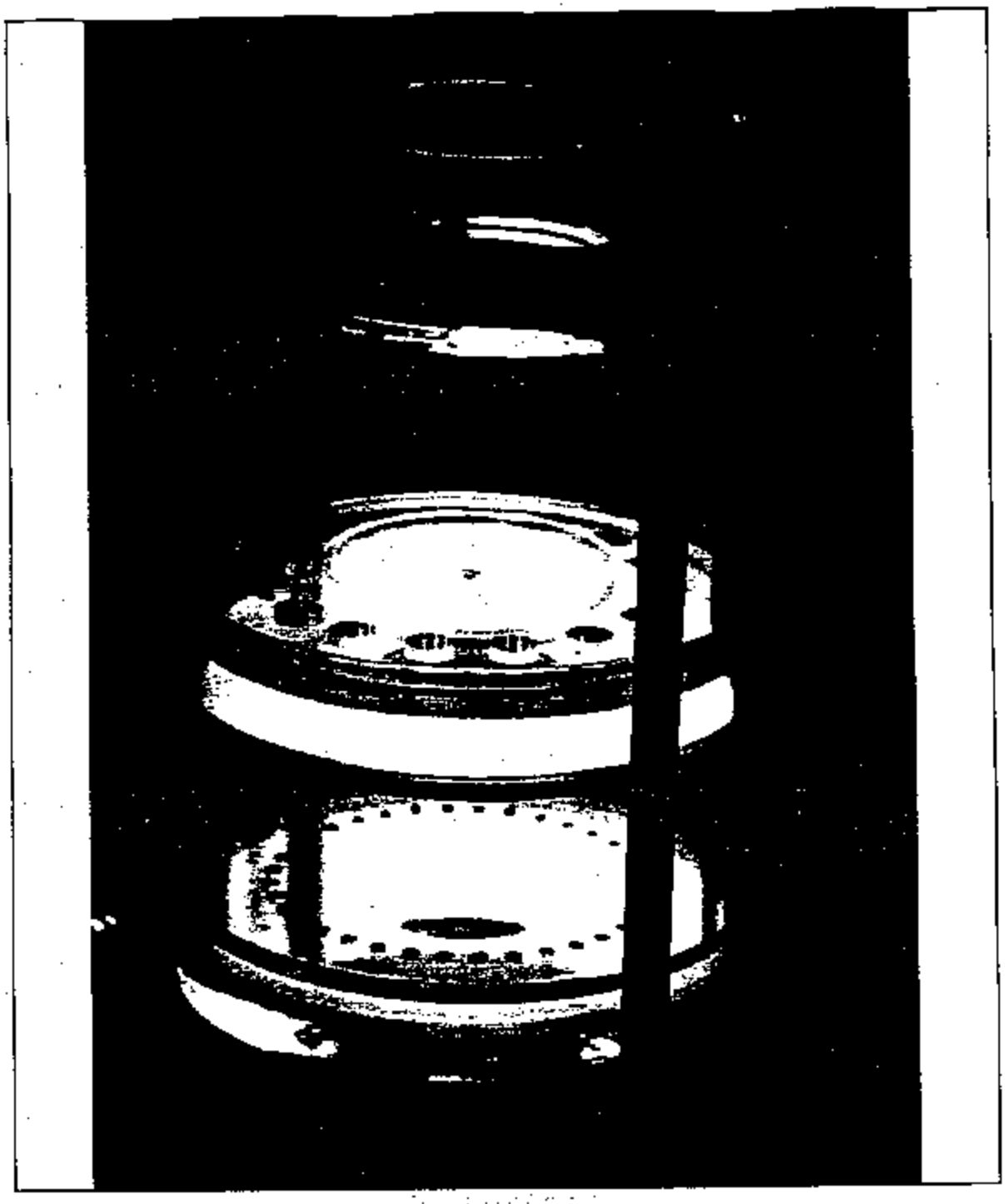


Figure 3-32. Two-stage ETH fog impactor.

in proportion to their size around the dump spot of the laser and into the collecting optics, where the light is condensed onto a photodetector.

The CSASP can measure the size distribution of fog droplets from 0.5 to 47 μ with 4 ranges. Each range contains 15 evenly spaced channels between each range maximum and minimum. Range 0 measures the distribution from 3 to 47 μ, Range 1 measures the distribution from 2 to 32 μ, Range 2 measures the distribution from 1 to 16 μ, and Range 3 measures the distribution from 0.5 to 8 μ. Range 1 provided the best coverage of drop size distributions measured during IMS95.

Field operations of the CSASP included field calibration checks with glass microspheres (from Duke Scientific Corporation, 15.7 μm ± 1.1 μm) before collecting data. The CSASP was operated to count particles in each range for 10 seconds, cycling through each range continuously until the CSASP was shut off. Postprocessing of the data included selecting out only Range 1 and then converting the particle counts per 10 seconds to particle counts per cc of air sampled. The manufacturer's specified flow rate of 12.5 cc/s was used to make the conversion. In some cases, the number of droplets counted in a particular channel exceeded the permitted maximum.

3.3.3.2.2 Berner Low-Pressure Impactor

Aerosol measurements were made at the Candelabra Tower by a Berner low-pressure impactor (Hauke Model LPI/30/0.06). This aerosol cascade impactor features 8 stages, with size cuts ranging from 0.06 to 8 μm in diameter and a blank stage. The inlet stage is designed to remove particles larger than 16 μm in diameter. Flow through the impactor is controlled by a critical orifice at 28.2 l/min.

Tedlar substrates collected impacting particles on each stage during IMS95. These substrates were coated with silicon spray to minimize particle bounce. Aqueous extracts of the substrates were analyzed by ion chromatography for major ions.

3.3.3.2.3 Annular Denuders

Annular denuders (Oberholzer et al. 1992) sampled gaseous ammonia, nitric acid, and SO_2 during the fog study at the Candelabra Tower. Flow rates through the denuders were controlled by critical orifices and measured by a flow meter. Three different coatings were used for the denuders: 0.2 M phosphoric acid to collect ammonia, 0.5 M potassium hydroxide to collect SO_2, and 0.5 M sodium fluoride to collect nitric acid. Although the potassium hydroxide coating also collects nitric acid, the potential oxidation of nitrogen dioxide to nitric acid on this strongly basic coating makes the sodium fluoride coating preferable for nitric acid measurements, especially in high NO_X environments like the SJV.

The annular denuders were extracted with 3 ml of deionozed (DI) water after sampling. These aqueous extracts were analyzed by ion chromatography for ammonium, nitrate, and sulfate. A small quantity of hydrogen peroxide was added to the sodium hydroxide denuder extract before analysis, to ensure that all sulfur was oxidized to sulfate.

The collection efficiency of the denuders depends on the gas sampled, ranging from approximately 82% for nitric acid to 96% for ammonia. Separate collection efficiency experiments made with the denuders have determined that the collection efficiencies are very close to the theoretical values.

3.3.3.2.4 Dual-Channel Peroxide and Analyzers

Two dual-channel peroxide analyzers were operated during IMS95 in a joint effort by the National Center for Atmospheric Research (NCAR) and CSU. Initially, both instruments were collocated at the KWR core site for an intercomparison. The NCAR instrument was later relocated to Fresno and then to Bakersfield, for several days each, to obtain information about spatial variability in SJV peroxide concentrations. The two instruments were also operated at the Candelabra Tower, with one at the base and one at the top of the tower.

The dual-channel hydrogen peroxide and total organic hydroperoxide instrument is a continuous method developed by Kok and Lazrus (Lazrus et al. 1986) and has a typical hydrogen peroxide detection limit of 20–30 pptv, with 10% precision and 15% accuracy for gas phase concentrations around 1 ppbv. The instrument's time response is 30 s.

The analysis procedure using this method consisted first of quantitatively transferring soluble gases into distilled water flowing through a coiled glass tube. The hydroperoxides in the collected solution were reacted with p-hydroxyphenylacetic acid under conditions of enzymatic catalysis to produce a fluorescent biphenyl derivative. Spectroscopic monitoring of the fluorescence emission at 420 nm allowed quantitative determination of hydroperoxides in the aqueous solution.

An estimate of the relative contribution of hydrogen peroxide to total hydroperoxides was measured by introducing catalase into a second aqueous flow channel, to preferentially destroy hydrogen peroxide before quantification. The dual-channel instrument yielded only semiquantitative organic hydroperoxide information, because catalase can also react with organic hydroperoxides. The principal interference is problematic when the contribution of the organic hydroperoxides to total hydroperoxides exceeds 50%. In this situation, the accuracy of the hydrogen peroxide measurement was reduced significantly. However, the ability to quantify total hydroperoxides was unaffected. To minimize this interference, the

catalase concentration was regularly monitored and controlled to limit hydrogen peroxide destruction to 90% or less. If the hydrogen peroxide destruction efficiency was found to have changed significantly, then the catalase concentration was adjusted to guarantee reliable measurements.

Calibration was accomplished with gas and liquid phase standards. The gas phase standards permitted quantification of any losses in the sample inlet lines. If significant losses were detected, the inlet line was cleaned and replaced.

3.3.3.2.5 Trace Gas Monitors

Trace gas concentrations were measured at the Candelabra Tower by monitoring systems at the base of the tower in an abandoned control room and in a two-story enclosure at 427 m agl near the top of the tower. Table 3-12 itemizes the instruments at these two locations. Quality control procedures and results are in Richards et al. (1997).

Table 3-12
Trace Gas Sampling Instrumentation

Parameter	Manufacturer	Analysis Technique	Range	Time	Approx.
NO/NO_y	TEI 42S	Chemiluminescence	200 ppb	<20 s	0.1 ppb
O_3	ML 8410E	Chemiluminescence	200 ppb	20 s	2.0 ppb
SO_2	TEI 43S	Pulsed fluorescence	50 ppb	15 s	0.5 ppb
Data logger	CSI CR-10	A/D conversion with data storage	N/A	Records data	0.005 VDC
Calibrator	TEI 146	Dynamic calibration	N/A	NA	NA
Transfer Standard	Dasibi 1003 AH/PC	UV photometry	500 ppb	<25 s	1.0 ppb

3.3.3.2.5.1 NO/NO_y Monitor

A TEI Model 42S monitor was employed to continuously monitor the ambient air for NO and NO_y via the chemiluminescence analysis technique. The monitor was a modification of TEI Model 42B, which has received EPA equivalence status. The modification involves removing the catalytic converter from the instrument housing and placing it immediately downstream of the sample inlet. A Teflon tee immediately upstream from the converter permitted sampling of either calibration gas or ambient air. The ambient air entered through an inverted Nalgene funnel, which prevented rain from entering the sample line, and passed through a 5.0-μm Teflon filter in a Teflon filter holder. All sample air and calibration gas lines

Teflon tubing. Multipoint calibrations and precision checks were performed through the calibration gas line. The Teflon particle filter was replaced at the base of the tower on January 23, after two weeks of sampling. Additional particulate filters were installed inline just prior to the instrument's inlet for both the NO and NO_y sample lines, but these filters were not replaced during the sampling program.

3.3.3.2.5.2 SO_2 and O_3 Monitors

The internal sampling configuration of each instrument remained unchanged throughout the study. Sample lines were kept to a minimum and were attached to an ARB-provided borosilicate manifold. Air was drawn into the manifold through an inverted Nalgene funnel, which prevented rain from entering the sample line, followed by a 5-μm Teflon filter in a Teflon filter holder, a Teflon tee to admit calibration gas, and a Teflon tube through a sample cane. All sample air and calibration gas lines used 6-mm Teflon tubing. Multipoint calibrations and zero and span checks were performed by supplying calibration gas to the Teflon tee. The Teflon particle filter was replaced biweekly. Additional particulate filters were installed inline just prior to the instrument's inlet for all sample lines, but these filters were not replaced during the sampling program.

3.3.3.2.6 Time-Lapse Video

Time-lapse video images were recorded at the top of the tower by a Panasonic Model AG-6730-P Super VHS time-lapse recorder. During January 13–19, the recorder was set at 240 hours per tape, which yields a playback time of 12 minutes for 24 hours of recording. The recorder was set at 480 hours per tape during January 9–13 and again on January 19, when the CSU measurements at the tower ended. At this speed, the playback time for 24 hours of recording is 6 minutes. The recording speed, time, and date of each image were displayed at the bottom of each frame. The video recorder is designed to stop recording each night. It was set so the downtime was only a few minutes near midnight.

A Sony SSC-S20 camera was mounted in a Pelco EH-4500 camera enclosure on a railing outside the building at 427 m agl on the tower. The camera was aimed to the east and focused on the KCRA tower, which provided a reference to indicate the depth of the fog. The strobe lights at several heights on the KCRA tower, as well as automobile headlights and other surface lights, gave an indication of the presence and depth of fog at night.

The Super VHS tapes were edited and transcribed onto a Super 8 tape, which was then used to make VHS tapes for distribution. The time-lapse video images began at 1140 PST on January 9 and ended on February 6.

3.3.3.3 Upper Air and Surface Meteorology

Meteorological measurements were obtained during the Fall and Winter studies. Surface meteorological measurements were obtained during the Fall study at one site, whereas surface and aloft measurements of meteorological parameters were obtained during the Winter study. Several point measurements were obtained during the vertical fog study in the northern SJV that preceded the main portion of the Winter study. Similar surface sensors were used throughout IMS95.

3.3.3.3.1 Upper Air

Upper air meteorological measurements were made either continuously via sodars and RWPs with RASS or intermittently via rawinsondes. These measurements are described below.

3.3.3.3.1.1 RWP/RASS Instruments

The 915-MHz boundary layer RWPs were pulsed Doppler radars that measure vertical profiles of winds in the boundary layer and lower troposphere. With the addition of a RASS, the RWP can measure profiles of virtual temperature (T_v). T_v is the temperature that a sample of dry air would have if its pressure and density were equal to those of the moist air parcel. Thus, an air parcel's T_V is always higher than its dry bulb temperature. The 915-MHz RWP technology was developed by the National Oceanic and Atmospheric Administration (NOAA) Aeronomy Laboratory. The RASS was developed in the 1970s by NOAA's Wave Propagation Laboratory and was adapted to the 915-MHz RWP in 1987. Radian International LLC manufactures the 915-MHz lower atmospheric RWP (LAP-3000) and RASS through a cooperative research and development agreement among NOAA, Radian, and STI.

Figure 3-33 shows the LAP-3000 RWP and RASS installed at MKR. The LAP-3000 consists of a single phased-array antenna. The radar beam is electronically pulsed vertically and 23° from vertical in any of four orthogonal directions. A "clutter fence," a rigid screen designed to suppress signals that are reflected from nearby obstacles, surrounds the antenna. The LAP-3000 includes electronic subsystems that control the radar's transmission, reception, signal processing, and RASS. The LAP-3000 also includes a communications computer (called the LAP Gateway system) that lets users download data and remotely control profiler operations. Each RASS unit consists of four vertically pointing acoustic sources (which are equivalent to high-quality loudspeakers) placed around the radar antenna and an electronics subsystem (an acoustic power amplifier and signal-generating circuit boards). The acoustic sources were enclosed by noise-suppression shields to minimize nuisance effects that might have bothered nearby neighbors or others working near the instrument. Each acoustic source transmitted approximately 75 W of power and produced acoustic signals of about 2,020–2,100 Hz.

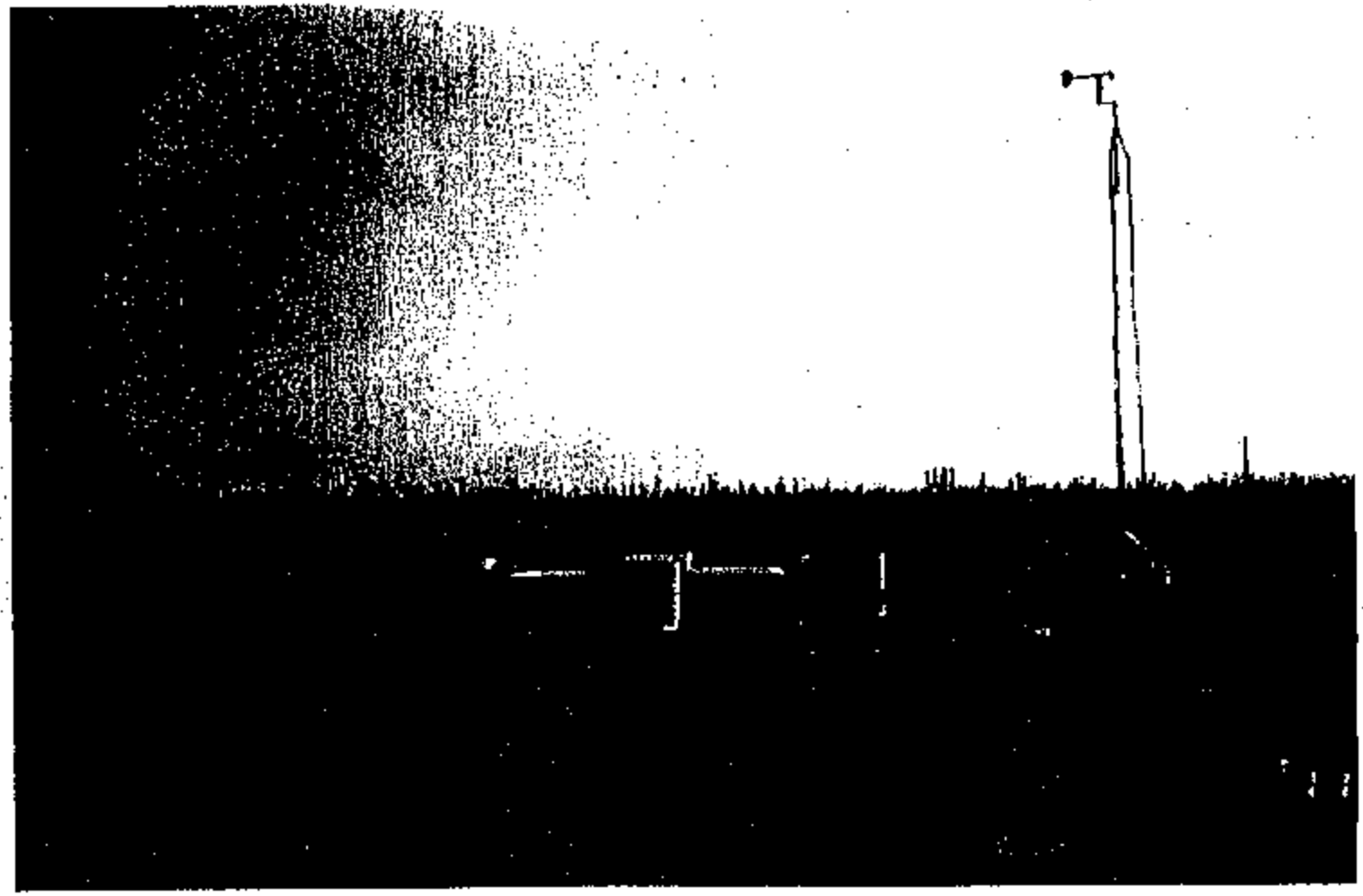


Figure 3-33. RWP and RASS at the Mouth of the Kings River site.

The principles of profiler operation are relatively straightforward. Basically, the radar transmits an electromagnetic pulse along one of the beam directions. The duration of the radar transmittal determines the length of the pulse emitted by the antenna, which in turn corresponds to the volume of air illuminated (in electrical terms) by the radar beam. These radio signals are then scattered by small-scale turbulent fluctuations that induce irregularities in the atmosphere's radio refractive index. The radar is most sensitive to scattering by turbulent eddies whose spatial scale is half the wavelength of the radar, or approximately 16 cm for a 915-MHz profiler. Signals can also be scattered by "hard" targets such as raindrops, trees, buildings, and birds. The receiver measures small amounts of the transmitted energy that are scattered back toward the radar (referred to as "backscattering"). These backscattered signals are received at a slightly different frequency than the transmitted signal. This difference, called the Doppler frequency shift, is directly related to the velocity of the air moving toward or away from the radar profiler along the pointing direction of the beam.

An averaged spectrum of the backscattered energy as a function of frequency is computed for each altitude (called a "range gate"). The mean Doppler shift for each range gate is then calculated, and the peak in the Doppler spectrum is identified, along with the zero, first, and second moments of the peak. These moments represent, respectively, the returned signal power, the radial velocity (the velocity of the air toward or away from the radar along the beam), and the spectral width of the peak (defined as the standard deviation of the radial velocities contained in the peak). This process is then repeated for the other beams. It takes approximately 1–2 minutes to complete a sampling cycle for all the beams.

The radial velocity measured by the tilted beams is the vector sum of the horizontal motion of the air toward or away from the radar and any vertical motion present in the beam. By using appropriate trigonometry, the three-dimensional meteorological velocity components (u, v, and w) and wind speed and wind direction are calculated from the radial velocities, with corrections applied for vertical motions. The LAP-3000 uses a technique called "consensus averaging" to compute averaged wind profiles. In this technique, the software operating the radar selects the largest subset of the radial velocities measured during the averaging period that Fall within a user-selectable velocity window (typically 2 m/s). For IMS95, at least 60% of the radial velocities were required to fall within 2 m/s of each other; if they did not, the winds (or temperatures) at that altitude failed the consensus test, and no data were reported.

For IMS95, the LAP-3000 profilers were cycled between a so-called "low mode" and "high mode" for measuring winds aloft. The low mode had a low altitude coverage with a fine vertical resolution, while the high mode had a greater altitude coverage with a somewhat coarser vertical resolution. The radar profilers

measured winds from about 110 m agl to 3–4 km agl with a combination of 57-m (low mode) and 101-m (high mode) vertical resolutions.

Vertical profiles of T_v were measured by the RASS subsystems. T_v was measured from about 110 m agl to 1.5 km agl in 105-m increments. The operating principle behind RASS is that, when the wavelength of the acoustic signal matches the half-wavelength of the radar (called the Bragg match), enhanced scattering of the radar signal occurs. During RASS operation, acoustic energy transmitted into the vertical beam of the radar produces the Bragg match and allows the radar profiler to measure the propagation speed of the acoustic signals. Once the speed of sound is known as a function of altitude, T_v profiles can be calculated with appropriate corrections for vertical air motion. As a rule of thumb, a vertical velocity of 1 m/s can alter a T_v observation by 1.6° C. For IMS95, T_v was not adjusted for vertical air motion; instead, any questionable T_v data were identified and removed from the data set or flagged by an appropriate QC code during data validation (Lindsey et al. 1996).

Each RWP with a RASS measured hourly averaged profiles of wind speed, wind direction, vertical velocity, T_v and returned signal strength (signal-to-noise ratio). The temperature data were collected for the first 5 minutes of each hour, and then winds were measured during the remaining 55 minutes. Sampling specifications and data quality objectives for the wind and T_v data are in Table 3-13.

Table 3-13
Sampling Configurations and Data Quality Objectives for RWP/RASS Instruments

Specification	Winds	T_v
Averaging period (min)	55	5
Reporting interval (min)	60	60
Time standard	PST	PST
Time convention	Begin	Begin
Vertical resolution (m)	57 (< 565 m agl) and 101 (> 565 m agl)	55
Minimum altitude (m agl)	110	112
Maximum altitude (m agl)	3,914	1,477
Manufacturer's reported accuracy	1 m/s and 10°	1°C
Precision	m/s and 20°	1°C
Data recovery rate (% of possible)	80% @ 1.5 km	80% @ 0.75 km
Range	0 to 24 m/s (per beam) and 0 to 360°	-10° to +25°C
Sample frequency (sec)	25	15

As discussed earlier, each radar profiler operated in a so-called low and high mode, which produced two wind profiles each hour. Low mode winds were measured with a 57-m vertical resolution, and high mode

winds were measured with a 101-m vertical resolution. These low and high mode winds were merged into a single data set to produce one wind profile per hour. The finer resolution 57-m wind data were used in the lowest altitudes up to 565 m agl. Above that altitude, the 101-m resolution winds were used up to about 4,000 m agl. The altitude where the resolution of the winds changed from 57 m to 101 m was chosen so as to take into account the data recovery rates and the need to minimize any gaps or missing wind data in the merged data set.

3.3.3.3.1.2 Rawinsonde Sounding Systems

The rawinsonde sounding systems used by STI during IMS95 were VIZ Manufacturing, Inc. (VIZ) Model W-9000 Loran-based sounders. These systems used a radiosonde ("sonde") attached to a helium-filled weather balloon to measure aloft wind speed, wind direction, atmospheric pressure, temperature, and RH as the balloon ascended. VIZ Mark-II radiosondes carried aloft by 100-g balloons were used with the sounding systems. In the Mark-II, a capacitance aneroid barometer measured atmospheric pressure, a rod thermistor measured temperature, and a carbon hygristor measured RH. A Loran receiver relay on the Mark-II measured times of arrival (TOA) and time difference (TD) values of Loran signals from three or four Loran stations. All sensor outputs (including the Loran signals) were fed to a low-power 403-MHz transmitter on board the radiosonde and were transmitted to a ground-based receiver and data acquisition system. Figure 3-34 shows a VIZ Mark-II radiosonde attached to a helium-filled weather balloon and ready for launch, as well as the antenna of the ground-based receiver/data processing system.

The data acquisition system consisted of a VIZ ZEEMET instrument rack equipped with data processing electronics, and a DOS-based personal computer that summarized the data in near-real time to produce vertical profiles of winds and thermodynamic variables. The data acquisition system converted the radiosonde data into engineering units by using calibration coefficients provided with each sonde. The data acquisition computer stored the data on a hard disk, and the data were copied to floppy diskettes at the conclusion of each sounding.

The VIZ-9000 system calculated wind data by measuring the horizontal and vertical position of the balloon at regular intervals. The balloon's altitude was computed by integrating the hydrostatic equation with the observed pressure, temperature, and moisture data. The sonde's horizontal position was determined by using the Loran TOA and TD signals, which were converted to latitude and longitude. The rate of change of horizontal position and altitude was used to compute wind speed and wind direction in near-real time, as described below.

Four soundings were made each day during the study period except for December 16–18, when

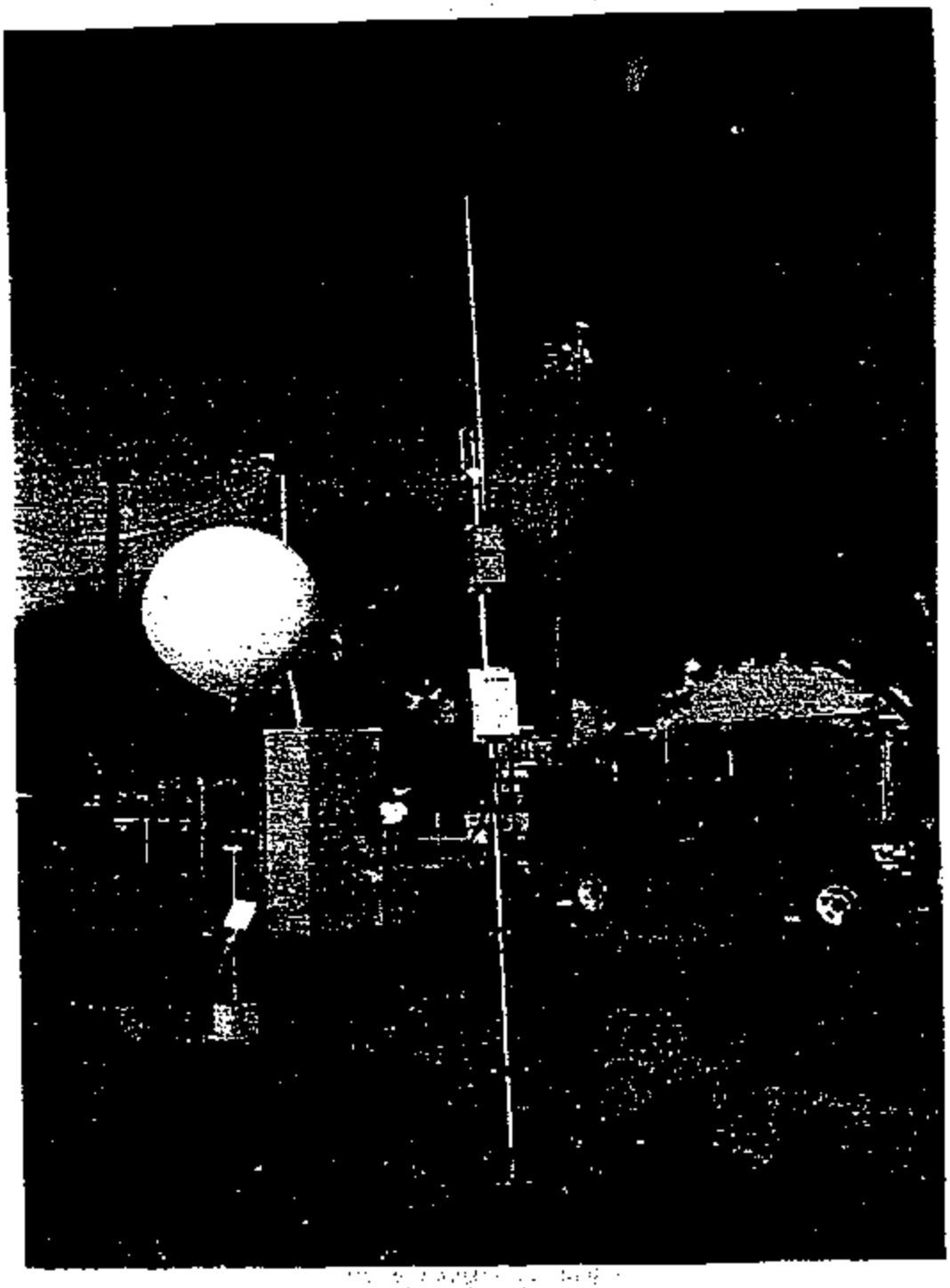


Figure 3-34. VIZ Mark-ii radiosonde attached to helium balloon before launch.

operations were halted because of rain. The soundings were made at 0400, 1000, 1600, and 2200 PST. The 100-g weather balloons were inflated so that the average rate of ascent was 150 m/min to 180 m/min for all soundings. Data from the VIZ sondes, including the Loran information, was sampled approximately once every 3 seconds as the balloon ascended. Given this sampling rate, the vertical resolution of the thermodynamic data in the soundings was approximately 7–9 m. Table 3-14 lists the specifications for the VIZ-9000 sounding system; the information on instrument performance was provided by the manufacturer.

Table 3-14

Instrument Specifications for VIZ-9000 Sounding System

Parameter	Specification
Radiosonde	
Model	Mark-II Microsonde
Frequency	403 ±3 MHz
PTU Data	
Pressure:	
Range	1,050 to 5 mb
Accuracy	1.0 mb
Resolution	0.1 mb
Sampling rate	3 sec
Temperature:	
Range	90° C to +50° C
Accuracy	0.5° C
Resolution	0.1° C
Sampling rate	3 sec
RH:	
Range	5% to 100%
Accuracy	3.0% RMS
Resolution	1.0%
Sampling rate	3 sec
Wind Data	
Position	LORAN-C
Wind speed:	
Range	min. 0.5 m/s
Accuracy	0.5 m/s
Resolution	0.1 m/s
Sampling rate	See Table 3-15
Wind direction:	
Range	1° to 360°
Accuracy	5°
Resolution	1°
Sampling rate	See Table 3-15

For the IMS95 rawinsonde systems, wind observations were computed from the Loran data in the following manner. The raw Loran data, sampled at the same frequency as the thermodynamic data (i.e., every 3 seconds), were fitted with a least-squares curve, which was applied over a user-selectable "smoothing interval." The data were smoothed to reduce erroneous variability in the position information from the Loran receiver. Points were then picked from the least-squares fit at user-selectable subintervals, called "computation intervals." Finally, wind speed and direction were calculated from this Loran position information. For example, if the smoothing interval was 60 seconds, the computation interval was 15 seconds, and the ascent rate was 3 m/s, then the winds were smoothed over a 180-m layer, and the reported wind speed and direction at each altitude were averaged over a 45-m-thick layer. Table 3-15 lists the intervals used to compute the winds at BFK and FRE.

Table 3-15

Wind Computation Setup for VIZ Sounding System

Elapsed Time (sec)	Altitude (m msl)	Smoothing Interval (sec)	Computation Interval (sec)	Wind Layer Thickness (m)
0–180	20–630	60	15	5
180–end	630–end	120	15	45

3.3.3.3.1.3 DAS and Sodar

A REMTECH phased array Doppler sodar or DAS was used to measure wind speed and direction at KWR in 50-m increments up to 600 m, with its lowest gate centered at 50 m. Wind speed and direction were averaged to 15 minutes and to hourly averages. This system was collocated with a 10-m tower by using a standard surface meteorological system for wind speed and direction, temperature, humidity, and solar radiation, as described below. The sodar antenna array was atop the instrument trailer near the center of the site, while the 10-m tower was 30 m north of the instrument trailer.

A single sodar was located at FEL to obtain the mixing heights throughout the study period. No information is available on the type of instrument used.

3.3.3.3.2 Surface

Surface meteorological measurements were performed with standard meteorological sensors whose wind speed threshold is about 0.5 to 1 m/sec and sonic anemometers whose wind speed threshold is about

0.05 m/sec. The latter estimated wind speeds during calm wind conditions that often occur in the valley during the winter.

3.3.3.3.2.1 Standard Surface Meteorological Sensors

Surface meteorological monitoring stations were installed at 10 sites, as shown in Figure 3-6; their geographic information is in Table 3-1. The locations included the four sites where there was an RWP with a RASS (ELN, COR, MTL, and MKR), as well as FEI, KWR, SWC, CRT, FEL, and KRN. An eleventh site was included with TSS 5A, but it did not operate during the complete study period, although it operated during the last two episodes. At all sites, wind speed and wind direction were measured at a height of 10 m, with most sites using an R.M. Young wind monitor or a Met One system (the ARB sites, ELN, and COR), as illustrated in Figure 3-35. No information was obtained for the type of sensors used at FEL and KRN. The R. M. Young and Met One instruments were integrated wind speed/wind direction sensors, which measure wind direction by the rotation and alignment of the sensor's vane-type body with the wind and measure wind speed by a rotating propeller attached to the front of the wind monitor. RH and temperature were measured by Vaisala or Met One sensors. These instruments used a capacitance element to measure RH and a thermistor element to measure temperature. The systems were mounted in a naturally aspirated radiation shield at about 2 m agl, except at COR and ELN, where they were at 5 m agl. As an example, sensor information and specifications for the R. M. Young and Vaisala systems are in Table 3-16; Met One systems are similar. The data quality objectives (DQOs) established for the IMS95 surface meteorological data are in Table 3-17.

Total solar radiation was also measured at KWR by a LI-COR (LI 200s) pyranometer that reported radiation in W/m^2.

Campbell Scientific, Inc. (CSI) CR-10 data loggers acquired and recorded the data at the surface meteorological monitoring sites. At the sites where the surface meteorological stations were collocated with the radar profilers, the CR-10 data logger was connected to the radar profiler's LAP Gateway communications computer via a serial interface. The data were transferred to the Gateway computer once per hour via software developed by CSI and STI, and the Gateway computer was polled at least once per day to transmit the data to STI. At the four standalone surface meteorological sites (FEI, SWC, KWR, and CRT), the data were polled at least once per day via modem and transmitted to the contractor who was responsible for the data.

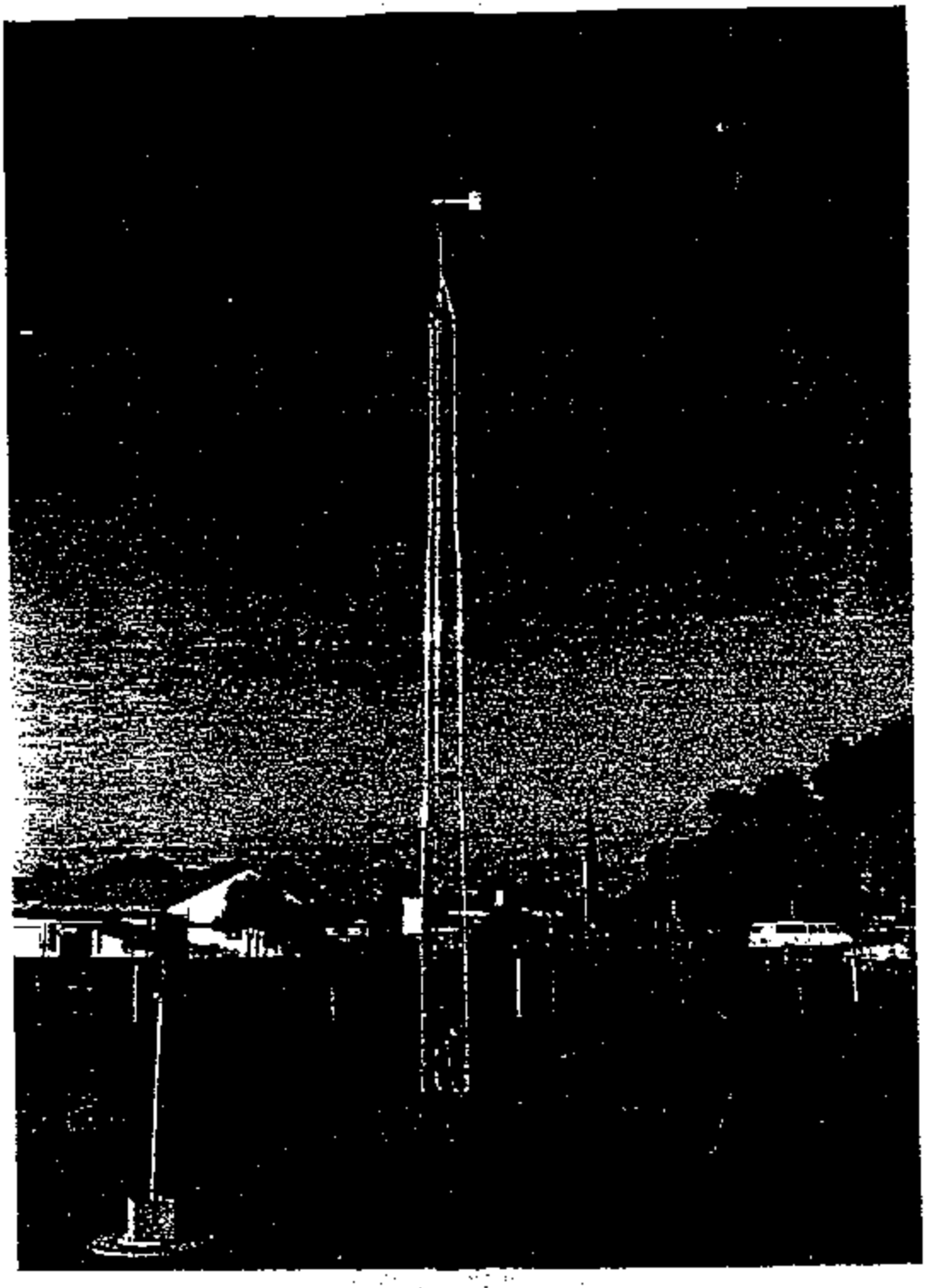


Figure 3-35. 10-m surface meterorological tower.

Table 3-16

Sensors at Surface Meteorological Stations

Measured Parameter	Sensor Manufacturer	Sensor Model	Sensor Specifications
Wind velocity	R.M. Young	5305-AQ Wind Monitor	Range: 0–40 m/s Distance constant: 2.7 m for 63% recovery Threshold sensitivity: 0.4 m/s Sampling frequency: 0.5 Hz
Wind direction	R.M. Young	5305-AQ Wind Monitor	Range: 0–360° with 5° deadband from 355–360° Threshold sensitivity: 0.5 m/s @ 10° offset; 0.7 m/s @ 5° offset Delay distance: 1.2 m for 50% recovery Damping ratio: 0.45
Temperature	Vaisala, Inc.	HMP35C[1]	Range: -33° C to +48° C Accuracy: ±0.4° C
RH	Vaisala, Inc.	HMP35C[1]	Range: 5–100% RH Accuracy: ±3%

[1] The temperature/RH sensor was mounted in an R.M. Young naturally aspirated "Gill" radiation shield.

Table 3-17

Data Quality Objectives for Surface Meteorological Stations

Parameter	Data Quality Objective
Wind speed	±0.25 m/s (ws 5 m/s) ±5% (ws > 5 m/s)
Wind direction	±5°
Temperature	±1.0° C
Equivalent dew point temperature	±1.5° C

The CR-10 data logger at each surface meteorological station was programmed to read the output from the wind speed/wind direction, temperature, and RH sensors once every 2 seconds. The data logger then converted the sensor outputs to engineering units and computed the dew point temperature from the temperature and RH observations. The 2-second data values were stored temporarily and used to compute 5-minute and hourly averages at all sites except KWR, where only hourly averages were reported. Standard deviations of all the parameters were also reported.

3.3.3.3.2.2 Sonic Anemometers

Sonic anemometers (sonics) were located at 6 sites throughout the SJV, as indicated in Table 3-1 and Figure 3-6. Of these sites, 5 were standalone sites where only the sonic was located. The other site was TSS 5A; 12 sonics were located at that site, along with other measurement instruments in a 0.5-km2 area, as described in Section 3.2.5 and in Gray et al. (1996). The 5 standalone sites where in areas were low wind speeds might be expected. The purpose of these sites was to evaluate how low the wind speeds are during calm conditions and to evaluate the spatial representativeness of the TSS 5A site.

Sonics measure wind velocity by sensing the effect of the wind on transit times of acoustic pulses traveling in opposite directions across a known path length. The 5 sonics used in this study were designed to collect wind velocity components in three axes (u, v, and w). Since there are no moving parts to come into dynamic equilibrium with the air flow, the sonic responds extremely rapidly and linearly to wind velocity fluctuations and is free from contamination from other velocity components as well as pressure, temperature, and RH. The sonics measure wind velocity at 100 Hz, averaged to 10 Hz for the output. The wind direction accuracy is typically ± 0.1°, and the wind speed accuracy is typically ± 0.05 m/s. The wind speed threshold is 0.05 m/s and can be resolved to the nearest 1 cm/s.

3.3.3.3.3 TSS 11 - Vertical Fog Study, Northern Valley

Four vertical levels of temperature and RH measurements were obtained at the Candelabra Tower during TSS 11. The sensors used were the same as those used in the southern SJV. Sensors were operated at a nearby tower at approximately ground level, 122 m, 244 m, and 366 m agl. The nearby tower was chosen because the ARB already had meteorological sensors there, which were used or upgraded for IMS95.

3.3.4 Laboratory Measurements

Laboratory measurements included the chemical analysis of (1) inorganic and organic aerosol species and gas phase inorganic species collected on filters and (2) gas phase organic species collected via cartridges and canisters.

3.3.4.1 Filter-Based Samples of Aerosol Species

Filter-based samples were collected via several types of samplers: SFSs, SGSs, portable samplers, and low-volume and high-volume DVIs. The samplers are described in Section 3.3.1 and 3.3.2.

3.3.4.1.1 Inorganic and Organic Aerosol Species Collected by SFSs, SGSs, and Portable Samplers

The field measurement methods for filter-based sampling via SFSs, SGSs, and portable samplers are described in Sections 3.3.1 and 3.3.2, with schematics of the sampling protocols in Figures 3-18 through 3-24. Below is a brief description of the methods used to determine the chemical composition of the collected samples.

3.3.4.1.1.1 Filter Media

Particles and gases were collected on several substrates configured both in series and in parallel for the Fall and Winter studies. Different substrates and configurations were needed to allow collection and analysis of the different chemical compounds of interest, such as inert Teflon filters for mass, impregnated fiber filters to collect reactive species, and heat-treated quartz filters for organic species. Lippmann (1989), Lee and Ramamurthi (1993), Watson and Chow (1993a, 1994), and Chow (1995) evaluated substrates for different sampling and analyses. On the basis of these evaluations, the 47-mm filters used for the Fall and Winter studies were (1) Gelman (Ann Arbor, Michigan) polymethylpentane-ringed, 2.0-mm pore size, PTFE Teflon membrane filters (serial number R2PJ047) for particle mass, light absorption, and elements; (2) Pallflex (Putnam, Connecticut) quartz fiber filters (serial number 2500 QAT UP) for carbon and ions; and (3) Whatman 31ET cellulose fiber filters (serial number 1441047) impregnated with citric acid for ammonia measurements or impregnated with sodium chloride for nitric acid measurements. Standard QA procedures were employed to check each filter by lot and batch to assure that blank values were within tolerance, that Teflon filters had no holes, and that filters requiring pretreatment had been pretreated properly. Details are in Chow et al. (1994).

3.3.4.1.1.2 Chemical Analysis

The Teflon membrane filters were analyzed for mass by gravimetry, for light absorption (B_{abs}) by densitometry, and for 40 elements (Na to U) by XRF (Dzubay 1977, Watson and Chow 1997). The front quartz fiber filters were analyzed for water-soluble chloride (Cl^-), nitrate (NO_3^-), and sulfate ($SO_4^=$) by ion chromatography (Mulik et al. 1976, Chow and Watson 1997); for ammonium (NH_4^+) by automated colorimetry (Bolleter et al. 1961); for soluble potassium (K^+) by atomic absorption spectrophotometry (Rodes et al. 1989); and for OC and EC by thermal/optical reflectance carbon analysis (Chow et al. 1993a, Watson and Chow 1993, 1994). The backup quartz fiber filter determined artifact OC by thermal/optical reflectance carbon analysis. The NaCl-impregnated cellulose fiber filters were analyzed for nitrate by ion chromatography to determine HNO_3. The citric-acid-impregnated cellulose fiber filters were analyzed for ammonium by automated colorimetry to determine NH_3.

3.3.4.1.2 Organic Aerosol Species Collected by HVDVI

In the laboratory, the quartz fiber filter samples collected by the HVDVI (see Section 3.3.2.1.3.1) were extracted via a sequential extraction protocol that was designed to optimize the removal of nonpolar and polar organic compounds from the quartz fiber filters (Rogge et al. 1993a, Rogge 1993, Schauer et al. 1996). Hexane (2 x 30 ml) and then benzene/isopropanol (2:1 mixture, 3 x 30 ml) were added sequentially to the filter composites. After mild sonic agitation, each extract was filtered and combined into a single flask via a custom-designed transfer line assembly. The combined sample extract was then reduced to a volume of 300 to 500 ml by rotary vacuum distillation (27° C and 640 mm Hg of pressure) followed by gentle solvent evaporation with a high-purity stream of N_2. The concentrated extract was divided into two aliquots; one was reacted with freshly produced diazomethane to convert organic acids and acidic hydroxy compounds to their methyl ester and to methoxy analogues, respectively.

Extracts from the fine carbon particle samples were analyzed by a Hewlett-Packard Mass Sensitive Detector system (GC Model 5890, MSD Model 5972) with a 30-m fused silica HP-1701 column. Compounds were quantified by selective ion monitoring (SIM) via the MS data systems. Relative ion counts were converted to compound mass concentrations by using relative response factors obtained via injection of external standards that contain the compound of interest. The organic compounds used in the organic chemical tracer model of Schauer et al. (1996) are listed in detail in Table 3-10. They form a targeted list of chemical substances that were sought by reduction of the GC/MS data.

3.3.4.2 Cartridge and Canister Samples of Gas Phase Organic Species

3.3.4.2.1 Carbonyl Species

DNPH cartridges were prepared, typically in batches of 150 with purified DNPH (~99.9996%) and phosphoric acid. The impregnating solution as well as several finished cartridges from each batch were analyzed for formaldehyde background before using them for impregnation. The cartridges were sealed by plugs and kept individually inside capped vials to prevent unwanted exposure. Approximately 40 of these cartridges were packaged in quart-size metal cans for storage in a refrigerator and shipment to the field via overnight delivery.

Carbonyl cartridge samples were analyzed in the laboratory in batches of approximately 20 to 40. Analysis was performed by injecting each sample cartridge with a known amount of an internal standard (hexanal-DNPH) and eluting with 2 ml of acetonitrile. The eluent was collected into a 2-ml septum vial and injected by an autosampler into an HPLC (Shimadzu LC-6) for separation and quantitation of the hydrazones (Fung

and Grosjean 1981). Species determined by this method include formaldehyde, acetaldehyde, acetone, propanal, methyl ethyl keytone (MEK), benzaldehyde, cyclohexanone, pentanal, hexanone, and hexanal, which was used as the internal standard. The analytical conditions were as follows. The column used was Axxiom 10 cm ODS 3u, and the species were eluted by gradient elution of a varying mixture of water and CH_3CN. Upon elution from the HPLC, the species were detected at 365 nm.

QC for the measurement included collection of field blanks and duplicates, which constituted approximately 10% of the samples. QC in the laboratory included instrument calibration for each batch of samples, replicates of standards, and the use of approximately 10% of the samples for estimating analytical precision.

Precision, accuracy, and stability results for sampling carbonyl compounds via the DNPH cartridge method are in Solomon and Thuillier (1995). The results presented were based on the extensive data set collected during the 1990 SJVAQS.

3.3.4.2.2 TNMOC, CO, CH_4, CO_2 and Speciated VOCs

CO, CH_4, and CO_2 were measured in the canisters by GC with an FID (GC-FID). Methane (CH_4) was measured directly by an FID after the column, whereas CO and CO_2 were first reduced to CH_4 over an Ni catalyst at 400° C and reported as CH_4 equivalent.

TNMOC in canisters was determined according to EPA Method TO-12. This method used a GC-FID instrument that detects simple hydrocarbons (compounds containing only hydrogen and carbon) with great sensitivity as well as hydrocarbons containing other elements besides hydrogen and carbon (such as oxygen, chloride, and other heteroatoms). However, under usual operating conditions and in the usual sample sizes, hydrocarbons containing heteroatoms are typically below the detection limit of the GC-FID method. For this reason, TNMOC by this method is often called total nonmethane hydrocarbons (TNMHC), in which the species containing other elements are corrected for or ignored.

Hydrocarbon speciation analysis on the air samples was performed via dedicated GC-FID systems. The FID provides high sensitivity for all hydrocarbons, as mentioned above. All canister samples collected during episodic periods were also analyzed via GC-MS, as described below. Tenax cartridge samples were analyzed only by GC-MS. The GC-FID method used for this analysis was based on EPA Method TO-14 for GC analysis of SUMMA® canister samples. In the present study, the GC-FID method is called the "conventional" hydrocarbon speciation method, in which a 500-ml sample aliquot is used, whereas the "improved" method processes a 5,000-ml sample aliquot to better determine the low concentrations of

species containing over 10 carbons—that is, species above decane (C_{10}). Both the conventional and improved methods were used for IMS95 sample analysis. In the conventional method, samples were analyzed by directly trapping a 250-ml or 500-ml aliquot of the sample by drawing it through a 1/8" x 6" stainless steel loop packed with glass beads, which was immersed in liquid oxygen. For the improved method, a cation dryer was used before the freeze-out loop to remove water, which allowed up to 5,000 ml of a sample to be processed. The trapped hydrocarbons were desorbed into a capillary cryofocusing loop by immersing the stainless steel freezeout loop in hot water at 90° C. Hydrocarbons were separated by a 60-m, 0.25-mm inside diameter (ID), 1.0-μ column. The column temperature was held at -20° C for 3 minutes or at -60° C for 5 minutes and then temperature-programmed to 200° C at 3° C/min. The total analysis time was about 70 minutes.

Samples were also analyzed by GC-MS full scan, which required large sample volumes. Typically, 5,000 to 50,000 ml of air were processed to obtain sufficient sample volume for GC-MS analysis on the numerous small peaks in the chromatograms. The analysis was optimized on loadings of 1 to 4 μg of analyte cryofocused on the head of the column. Therefore, it was essential to know the TNMOC concentration ($\mu g/m^3$) in the sample before performing the GC-MS run. Generally, this concentration was determined by the TO-12 method or from an independent GC-FID analysis. With GC-MS full scan sensitivities for most compounds at 0.1 ppbv, it is possible to identify many of the "hydrocarbon" components traditionally allocated to the large number of unidentified peaks in the speciated hydrocarbon analyses of nonurban and remote rural air samples. All canister and Tenax cartridge samples were analyzed via the GC-MS method.

Details of the operating conditions, precision, accuracy, and stability results for sampling TNMOC, CO, CH_4, CO_2, and speciated VOCs are in Solomon and Thuillier (1995). Their results are based on the extensive data set collected during the 1990 SJVAQS.

3.3.4.3 Chemical Species Analyzed in Fog Samples

The chemical species analyzed in IMS95 fog samples are in Table 3-18. Some of these samples were analyzed in the field, immediately after collection, whereas others were analyzed in the CSU laboratory. Several of the more unstable species were stabilized immediately after field collection, for later laboratory analysis. All stored samples were refrigerated until the analysis was performed.

Each fog collector was cleaned with deionized water before each event. After cleaning and before each event, a blank of each collector stage was taken by rinsing the collection surface and sample flow path with deionized water and collecting the rinse water in a sample vial. Blanks were handled and analyzed in the same fashion as the samples, as described below.

Table 3-18

Species Measured in SJV Fogwater

Species	Analytical Method	Detection[a]	Precision[b]
Cl^-	Ion chromatography	2 µN	10%
NO_3^-	Ion chromatography	2 µN	5%
SO_4^{2-}	Ion chromatography	2 µN	5%
Na^+	Ion chromatography	2 µN	5%
K^+	Ion chromatography	2 µN	10%
NH_4^+	Ion chromatography	2 µN	5%
Mg^{2+}	Ion chromatography	2 µN	10%
Ca^{2+}	Ion chromatography	2 µN	10%
Formate	Ion chromatography	5 µN	10%
Acetate	Ion chromatography	5 µN	10%
Propionate	Ion chromatography	5 µN	10%
Pyruvate	Ion chromatography	5 µN	10%
Oxalate	Ion chromatography	5 µN	10%
Total organic carbon	TOC analyzer	100 ppb	10%
Soluble hydroperoxides	Fluorescence	0.1 µM	5%
S(IV)	Absorbance	0.3 µM	5%
Hydroxymeth-anesulfonate	Absorbance	0.5 µM	5%
Formaldehyde	Fluorescence	0.5 µM	5%
Fe	Atomic absorption	5 ppb	10%
Mn	Atomic absorption	5 ppb	10%

[a] Based on past experience, not IMS95 results; see Collett et al. (1997) for IMS95 results.
[b] Relative standard deviation of replicate analyses.

Sample pH was measured onsite with an Orion electronic pH meter (Model 250 or 290) equipped with a Microelectrodes, Inc. combination microelectrode (Model MI-710). This electrode can measure pH in samples as small as 10 µl, thus enhancing the ability to characterize the pH among small-volume samples from the ETH and IESL fog impactors. Before sample measurement, the electrode was calibrated with pH 4 and 7 buffers.

Sample aliquots for major ion analysis were removed in the field, placed in clean polyethylene or polypropylene vials, and refrigerated until analysis. Major anions and cations were analyzed via ion chromatography (IC) with conductivity detection. Chloride, nitrate, and sulfate anions were analyzed via a Dionex DX500 series ion chromatograph with an AS4A column equipped with an AG4A guard column and a self-regenerating anion suppressor. The latter was used for background suppression. Sodium carbonate/sodium bicarbonate in DI water was used as the eluent.

Ammonium, sodium, potassium, calcium, and magnesium cations were analyzed on a second Dionex DX500 ion chromatograph using a CS12 separator column equipped with a CG12 guard column and a self-regenerating cation suppressor. The latter was used for background suppression. Methane sulfonic acid in DI water was used as the eluent.

Samples were introduced into the ion chromatograph by a Dionex AS3500 autosampler. Through the autosampler and manual microinjection techniques, samples as small as 25 µl were analyzed. Detection limits for analyses of ionic species to be measured by IC range from 1 to 5 µN, depending on the species. These limits are well below the historical levels of these species measured in SJV fog water.

Immediately after collection, sample aliquots for organic acid analysis were placed into precleaned glass vials with Teflon-lined caps. A small amount of chloroform was added to each vial to prevent degradation of the organic acids from microbial action. The preserved aliquots were refrigerated until analysis. The samples were analyzed for formate, acetate, propionate, and pyruvate on the Dionex DX500 series ion chromatograph using an AS11 separation column equipped with an AG11 guard column and a self-regenerating anion suppressor. To achieve the maximum separation and quantitation, gradient elution was performed with a sodium hydroxide eluent. Detection limits are below 5 µN for all species.

Sample aliquots for formaldehyde determination were stabilized in the field by reacting the formaldehyde with a buffered bisulfite solution to form the stable hydroxymethanesulfonate (HMS). Formaldehyde concentrations were determined in the stabilized samples by reacting the HMS with 2,4-pentanedione and ammonia to form diacetyldihydrolutidine (DDL). The concentration of DDL was then measured on a Shimadzu RF-1501 fluorescence spectrophotometer. The detection limit for formaldehyde in this technique is 1 µM.

Sulfur (IV) exists in fog water in several forms—as dissolved SO_2, sulfite, possibly other inorganic forms, and in a complex with formaldehyde as HMS. Therefore, two types of S(IV) aliquots were prepared in the field, for later laboratory analysis. One aliquot was stabilized by reaction with a buffered formaldehyde solution to form HMS. This aliquot was used to determine total S(IV). In the second aliquot, the same procedure was used after the addition of hydrogen peroxide, which rapidly oxidizes free S(IV) to S(VI) and leaves only hydroxymethanesulfonic acid (HMSA). Thus, total S(IV) is measured, and then HMSA is measured by itself and S(IV) is determined by difference. The preserved aliquots were refrigerated until analysis. Before chemical analysis, the HMS is dissociated by adding a strong base. The free S(IV) and formaldehyde are reacted with acidic pararosaniline to form a purple

product that was quantified by absorbance at 580 nm via a Hitachi U-2000 UV/Vis spectrophotometer. The detection limit for each compound is 1 μM.

Soluble hydroperoxides were stabilized in solution by adding a buffered preservative solution containing parahydroxyphenylacetic acid (POPA) to form a stable dimer. Preserved aliquots were refrigerated until analysis. Peroxide concentrations as the dimer were later detected by a Shimadzu RF-1501 fluorescence spectrophotometer at an excitation wavelength of 320 nm and a monitoring fluorescence wavelength of 400 nm. The detection limit for this technique is 0.05 μM.

Aliquots for iron and manganese determination were placed into clean polyethylene vials, acidified to 0.16 M by addition of trace-metal-grade nitric acid, and refrigerated until analysis. Total iron and manganese were measured in the preserved aliquots by graphite furnace atomic absorption via a Zeeman-corrected Varian Spectra A-600Z Graphite Furnace Atomic Absorption System. Detection limits for iron and manganese were about 2 and 1 μg/l, respectively.

In the field, aliquots were prepared for TOC analysis by addition of a biocide and storage in a glass vial with a Teflon-lined cap. Samples were refrigerated until analysis. Analysis was performed by combustion via a Shimadzu Model 5000A TOC analyzer with detection limits of about 4 ppb for a 2.5 ml injection. With smaller sample injections, the detection limit rises. Previous analysis of TOC content in Bakersfield fog water indicates that concentrations are likely to be in the ppm range.

Chemical concentrations of the analyzed species were determined on the basis of multipoint calibration curves generated from analysis of a series of standard solutions whose concentration range spanned that of the analyzed samples. Standard solutions were prepared by dilution of stock solutions prepared from analytical-grade chemical reagents. Analytical results from the laboratory were tested by using replicate samples. To check for the reproducibility of analytical results, 5% of all samples were analyzed in duplicate. Standard solutions were interspersed with samples at a rate of at least 5% to provide a check on drifts in calibration. Procedural details, precision results, instrument detection limits, and results from preliminary data analysis are in Collett et al. (1997). Nominal values for these parameters, on the basis of past work, are in Table 3-18.

3.3.5 Emissions Activity Measurements

Emissions activity measurements consisted of daily visual surveys around each of the PM monitoring sites by using video and site logs, collecting traffic count data near many of the PM monitoring sites, and collecting road dust samples for soil silt loading determination. At saturation and core monitoring sites,

full-time field observers documented visible releases or changes in the surroundings that may have occurred between site visits and may have resulted in PM emissions. At boundary and flux plane sites, site operators documented the emissions activities in a log book; however, daily video was not obtained at those sites.

3.3.5.1 Daily Emissions Activity Measurement at PM Monitoring Sites

3.3.5.1.1 Surveys

The collection of emissions data to support IMS95 modeling and data analysis activities is an extensive undertaking. Activity data and emissions factors are needed to determine emissions estimates. Emissions factors are usually estimated from a few measurements and extrapolated to broader categories. However, emissions factor development can be costly and time-consuming and does not necessarily need to be performed concurrently with a field monitoring study, such as IMS95.

Activity data, on the other hand, are usually approximated from broad data (county or state, annual or monthly) to the specific time and place of interest, often by using surrogates (such as population density). This step leads to considerable uncertainty in the emissions estimates. Therefore, collection of day-specific activity data in the local area surrounding each monitoring site is important in understanding the temporal and spatial fluctuations in emissions, particularly for directly emitted PM. Such data thereby reduce the uncertainty in the emissions estimates. Activity data, however, especially for primary PM, often must be collected during the field study, because they cannot be "reconstructed" after the activity has occurred. For this reason, near-term IMS95 emissions data collection tasks focused on collecting activity data that occurred during each of the sampling days as well as developing micro land use surveys around each monitoring site.

The surveyors had been trained to document visible and potential PM sources and their locations, and to videotape these sources. Locations of PM sources were recorded on maps that acted as data sheets, such as in Figure 3-36. This data collection was performed only once in the Winter study, during a 3-day hiatus, to provide a baseline for the area. Recent areal photographs served the same purpose for the fall study, but they were too expensive to obtain for the much larger Winter study domain. Both land use displays are in the site description report (Solomon et al. 1997). Daily activity measurements performed by the surveyors included g a 360° videotape of each site; recording the location of activity data on maps; taking notes; and driving around each site in about a 1.6-km radius, noting changes in the surroundings caused by current activities or activities that may have occurred between visits. In urban areas, where the line of sight was limited, the surveyors drove through the surrounding areas to ascertain conditions.

Initials: _____ Time Arrive in Area: _____

Date: _____ Time Depart: _____

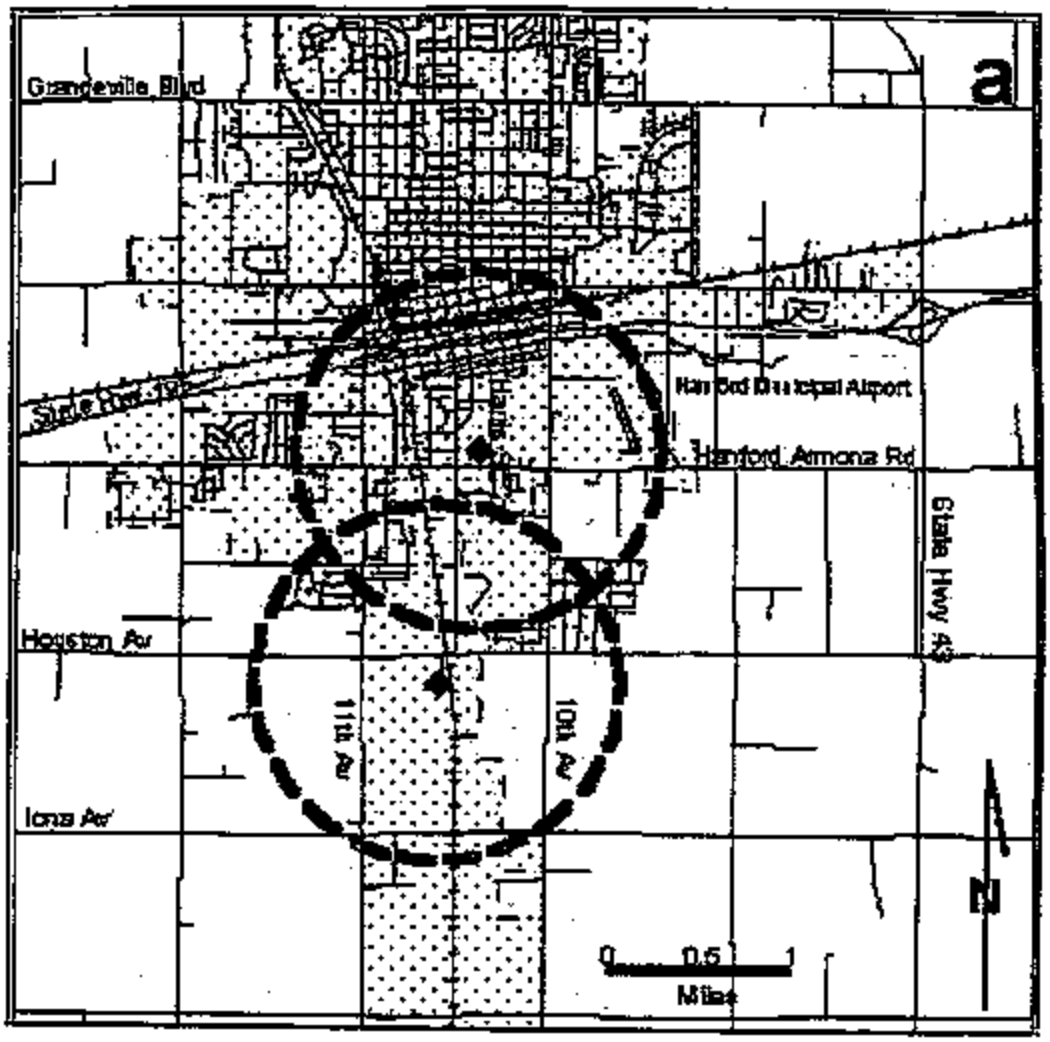


Figure 3-36. Sampler data sheet for indicating locations of PM sources around each monitoring site (◆).

3.3.5.1.2 Micro Land Use

One-time surveys were obtained to provide a baseline for the land use observed during the Fall and Winter studies. The land use surveys included maps of land use types and videos and photographs of the sites and surrounding areas. These surveys were the basis for the site descriptions report (Solomon et al. 1997). Sources surveyed included (but were not limited to) vacant lots, storage piles, agricultural acreage, livestock, paved and unpaved roadways, industrial operations, construction sites, and parking lots. In addition, the presence or absence of chimneys was noted within the few blocks surrounding each site. The microinventory was available to update and assess the adequacy of the baseline inventory. Data analysis also used the surveys to identify locations of possible sources that might have impacted a receptor site of interest.

3.3.5.1.2.1 Area Maps

During the Fall study, areal photographs were obtained from the county offices of the Agricultural Conservation Service. Most areal photographs were taken during the summer of 1995. The area maps (Solomon et al. 1997) can identify general land use characteristics around each site. A trained observer can use these maps to identify crop types and acreage.

During the Winter study, land use maps were developed by the surveyors who were collecting the daily activity data. Areal photographs were not obtained for the Winter study, because of the large number of expensive photographs needed to cover the Winter study domain. The land use surveys consisted of identifying land use types within a radius of about 1–2 km around each monitoring site. This was done by marking land use types on printed maps that show the sites and by drawing a circle with a 1-km radius around each site. Land use data were indicated on the maps during a 3-day hiatus (because of rain in the study domain) near the beginning of the study. These maps are in Solomon et al. (1997).

3.3.5.1.2.2 Photographs and Videotapes

Videos and photographs were obtained at every primary site. The photographs are included in the site descriptions report, and the videos supplement that report (Solomon et al. 1997). At each site, with the sampler location as the center of a circle, 360° line-of-sight videos were made. Additional video footage was taken of the area surrounding each site by driving around the rural sites at about a 1.5-km radius and around the urban sites at a radius of several blocks.

3.3.5.1.2.3 Day-Specific Activity

During the Fall and Winter studies, daily surveys were performed to characterize significant emissions-related activities that occurred within about a 25-km radius around the core and Boundary A air quality sites (COR during the fall; BFK, FEI, KWR, and SWC during the winter). This was accomplished by performing daily activity surveys within a radius of about 1–2 km around each core and saturation site. The characterized activities included (but were not limited to) farming operations, agricultural burning, construction and demolition, residential fireplace usage, and traffic events. Details of the approach are in Coe et al. (1996). In summary, observations were performed at each site, every day, during daylight hours. If activities occurred when the operator was present, their timing was documented on data sheets. Since operators visited each site only once per day for about 20 minutes, they also noted activities that had occurred during their absence (e.g., a field that had been plowed, streets that had been cleaned, or garbage cans that had been left on the curb). Operators also estimated the location of the activity. After the field study, surveyors' notes and videotapes were reviewed, and a database of activity, location, and time was constructed. A program was developed in Visual Basic to search the database when the site and time information are given (Coe et al. 1996). The input form for the search is illustrated in Figure 3-37. Data analysts and modelers could use this database to investigate aspects of the potential occurrence of intermittent emissions during the study, such as the following:

- Which PM sources were observed between specified dates,
- Which PM sources were within a variable radius from a particular monitor,
- How many times a specified source category was observed during the study period, near a particular monitor, or between certain dates.

The usefulness and success of this unique database were tested during the IMS95 data analysis process, which is described in Section 7.

One surveyor made observations during the Fall study, and three surveyors made observations of monitoring sites during the Winter study. Each surveyor worked 8 hours per day and drove 160–320 km per day. The amount of time each day that surveyors could spend in the vicinity of each monitoring site was 15 minutes to 1 hour for clustered sites.

After review of the videotapes and surveyor's notes, a Microsoft Access database was then constructed of the daily emissions activities, including summaries of the traffic count data, to allow simple queries of the data via a point-and-click program developed in Visual Basic. The database and user manual are described in Coe and Chinkin (1996). This database, including query capabilities, is part of the IMS95 data archive.

IMS-95 Fall Database Entry Form

Source Information:

Location:	Hanford-Corcoran
Source ID#:	1
Source Type:	Harvest
Source Subtype:	Cotton
Zone:	11
UTMx:	262.99
UTMy:	4019.82
Lon (degrees):	119.639
Lat (degrees):	36.286

Monitoring Sites Within 1 mile of Source:

Site 1	☒	Site 12	☐
Site 2	☐	Site 13	☐
Site 3	☐	Site 14	☐
Site 4	☐	Site 15	☐
Site 5	☐	Site 16	☐
Site 6	☐	Site 17	☐
Site 7	☐	Site 18	☐
Site 8	☐	Site 19	☒
Site 9	☐	Site 20	☐
Site 10	☐	Site 21	☐
Site 11	☐	Site 22	☐

Dates and Times Source was Observed: / **Weather Conditions:**

		Time arrived in observation area:	Time departed observation area:	Foggy:	Hazy:	Wind Strength:	Wind Direction:
Nov 1	☒	10:50	11:45	☐	☐	Weak	Northwest
Nov 2	☐			☐	☐		
Nov 3	☐			☐	☐		
Nov 4	☐			☐	☐		
Nov 5	☐			☐	☐		
Nov 6	☒	8:00	8:30	☐	☒	Weak	North
Nov 7	☐			☐	☐		
Nov 8	☐			☐	☐		
Nov 9	☐			☐	☐		
Nov 10	☐			☐	☐		
Nov 11	☐			☐	☐		
Nov 12	☐			☐	☐		
Nov 13	☐			☐	☐		
Nov 14	☐			☐	☐		

Figure 3-37. Sample Computerized Database Entry Form.

3.3.5.2 Traffic Counts and Silt Loadings on Roads

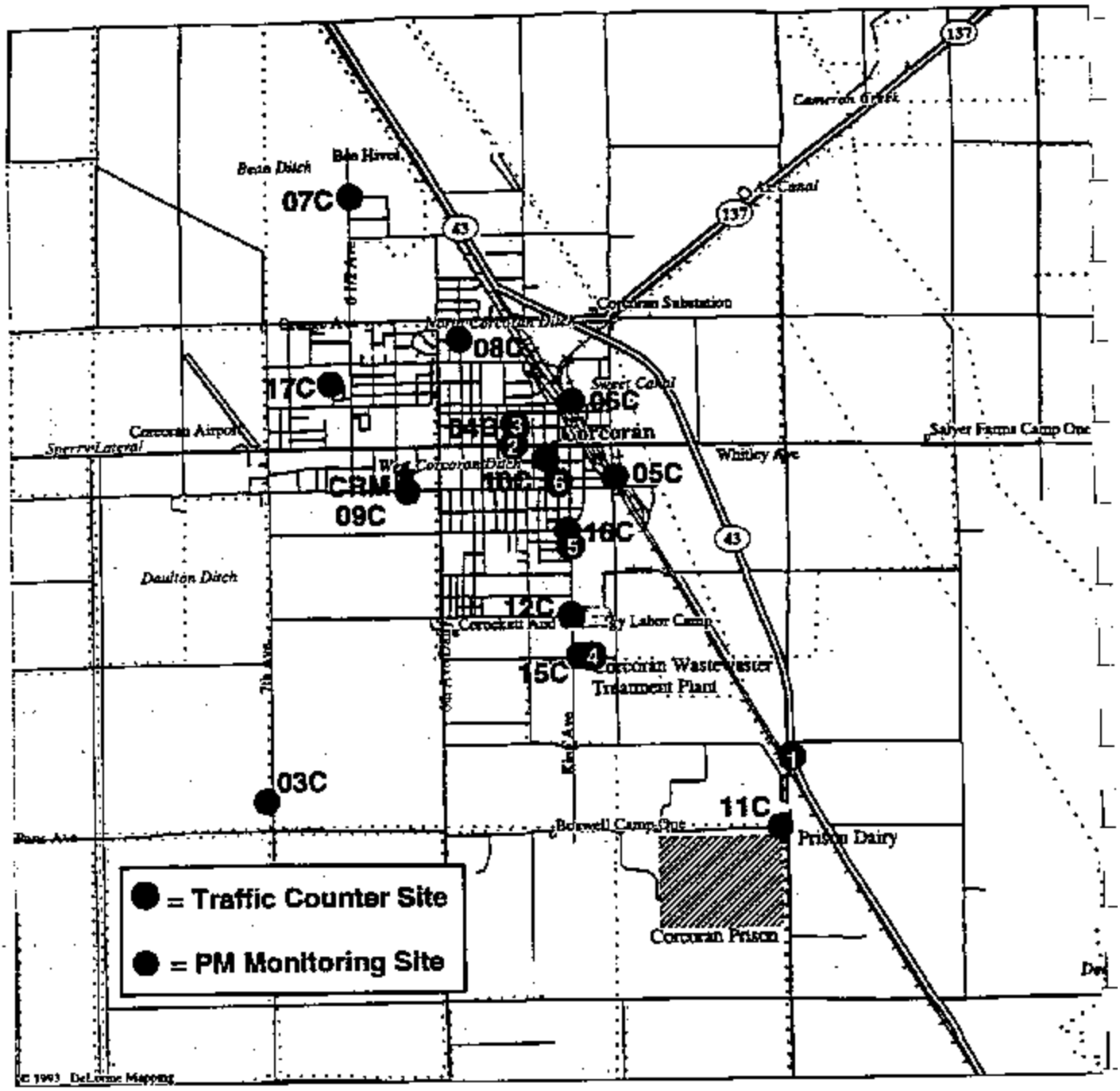
Automatic traffic counters, collecting continuous data, were operated at 6 locations during the Fall study and 18 locations during the Winter study. Locations of the counters are shown in Figures 3-38 to 3-41 for COR, FEI, BFK, and KWR, respectively. Each site reported hourly average traffic counts. At these same locations, road dust samples were collected and analyzed for silt content. The road dust sampling technician also noted the pavement surface condition and unusual activity in the area. During the Fall study, road dust samples were collected at 6 sites, but traffic counters were operated only after the end of the study. Road dust samples were collected via a commercial vacuum cleaner with a paper filter bag. The area vacuumed was carefully measured, and it varied from location to location to ensure that a sufficient sample was collected for further analysis. A separate tared bag was used for each sample. At the laboratory, the samples were then oven-dried, weighed, and sieved according to EPA procedures. These data will help to more fully characterize the impacts of on-road traffic on PM levels in the area.

3.4 Selection of Samples for Chemical Analysis

Owing to limited resources, not all samples collected during the Fall and Winter studies were submitted for chemical analysis. In the Fall study, resources for analyzing samples were available for about 6–9 days. In the Winter study, resources were available for 6 days. The final selection of which samples to analyze was based on a review of the mass data, which were obtained for all sites and all days.

Results of this anlaysis indicated that there were two distinct episodes during the Fall study—one during November 6–8 and another from November 10–14. For continuity, all samples were analyzed from the period November 6–14, a total of 9 days.

During the Winter study, there were four peak periods of PM buildup between storm fronts: December 9–10, December 20–22, December 25–28, and January 4–6. A review of the mass data indicated that peak values occurred at 23 sites during January 4–6, with the second highest number occurring during December 9–10. An examination the data by sites showed that the December 9–10 episode peaks occurred at boundary and flux plane sites (along the central flux plane, at 4 sites) and in the Bakersfield area (5 sites) and the Kern Wildlife Refuge area (5 sites). For the January 4–6 episode, the peak values were more evenly distributed at boundary sites (5 sites), and at saturation sites in Bakersfield (6 sites plus collocated sites) and Fresno (11 sites). Thus, the December 9–11 episode had the highest values in Bakersfield, the December 26–28 episode was completely dominated by Fresno sites (no others were present), while the January 4–6 episode had peaks of PM concentrations that were more uniform across the study domain. During December 9-11, rain only reached as far south as Fresno,



LEGEND

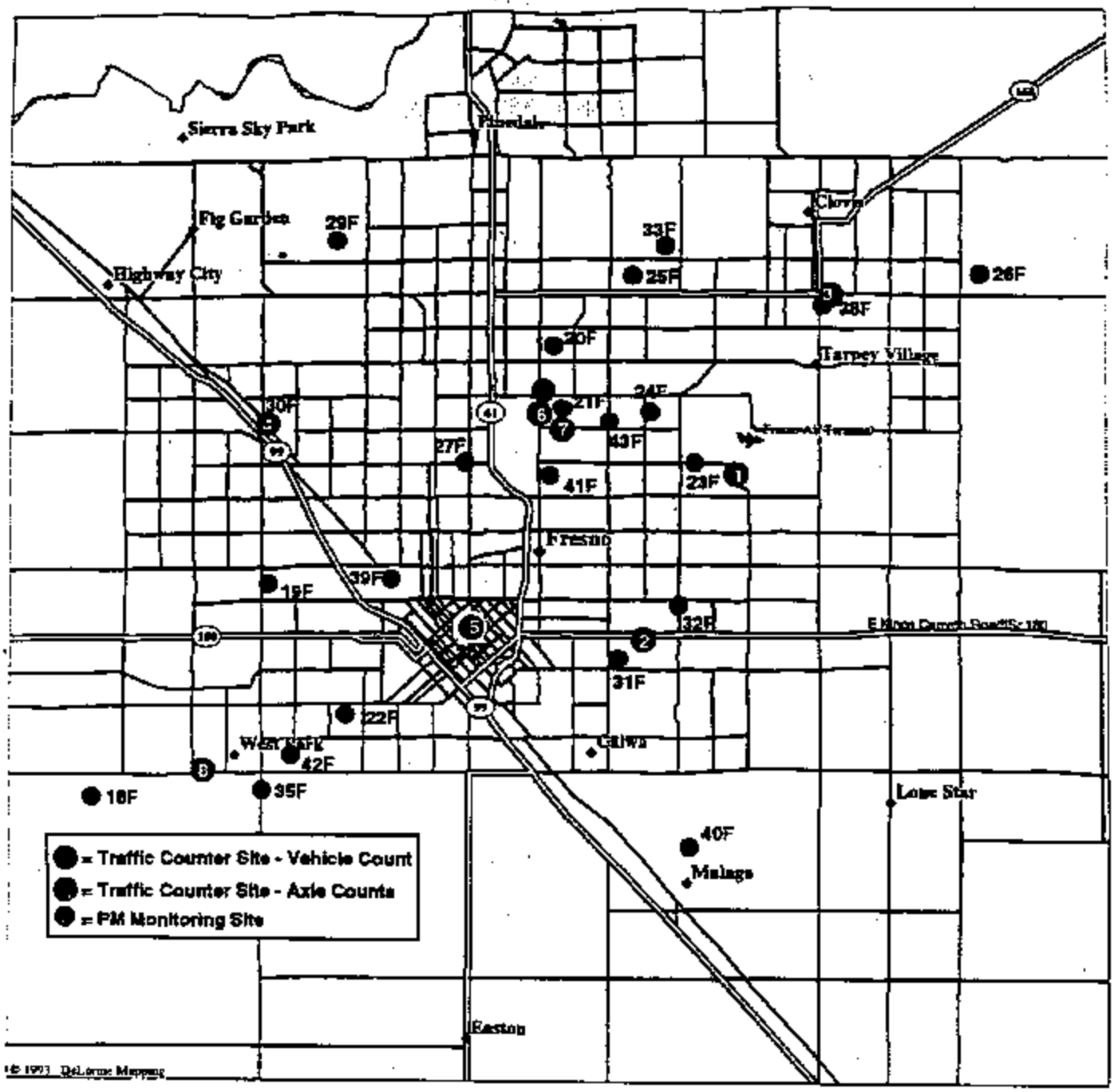
- State Route
- Geo Feature
- Town, Small City
- County Boundary
- Population Center
- Street, Road
- Major Street/Road
- State Route
- Railroad
- River
- Intermittent River
- Airfield
- Utility (powerline)

Scale 1:50,000 (at center)
5000 Feet
1000 Meters

File: CorcRoad.ovl13
Mag 13.00
Fri Feb 07 09:35:04 1997

Figure 3-38. Corcoran traffic counters and road dust sample collection sites for soil silt content—Fall study.

026 22-98-2



LEGEND

- State Route
- Town, Small City
- Large City
- Airfield
- Population Center
- Major Street/Road
- State Route

Scale 1:125,000 (at center)

2 Miles

2 KM

File: FreRoad.cvl
Mag 12.00
Tue Feb 11 15:24:07 1997

Figure 3-39. Fresno traffic counters and road dust sample collection sites for soil silt content—Winter study.

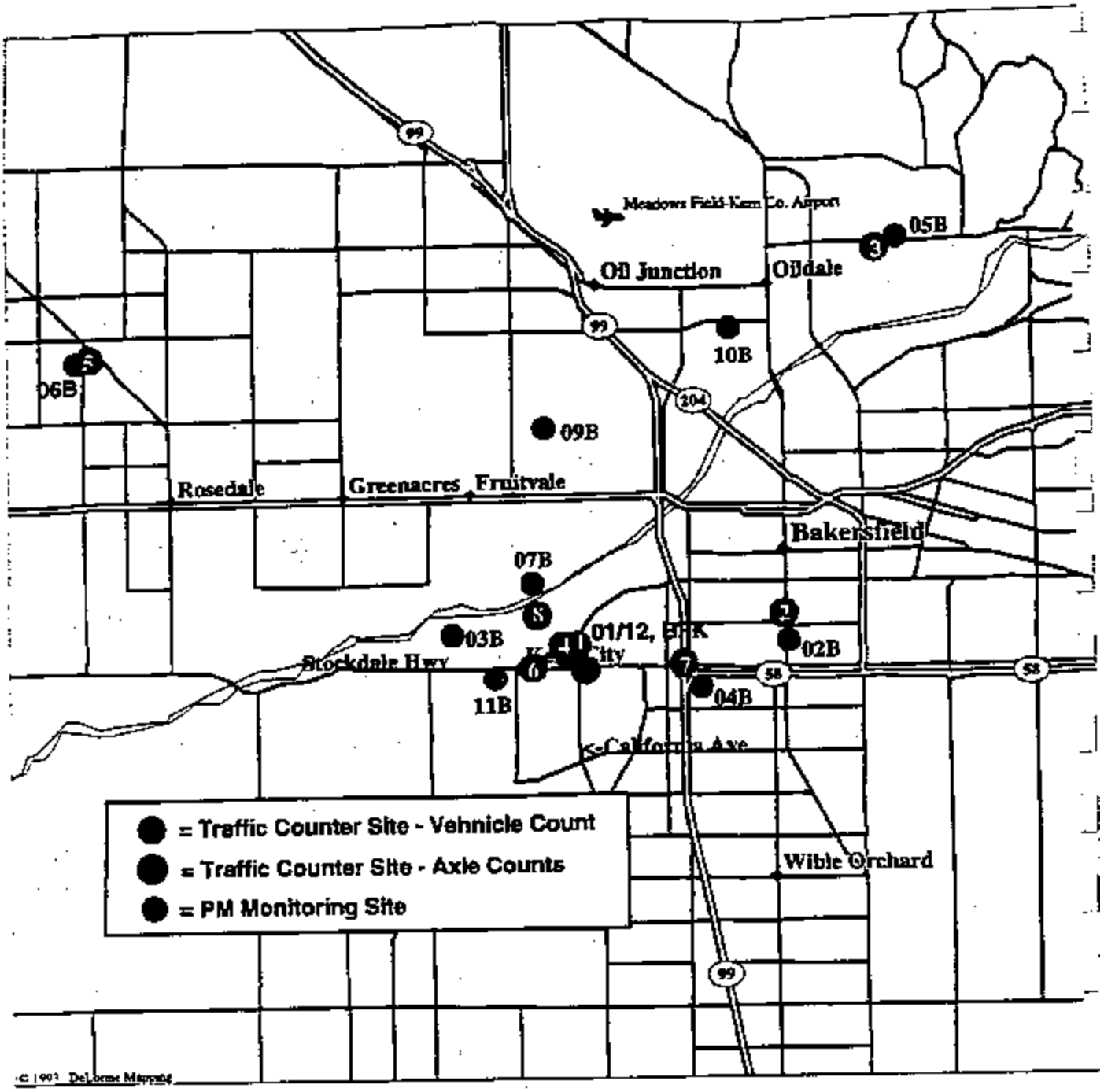


Figure 3-40. Bakersfield traffic counters and road dust sample collection sites for soil silt content—Winter study

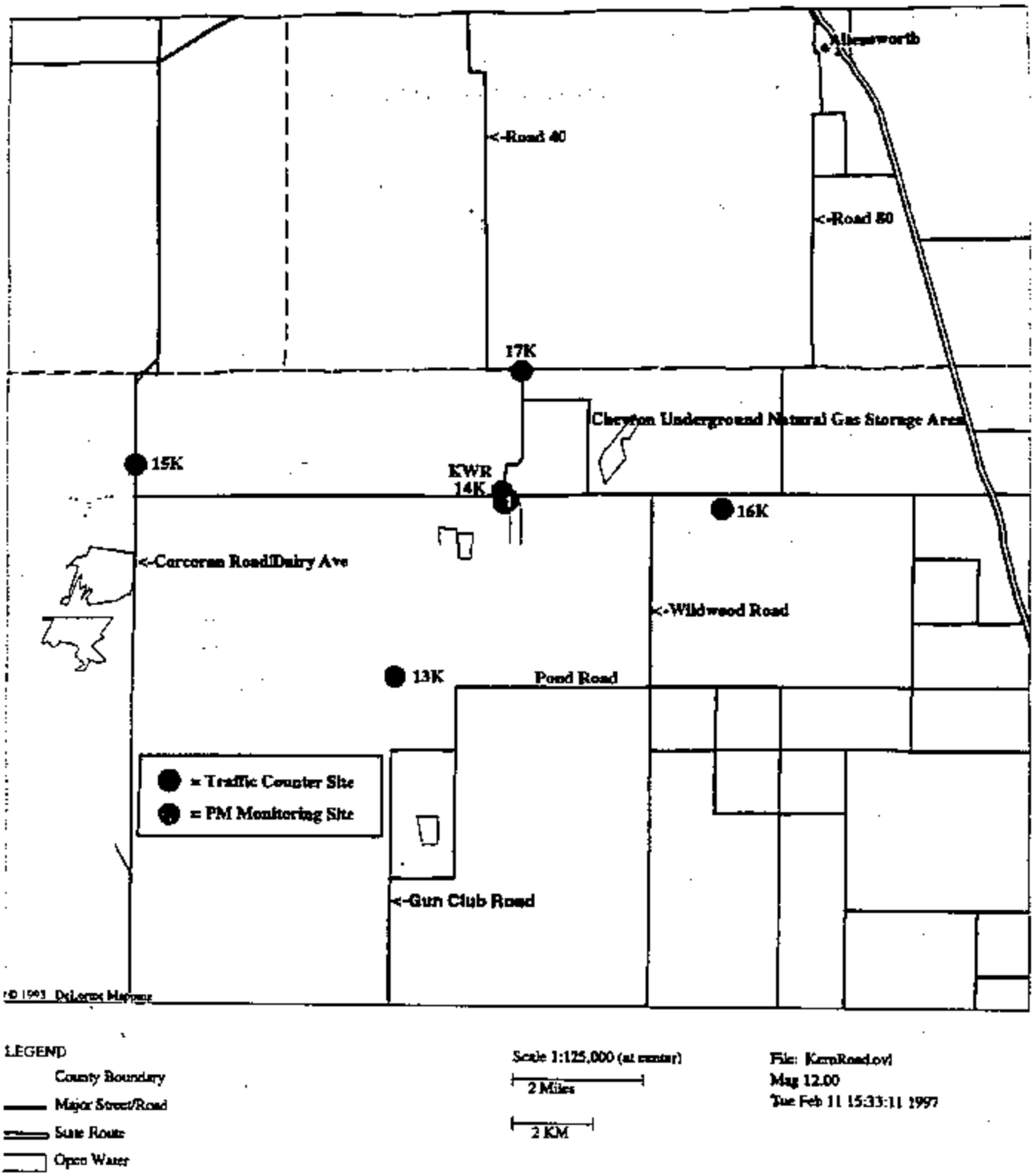


Figure 3-41. Kern Wildlife Refuge traffic counters and road dust sample collection sites for soil silt content—Winter study.

during December 26-28 it rained in Bakersfield, but not Fresno, and during January 4-6 the entire study domain was calm with no rain. Thus, meteorological patterns e.g., penetration of frontal systems into the valley, strongly influenced the spatical extent of PM buildup during IMS95.

The second highest peak value at sites during the study period occurred 18 times during the December 20–22 episode, followed by 13 times during the January 4–6 episode, and 11 times during the December 26–28 episode. The data indicated that the December 20–22 episode was dominated by sites in the north of the study domain (rain came up from Bakersfield), the January 4–6 episode's second-highest peak values were more evenly distributed, and the December 26–28 episode was again dominated by sites in the Fresno area and a few boundary sites.. The BFK core site was also high on December 26–28, but second-highest peaks did not occur at any other sites in the Bakersfield area.

Also noteworthy is the distribution of fog during the study. The major fog events occurred during the December 9–10 episode, with fog occurrences at all three core sites. During the remainder of the study, fog at the core sites was sporadic at best. In addition, the highest 3-hour PM values were at FEI during the December 25–28 episode. Complementary evidence indicated that this was probably due to wood burning in the FEI area; the filters were very dark and smelled like wood smoke.

On the basis of this analysis and related discussions during a conference call, the Technical Committee decided to analyze the following samples during the Winter study. For the December 9–10 episode, only the samples collected at the core sites were analyzed for chemical composition (PM_{10}, $PM_{2.5}$, gases [HNO_3, NH_3, and SO_2] that were collected by the filter-based methods, VOCs, carbonyl samples, and so on). This analysis provides important data to supplement the fog event data. For the December 25–28 episode, all samples collected for chemical analysis were analyzed for chemical composition; however, only short-duration samples, with collection times from noon on December 25 to noon on December 28, were analyzed for chemical composition, whereas all 24-hour samples were analyzed only for the December 26–27 episode. For the January 4–6 episode, all samples intended for chemical analysis were analyzed.

Section 4

AUDIT PROGRAM

4.1 External Quality Assurance Program (EQAP)

A comprehensive EQAP was an integral part of IMS95 and included field system and performance audits before the start of the measurement effort, as well as laboratory audits during the study. Audits were performed on the SFS sampler and five portable samplers during the fall study and during the winter study on virtually all air quality samplers and continuous analyzers, the surface and upper air meteorological measurements, and the four laboratories performing chemical analysis. The fall study used the same procedures as the winter study, which are described below. These audits were designed to ensure that data of known accuracy, precision, and validity would be obtained. A contractor and ARB personnel performed the audits. The EQAP was designed to determine the accuracy of the measurements and ensure proper operation of the instruments, while precision estimates, based on Level 1 span checks and/or replicated/duplicate measurements, were obtained from the contractors performing the field work.

The complete audit procedures used during the Fall and Winter studies are described in the quality assurance program plans (QAPPs) and standard operating procedures (SOPs) of the groups performing the audits (AeroVironment 1995, ARB 1995a). The QA contractor used ARB procedures, so both procedures should have been the same. Instruments at existing ARB or District sites were audited a month or so before the study, except for COP, BFK, and FEI, which were audited just before the study began. ARB also audited the criteria gas monitors at KWR and SWC.

Audit results, including estimates of the instrumentation's accuracy, are in Bush et al. (1996) and Miguel (1996).

4.2 Audit Program Scope

The objective of the audit program was to ensure that the established Data Quality Objectives (DQOs) were achieved. The two stages of the approach consisted of (1) reviewing the DQOs in the QA plan and the applicable measurement system SOPs to ensure that DQOs were adequate and realistic and that the proposed procedures were appropriate to those objectives and (2) testing the implementation of the SOPs through system and performance audits of each measurement system. The system audits documented and commented on how fully the DQOs were met by the level of adherence to the SOPs and recommended changes in site operations, if needed, to accomplish the objectives. The performance audits compared the response of the individual measurements to certified standards, to determine the deviation from the DQOs.

The remainder of this section details the IMS95 audit program, including the schedules, audit procedures, criteria, and reporting. Where project DQOs did not exist, the audit criteria were those recommended in the EPA monitoring guidelines, if available. For the radar profilers and RASSs, the audit criteria were based on prior experience.

4.3 Audit Schedules

Because of the study's short duration, all measurement systems were audited as soon as they were in place and operational, to identify and correct potential problems before they affected the measurement DQOs. All audits, except for the radar profiler and RASS performance audits and the fog sampler system and performance audits, were completed before the first day of monitoring. The radar profiler and RASS performance audits were carried out during the measurement period because of the lack of time to carry them out between the instrument setup and the onset of the study. Data collection was not disturbed during the audits, because they were based on comparisons between similar collocated measurement systems. The fog samplers were audited after the start of the monitoring period because they were not installed until after that date. These schedules were dynamic in that adverse weather or instrument problems could alter the audit dates. The audit dates are shown in Tables 4-1 and 4-2. Monday, December 4 and Friday, December 8 were reserved for core site audits that were not completed during the previous week.

4.4 Audit Standard Certification Procedures

4.4.1 Radar Profilers

Table 4-1

Audit Schedule for RWPs, RASSs, Sodars, and Surface Meteorological Measurements

Date		Audit Location and Action
Monday	November 27	System audits of MTL and MKR
Tuesday	28	System audits of ELN and COR
Monday	December 4	Set up audit sodar at MTL
Tuesday	5	Performance audit at MTL
Wednesday	6	Travel to MKR
Thursday	7	Performance audit at MKR
Friday	8	Travel to ELN
Monday	11	Performance audit at ELN
Tuesday	12	Travel to COR
Wednesday	13	Performance audit at COR
Thursday	14	Travel to TSS 5A site
Friday	15	Performance audit of TSS 5A sodar
Monday	18	Travel to PG&E sodar site
Tuesday	19	Performance audit of PG&E sodar
Wednesday	20	Return to AeroVironment Monrovia office

Table 4-2

Audit Schedule for Core Site Samplers and Rawinsondes

Date			Location	Observables
Sunday	October	29	COR	SFS and EPA portable TSP samplers
Monday	November	27	SWC	Core site samplers
Tuesday		28	FEI	Core site samplers
Wednesday		29	KWR	Core site samplers
Thursday		30	BFK	Core site samplers
Friday		31	BFK	Core site samplers
Tuesday	December	5	BFK	Fog samplers and rawinsondes
Wednesday		6	KWR	Fog samplers
Thursday		7	FEI	Fog samplers and rawinsondes

Audits were made of the upper air meteorological measurement instrumentation, as shown in Table 4-3.

Table 4-3

Upper Air Meteorological Measurement Instrumentation Audits

Location	Operator	RWP and RASS	Core	Sodar	Surface Meteorology[1]	Rawinsonde
MTL	STI	X			X*	
MKR	STI	X			X*	
ELN	ARB	X			X*	
COR	ARB	X			X*	
KWR	Multiuser		X		X*	
BFK	Multiuser		X	X		X
FEI	Multiuser		X			X
SWC	Multiuser		X		X*	
CAR	STI				X*	

[1] The surface meteorological measurements associated with the RWPs and RASSs at these sites consist of wind speed and wind direction at 10 m agl, ambient temperature, RH, and barometric pressure.

The audit standards consisted of a portable sodar to audit radar profilers and sondes to audit the RASS. Each of the associated certifications is described below.

4.4.1.1 Portable Sodar

The portable sodar was used to audit the 4 RWP systems and 2 sodar systems. These systems collected independent 15-minute average wind data that were compared with the collocated RWPs and sodars. The radar profiler audit locations were MTL, MKR, ELN, and COR, and the sodar locations were KWR and the TSS 5A site (west of Tulare and north of Corcoran). The audit sodar was an AeroVironment

Model 2000 3-axis system, whose performance was certified during an initial system checkout at AeroVironment's Monrovia headquarters and during checks before each of the individual audits.

4.4.1.2 System Checkout and Acceptance

Before field deployment, portable sodar operation was verified against a known audit standard. The standard was an AeroVironment responder (AVR), which generates a known Doppler-shifted frequency and timing interval.

To verify system operation, the sodar was operated in its normal mode. At least three complete averaging intervals (5 minutes long) were run for each of the three antennas that used the AVR. The signal produced by the AVR showed in the data output of the antenna where it was located as a zero wind speed at the 300-m range gate. Criteria for acceptable operation were 300-m wind speeds of 0.0 m/s ± 0.2 m/s. If the sodar data fell within this accuracy bound, then the sodar was considered suitable for use as an audit device.

To optimize the sodar's vertical range and minimize the potential influence of reflective sources, the sodar was expected to be operated with a 20° zenith angle.

4.4.1.2.1 Sodar Operational Verification before Each Audit

Before each audit by the portable sodar, its operation was verified by the AVR. This check was performed via the same procedure as the system checkout.

The portable sodar orientation was determined via a Brunton Pocket Transit Model F5007LM. The transit is tripod-mounted and can be read to an accuracy of approximately ± 0.5°. This magnetic alignment was corrected to true north by using the local magnetic declination. When possible and when the cloud cover allowed, the orientation was also verified by using the solar azimuth angle and site latitude and longitude.

4.4.2 RASS

Each RASS was audited by releasing airsondes and comparing the calculated T_V profile with the RASS profile. Before release, the sondes' output was verified against the surface pressure and temperature readings of an audit device. Surface pressure was measured by a Peet Brothers Ultimeter Model 3. This barometer was certified by single-point comparison with the AeroVironment standard barometer as well as periodic comparisons with airport pressure readings in the field. Temperature was measured by a Brooklyn Thermometer Company 76-mm immersion mercury-in-glass thermometer. This thermometer

was certified against AeroVironment's laboratory standard thermometer, a Brooklyn Thermometer Company NIST-traceable mercury-in-glass thermometer.

4.4.3 Wind Speed

The R.M. Young anemometer drive (Model 18801) is certified quarterly. A photo tachometer determines the actual rotational speed of the anemometer drive shaft, for comparison with the rotational speed indicated by the anemometer drive display. Readings are made at six speeds that are evenly spaced through the instrument's entire operating range.

No certification of the anemometer drive's torque disk was required.

4.4.4 Wind Direction

No certification of the compass or its torque disk was required.

4.4.5 Ambient Temperature

Upon being purchased, the mercury-in-glass thermometer for the audit was compared with AeroVironment's NIST-traceable standard thermometer. The two thermometers were immersed in water baths of approximately 0°, 10°, 20°, 30°, and 40° C. Periodic comparisons with the standard thermometer were not required.

4.4.6 Psychrometer Mercury-in-Glass Thermometers

Upon being purchased, the psychrometer mercury-in-glass thermometers were compared with AeroVironment's NIST-traceable standard thermometer. The two psychrometer thermometers and the standard thermometer were immersed in water baths of approximately 0°, 10°, 20°, 30°, and 40° C. Periodic comparisons with the standard thermometer were not required.

4.4.7 Precipitation

The volume of the graduated cylinder that was used to determine the audit volume of water was NIST-traceable.

4.4.8 Barometric Pressure

The audit barometer (Peet Brothers Ultimeter Model 3) was compared with a standard barometer yearly by Temperature Standards, Inc. The last certification before the study began was performed on May 10, 1995.

4.4.9 Total Solar Radiation

4.4.9.1 Pyranometer

The audit pyranometer is certified yearly. Li-Cor Inc., the manufacturer of AeroVironment's audit transfer standard, performs this certification.

4.4.9.2 Voltmeter

The voltmeter that reads the audit pyranometer outputs is certified yearly. Shaffer Engineering, Inc. of Irwindale, California performs the certification for AeroVironment. The last certification before the study began was performed on July 6, 1995.

4.4.10 Rawinsondes

4.4.10.1 Audit barometer

The audit barometer (Peet Brothers Ultimeter Model 3) was compared with a standard barometer yearly by Temperature Standards, Inc. The last certification before the study began was performed on May 10, 1995.

4.4.10.2 Psychrometer Mercury-in-Glass Thermometers

Upon being purchased, the psychrometer mercury-in-glass thermometers were compared with AeroVironment's NIST-traceable standard thermometer. The two psychrometer thermometers and the standard thermometer were immersed in water baths of approximately 0°, 10°, 20°, 30°, and 40° C. Periodic comparisons with the standard thermometer were not required.

4.4.11 Flow Measurements

4.4.11.1 QA Standards

AeroVironment at its QA laboratory in Monrovia, California, maintains a set of flow standards for certifying the flow transfer standards that are used in the field. Table 4-4 summarizes the QA flow standards.

Table 4-4

QA Flow Standards

Device	Manufacturer	Model	Element	Range
Laminar flow meter	Meriam	50MK10	725250-C1	0–50 cc/min
Laminar flow meter	Meriam	50MK10	725250-C2	0–1 l/m
Laminar flow meter	Meriam	50MJ10-½	700310-T2	0–10 l/m
Laminar flow meter	Meriam	50MJ10-½	700310-T1	0–50 l/m
Laminar flow meter	Meriam	50MW20-1	700310-T3	0–200 l/m

An external laboratory certifies the laminar flow devices yearly against a primary flow standard. The bubble flow meter is a primary flow measuring device and therefore requires no certification.

4.4.11.2 Mass Flowmeters

Three Hastings mass flow meters were used as transfer standards. Their operating ranges are as follows:

- Model HS-10KS, serial number 16045; range: 0–10 l/m
- Model HS-50JS, serial number 16944; range: 0–50 l/m
- Model HS-10S, serial number 17259; range: 0–150 l/m

All mass flow meters were certified at AeroVironment's QA laboratory before field use. Certifications consisted of a comparison of the mass flowmeter with the appropriate QA laminar flow element at 10 different flows evenly spaced across the mass flow meter's range.

4.4.11.3 Roots Meter

The Roots meter was typically maintained at AeroVironment's QA laboratory. However, this meter was used as a field standard to measure flows in the 150–800 l/m range. The Roots meter is a primary standard, and by definition it requires no further certification.

4.4.11.4 High-Volume Orifices

AeroVironment maintains a set of top-loading high-volume flow measuring orifices typically used for measuring flows for standard high-volume total suspended particulate (TSP) and PM_{10} samplers. An external laboratory certifies these orifices yearly against a primary flow standard.

4.4.11.5 Dilution Standards and Gases

Multipoint audits were performed via a Dasibi Model 5009-PC dilution system (serial number 281) or a Dasibi Model 1009-MC dilution system (serial number 032). AcroVironment's QA department maintains these systems and certifies the flow rates. The zero air source was a cylinder of Ultra-Pure Air supplied by Scott-Marrin, Inc.

The span gases, except Dupont SUVA-134A, were provided by Scott-Marrin, Inc. The NO analysis was performed in accordance with EPA Protocol 2 by using chemiluminescence and was NIST-traceable. No EPA protocol or NIST-traceable standard for ammonia exists. Scott-Marrin certified the ammonia concentration to an accuracy of ± 10%; independent analysis of this gas shows that the accuracy exceeds this figure.

Dupont SUVA-134A refrigerant was used to audit the nephelometers. This compound has a known scattering coefficient that is within the nephelometer measurement range and replaces Freon-12 and Freon-22.

4.5 System Audit Procedures

The purpose of the system audit was to assess the consistency of measurements with the QA plan and the applicable SOPs.

4.5.1 RWP's and RASSs

Little guidance existed, regulatory or otherwise, for the QA of remote sensing systems. For this reason, EPA guidelines were used as a starting point for the system and performance audit procedures. These guidelines were issued to help the instrumentation users obtain consistent data.

The system audit of the RWP consisted of inspecting the antenna and controller interface cables for proper connection. Since each installed RWP used a phased-array antenna system, in contrast to systems that have three antennas, the IMS95 procedures focused on the single-antenna system and its setup and alignment.

The antenna orientation was checked via a magnetic transit and tripod with the observed magnetic readings corrected to true directions by using the local magnetic declination. The alignment of the array was checked by using flags dropped from the antenna array that were visible from outside the clutter fence. The magnetic orientation measurements were also verified by using solar azimuth measurements and latitude and longitude information provided by the site operator. The antenna levels were measured

by a Pro SMARTLEVEL. Measurements were made in at least two directions on the bottom of the antenna array's support structure.

A vista diagram was prepared that documented the site surroundings. The diagram identified potential reflective sources for the radar signal, as well as potential active sources that could generate interference. The diagram also described the view in 30° increments around the antenna, including the elevation angle and the estimated distance to potential sources.

The settings of the controller and data collection devices were checked and noted to ensure that the instrument was operating in the proper mode and that the data being collected were those specified in the SOPs. Interviews assessed the site operator's knowledge of system operation and maintenance and his or her proficiency in performing QC checks. The station log books were reviewed for completeness and content.

Although no specific audit criteria exist for the orientation and level, values were used that were consistent with past audits and with the IMS95 data goals. For orientation, the value was ± 2°, and for level, the value was ±1°. No specific guidance was available for siting, other than the recommendation that radars be installed away from tall buildings, power lines, and other obstructions that may produce interference. Ground clutter was the primary problem; therefore, the desirable locations were on hilltops, away from trees or other tall objects. A system audit checklist for an RWP with a RASS ensured that all aspects of the audit were covered consistently.

4.5.2 Sodar

The system audit procedures for the sodars were the same as those described above for the RPS audits. Although the two systems differ in their operating frequencies, operating ranges, data intervals (range gates), and data handling, the system configurations are essentially the same.

4.5.3 Surface Meteorological Measurements

The system audits of the radar profiler surface meteorological sensing systems consisted of a site inspection to assess proper siting of the instrument sensors, a review of the station check logs and other site documentation, and an interview to assess the site operator's knowledge of the QAPP and SOPs. Siting criteria for meteorological sensors are specified in the EPA Quality Assurance Handbooks for Air Pollution Measurement Systems, Volume IV. Onsite forms and site logs were reviewed to ensure that the documentation conformed to the plan's specifications. A system audit form/checklist was used to

ensure that pertinent audit items were covered and to report the audit findings. The subjects addressed by the system audits were as follows:

- Network design and siting
  - Network size and design
  - Sensor exposure
  - Review of station
- Resources and facilities
  - Instruments and methods
  - Staff and facilities
  - Standards and traceability
- QA and QC
  - Status of QA program
  - Audit participation
  - Precision and accuracy checks

In addition, once the system audits of all sites were complete, the auditor checked for possible differences in operation among the various sites.

4.5.4 Rawinsonde

The system audits of the rawinsonde operations consisted of watching a launch and comparing its procedures with the SOP. Special attention was paid to ground station and sonde initialization procedures, balloon inflation (with regard to proper ascent rate), data acquisition, and flight termination. A rawinsonde system audit checklist ensured that all aspects of the audit were covered consistently.

4.5.5 Particulate Matter Samplers

The system audit of the particulate matter samplers consisted of a review of the sampler siting and observation of the sample loading and handling procedures. Much of the auditing of the IMS95 monitoring preceded the onset of actual monitoring. However, as time and scheduling permitted, an effort was made to observe the site technician during routine loading and unloading of the sampler to ensure that the sampler SOPs were being followed. The system audit verified at least the following aspects:

- Sample chain-of-custody
- Sample labeling

- Sample loading procedures
- Sample storage
- Sample shipping procedures
- Sample blanks
- Flow calibration and measurement procedures
- Training of the technician
- Sampler location
- Pump venting
- Presence of any obstructions or trees
- Sampler preventive maintenance and spare parts inventory
- Cyclone or impactor cleaning (if used)

A detailed system audit checklist assisted the auditor in documenting the results. In general, system audit results were compared with EPA siting and sample handling guidelines for PM_{10} and TSP samplers. The completed system audit checklist was included in the final audit report for the site.

Many samplers had unique requirements that were checked during the system audits. A discussion of these additional checks, by sampler, appears below.

4.5.5.1 SFS and SGS Samplers

Half of the SGSs used in this study employed denuders. The denuder use and maintenance were checked during the system audit. In addition, special attention was given to reviewing the procedures for checking leaks.

4.5.5.2 Portable PM_{10} Sampler

The portable PM_{10} samplers were battery-operated. The system audit included a check of battery charging procedures, including the tracking of batteries.

4.5.5.3 MOUDI Sampler

Because preparation and loading of the sample substrates was critical for successfully operating the MOUDI sampler, special attention was given to this procedure.

4.5.6 Fog Samplers

System audit procedures for the fog samplers incorporated all the checks described for the particulate matter samplers. Fog water samples required additional procedures for the following steps:

- Preparing the sample storage bottles
- Preparing the denuders
- Weighing the sample bottles
- Fixing the fog water samples
- Storing the samples and the fixing reagents
- Testing the fixing reagents

These additional procedures were verified during the system audit. When possible, the auditor observed the collection of fog samples during a foggy day for 3 hours to verify adherence to the operating procedures for each sampler.

4.5.7 Air Toxic Samplers

System audit procedures for air toxic samplers (VOCs and carbonyls) were essentially the same as for particulate matter samplers.

4.5.8 CSASP Optical Scatter Probe

The system audit of the CSASP probe consisted of reviewing the instrument's siting, maintenance, and operation. If the audit schedule and weather permitted, the instrument performance was qualitatively evaluated during a foggy period to verify that the instrument was operating properly.

4.5.9 Continuous Peroxide Analyzers, NH_3 Analyzers, and Nephelometers

The system audits of the continuous peroxide analyzers, NH_3 analyzers, and nephelometers incorporated a review of the following aspects:

- Probe height
- Probe exposure
- Proximity of sources
- Sample manifold and/or sampling line construction
- Sample residence time
- Calibration procedures
- Calibration standards and their certification
- Zero/span checks
- Preventive maintenance
- Spare parts inventory
- Data acquisition equipment and procedures

- Data chain of custody
- QC documentation (e.g., site logs and checklists)
- Support equipment, including station condition
- Training

The preparation and handling of the solutions used to calibrate the continuous peroxide analyzers was also checked.

4.6 Performance Audit Procedures

4.6.1 RWP and Sodar

The latest EPA guidance for QA of radar profilers defined a series of system checks inherent to profiler electronics. Collocated measurements via an audit sodar were conducted at each of the radar profiler and sodar sites. A portable AeroVironment Model 2000 was operated over 24 hours at each site for this purpose.

Performance audits were performed by collocation of a portable audit sodar with each radar profiler and sodar displayed for the study. Wind speed and wind direction data were collected at 30-m intervals up to 750 m. These data were collected in 15-minute intervals, validated, and averaged in both time and vertical space to match the intervals on the radar profilers and sodars, as necessary. Collocated data were collected over at least a 24-hour interval so as to include a variety of stability conditions. During the daytime hours, and while at the sites, logs were maintained on the observed conditions to help document the atmospheric stability during the audits. Before field deployment of the sodar, its operation was verified via the AVR.

Suggested criteria for RWPs and sodars were developed and used by AeroVironment for SARMAP (Gertter et al. 1993) and the Lake Michigan Ozone Study (LMOS) (AeroVironment 1995). These criteria assess the accuracy of the systems over the range of data that are collected by the sodar and are then averaged to correspond with the range gates of the radar profilers and sodars, as necessary. The criteria are ±1 m/s for wind speed and ±10° for wind direction (Table 4-5). This speed is consistent with the EPA suggested criteria for comparison with a tethersonde. No suggestions are provided for wind direction. It is important to note that, when the audit results do not fall within the audit criteria, this does not necessarily mean that the profiler failed the audit. It may mean that an observed condition produced different results on the different systems, which has happened in previous auditing programs. During one LMOS audit, meteorological conditions changed rapidly during a given hour, and the observed differences are believed to have arisen from the radar profilers' consensus averaging technique, thus

Table 4-5

Summary of Audit Observables and Audit Instrumentation—RWP and RASS

Instrument	Observable	Audit Device	Audit Device Traceability	Audit Device Precision	Audit Device Accuracy	Audit Criteria (DQOs)	Comments
RWP	Orientation	Brunton Pocket Transit Model F5007LM	NA	NA	± 1°	± 2°	Orientation measurement accuracy is based on the ability to read the compass and avoid magnetic aberrations. When possible, solar siting verifications were obtained.
	Level	Pro SMARTLEVEL with inclinometer verification	NA	0.2°	± 0.5°	± 1°	The SMARTLEVEL is calibrated in accordance with factory recommendations over the full operating range. Indicated accuracy and precision are conservative estimates; manufacturer claims ±0.1° accuracy.
	Wind Speed and Wind Direction	AcroVironment Model 2000 sodar	Sodar verification with AV transponder	0.1 m/s	± 0.2 m/s	± 1.0 m/s speed and ± 10° direction for collocated sites. For noncollocated sites such as Milstone Point, suggested criteria are ± 2.0 m/s speed and ± 20° direction.	Audit device precision and accuracy refers to the response of the sodar to the APT on a component-by-component basis. Audit criteria shown are based on vector resultant comparisons. See sodar below for more on the APT.
	Exposure	Brunton Pocket Transit Model F5007LM and inclinometer	NA	NA	NA	Minimize active and passive sources. Passive sources below 20° in the beam directions.	The evaluation is subjective.
RASS	(T_v)	AIR Airsonde	Cole Parmer RTD temperature device; Peet Bros. Ultimeter 3 for pressure	0.2° C 1 mb	± 0.3°C ± 4 mb	T_v ± 1.0°C	Temperature precision and accuracy refer to dry bulb thermistors. Devices used for traceability check the sondes before launch. Acceptable launch differences are ± 0.5° C and ±10 mb.

Table 4-5 (continued)

Summary of Audit Observables and Audit Instrumentation—RWP and RASS

Instrument	Observable	Audit Device	Audit Device Traceability	Audit Device Precision	Audit Device Accuracy	Audit Criteria (DQOs)	Comments
Sodar	Orientation	Brunton Pocket Transit Model F5007LM	NA	NA	± 1°	± 2°	Orientation measurement accuracy is based on the ability to read the compass and avoid magnetic aberrations. When possible, solar siting verifications were obtained.
	Level	Pro SMARTLEVEL with inclinometer verification	NA	0.2°	± 0.5°	± 1°	The SMARTLEVEL is calibrated in accordance with factory recommendations over the full operating range. Indicated accuracy and precision are conservative estimates; manufacturer claims +0.1° accuracy.
	Wind Speed and Wind Direction	Acoustic Pulse Transponder	Fluke Model 87 frequency meter for frequency. Quartz clock timing.	1 Hz 3 ms	± 1 Hz ± 3 ms	± 0.2 m/s component speed. ± 0.5 m/s speed. ± 5° direction resultant vector. ± one range gate for altitude response.	Audit device precision and accuracy are expressed in simulated Doppler shift frequency and echo delay. The respective response in m/s and altitude depends on operational parameters of the sodar audited. Audit criteria applies to the portable sodar and onsite sodars used to audit the radar profilers.
	Exposure	Brunton Pocket Transit Model F5007LM and inclinometer	NA	NA	NA	Minimize active and passive sources. Passive sources below 20° in the beam directions.	The evaluation is subjective. More details are provided in the work plan.

producing errors in the hourly average profile. This possible source of error in the averaging technique has been documented by Weber et al. (1993). In evaluating the comparison data, care was taken to determine whether a systematic problem existed or another isolated event with the averaging technique was producing the differences.

As a final step in the radar profiler and sodar audits, data from several days before the audit were reviewed for internal consistency. This type of review checked the indicated flags for data reliability or quality codes for consistency, the individual component intensity values for potential reflections, and the vertical profiles of the components and resultant values for internal consistency in space and time. This was a subjective review and had proved useful in past audits as a "second set of eyes" reviewing the data.

4.6.2 RASS

There was little information in the latest EPA guidance on performance auditing of RASS, other than performing manufacturer-provided system tests. These tests, however, do not provide for any comparisons to "known standards." The best method for gaining confidence in the RASS data is to compare them with independently collected Tv profiles, which will be collected by an airsonde system. This method has been used in the LMOS and other studies for auditing RASS.

Four airsondes were launched at each RASS site to collect profile data from which the comparisons over several stability conditions could be made. The collected Tv data were averaged into intervals consistent with the RASS reporting levels, and comparisons were made to a criterion of ± 1° C. Experience gained in the LMOS study showed that this criterion is readily achievable. However, differences outside this criterion do not mean that the RASS system failed; instead, they indicate that the data need further analysis to determine the reasons for the differences.

As in the wind profiles, data from several days before the audit were reviewed. The review focused on the internal consistency of the data in space and time and looked for the reasonableness of the Tv profiles.

4.6.3 Surface Meteorological Measurements

The performance audit procedures and criteria were those recommended in the EPA Handbook for Air Pollution Measurement Systems, Volume IV. Audit criteria are detailed in Table 4-6.

4.6.3.1 Site Operator

The goal of the performance audit was to establish the accuracy of the monitoring instrumentation. To achieve this goal, the station operator's assistance was required throughout the audit. Interaction between the site operator and auditor helped in understanding site operations and factors that may affect the data. The station operator had to prepare the station monitoring equipment for the audit and give the auditor the needed information for instrument evaluation.

4.6.3.2 Wind Speed

The wind speed audit began with an inspection of the wind speed cups or propeller(s) to ensure they were intact. The cups were then removed to produce a zero point. Next, the R.M. Young selectable-speed anemometer drive was connected to the sensor shaft to simulate wind speeds of approximately 10, 25, and 35 m/s. Actual values depended on the sensor model and were determined by multiplying the motor speed by a cup or propeller transfer coefficient supplied by the manufacturer. The data logger and chart recorder responses were entered into the AeroVironment Audit Software Package (AVASP), and the difference between them and the audit input values was calculated. The calculated difference for each wind speed was then compared with the audit criteria (Table 4-6).

The sensor bearings were then checked for excessive wear by manually turning the sensor shaft to determine whether there was any bearing drag. Next, the sensor was removed from the crossarm, and the R.M. Young torque disk was mounted on the sensor shaft. The starting torque was determined via the manufacturer-recommended procedures.

4.6.3.3 Wind Direction

The wind sensor crossarm alignment relative to true north was checked by using a Brunton surveyor compass mounted on a tripod. The angle of declination was taken into account when performing this check. The wind direction vane was then pointed toward the four cardinal directions, and the responses of the data logger and chart recorder were noted and entered into the AVASP for comparison with the audit input values. The difference calculated for each input wind direction was compared with the criteria (Table 4-6).

Table 4-6

Audit Criteria

Parameters	Criteria
Continuous gas analyzers	Slope - ± 15% of 1 Intercept - ± 3% of full scale
Sampler flow rates	± 10%
Nephelometer	± 10%
Surface wind speed	± 0.25 m/s; ws < 5 m/s * ± 5%; ws >= 5 m/s*
Surface wind direction	± 5° *
Surface temperature	± 1.0° C *
Surface relative humidity	± 1.5° C **
Solar radiation	± 70 W/m^2*
Rawinsonde temperature	± 1.0° C *
Rawinsonde relative humidity	± 1.5° C **
Rawinsonde barometric pressure	± 2 mb

* Audited by means of collocated sensors.
** Equivalent dew point temperature

The sensor bearings were then checked for excessive wear, first by manually turning the sensor shaft to determine whether bearing drag was present and then by using an R.M. Young vane-bearing torque gauge according to the manufacturer-recommended procedures.

4.6.3.4 Ambient Temperature

The temperature-sensing system was audited by immersing the system thermistor and a NIST-traceable mercury-in-glass thermometer in the same water bath and then using the AVASP to compare the thermometer readings with data logger and chart recorder outputs at approximately 0°, 20°, and 40° C. The difference calculated for each point was compared with the audit criteria (Table 4-6).

4.6.3.5 Delta Temperature

The delta temperature-sensing system was audited by immersing the two system thermistors and a NIST-traceable mercury-in-glass thermometer in the same water bath and then using the AVASP to compare the thermometer readings with the data logger and chart recorder outputs at approximately 0°, 20°, and 40°C. The difference calculated for each point was compared with the audit criteria (Table 4-6).

4.6.3.6 RH and Dew Point Temperature

The muslin wick of the wet bulb thermometer of the motorized psychrometer was wet with distilled water, then the motorized psychrometer was placed close to the RH or dew point sensor and allowed to run for at

least 5 minutes or until the thermometer readings stabilized. Once the readings stabilized, the audit psychrometer wet and dry bulb temperatures, the audit barometric pressure, and the station RH and ambient temperature or dew point temperature were read simultaneously. These readings were entered into the AVASP, where the audit RH or dew point temperature was calculated. If RH was present, then it was converted to an equivalent dew point temperature for comparison with the calculated audit dew point temperature. If dew point temperature was measured directly, then the station value was directly compared with the calculated audit value. The difference between the station equivalent or measured dew point temperature and the calculated audit dew point temperature was compared with the audit criteria (Table 4-6).

4.6.3.7 Precipitation

To audit precipitation, 1,000 ml of water was added to the precipitation gauge calibrator. The cap was secured in place, and the calibrator was upended into the rain gauge funnel. The calibrator metering valve allowed the water to flow into the rain gauge funnel at about 0.08 cm/min. Once the water emptied out of the calibrator, the precipitation indicated by the data logger and chart recorder during the audit period was compared with the value that corresponded to the audit volume that was calculated by using the diameter of the rain gauge funnel. The difference between the indicated rainfall and the audit value was compared with the audit criteria.

4.6.3.8 Barometric Pressure

Simultaneous readings of the data logger and chart recorder for barometric pressure and the audit barometer were made at the beginning and the end of each audit visit. These readings were entered into the AVASP. The AVASP calculated the percent difference between the station and the audit values, which was compared with the audit criteria.

4.6.3.9 Solar Radiation

Time constraints restricted solar radiation audits to the audit period, instead of over one diurnal period as recommended by the EPA guidelines. Five readings of the data logger, chart recorder outputs for solar radiation, and the audit pyranometer were compared. Meteorological conditions permitting, the five readings were taken over as much of the station pyranometer's operating range as possible. The audit data, in millivolts (mV), were converted to Langleys per minute (Ly/min) by using the audit pyranometer calibration factors. The station pyranometer data logger and chart recorder readings and the audit pyranometer readings were entered into the AVASP, which calculated the difference between the station outputs and the audit values. These differences were then compared with the audit criteria.

4.6.4 Rawinsondes

The instruments used to initialize sonde pressure, temperature, and humidity before each launch were audited to determine the individual accuracies as well as the relative accuracy between the two sites.

4.6.4.1 Pressure

The audit and reference barometers were placed in close proximity, and the readings were allowed to stabilize. Simultaneous readings of the reference and audit barometers were then made. These readings were entered into the AVASP, where the percent difference between the reference and the audit values were compared with the audit criteria (Table 4-6).

4.6.4.2 Temperature and Humidity

To audit temperature and humidity, the muslin wick of the wet bulb thermometer of the audit motorized psychrometer was wet with distilled water. The audit and reference psychrometers were then placed in close proximity and allowed to run for at least 5 minutes or until the thermometer readings stabilized. Once the readings stabilized, the readings of the psychrometers and the audit barometric pressure were noted. The audit and reference dry bulb temperatures were compared, and the difference was compared with the audit criteria for ambient temperature (Table 4-6).

The audit RH was calculated from the psychrometer and barometric pressure readings and was compared with the reference RH. The difference between these values was compared with the audit criterion of ±10%.

4.6.5 General Performance Audit Procedures for Air and Fog Samplers

Sampler flow rates were audited via the appropriate flow audit field standard. Table 4-7 summarizes the operational flow rates and corresponding audit device for the various samplers. All flow rates were measured as close as possible to the collection media. Measured audit flow rates were compared with the measured or nominal flow rates supplied by the site technicians. Site comparison flow rates should correspond to the flow rates that were used to calculate sample concentrations. The ambient temperature and atmospheric pressure were recorded for each flow rate audited, thus allowing audit flow rates to be reported in either volumetric or standard units, by using the following equations:

Table 4-7

Sampler Performance Audit Flows

Sampler	Flow Rate (l/m)	Audit Device
Particulates:		
SFS	113	0–150 MFM*
SGS	113 (total)	0–150 MFM
	20 (sample)	0–50 MFM
	73 (bypass)	0–150 MFM
Portable PM_{10}	5.0	0–10 MFM
$PM_{2.5}$ Federal Ref. Method	20	0–50MFM
HVDVI	500	Roots meter
TEOM	16.7 (total)	0–50 MFM
	3.0 (sample)	0–10 MFM
Beta gauge	16.7	0–50 MFM
VAPS	16.7	0–50 MFM
Aetholometer	8.6	0–10 MFM
Hi-Vol PM_{10}	1,000	Hi-Vol orifice
CE-CERT Sampler	5	0–10 MFM
MOUDI	16.7	0–10 MFM
CADMP	113 (total)	0–150 MFM
	20 (sample)	0–50 MFM
	36.5 (bypass)	0–50 MFM
Fog:		
ETH Impactor	410	Roots meter
IESL Impactor	1,500	Hi-Vol orifice
CASCC2	5,800	Not audited
SFCASCC	19,000	Not audited
Toxics:		
Carbonyls	0.9	0–3 MFM
VOC (Tenax)	0.05	0–.05 MFM
VOC (Canister)	0.05	0–.05 MFM

* Mass flow meter

$$Q_{std} = Q_{vol} * (P_a / 29.92) * (298 / T_a) \quad (1)$$

$$Q_{vol} = Q_{std} * (29.92 / P_a) * (T_a / 298) \quad (2)$$

where

Q_{std} is the flow rate at standard conditions (P = 29.92" Hg, T = 298° K),

Q_{vol} is the volumetric flow rate,

P_a is the ambient pressure in inches of Hg,

T_a is the ambient temperature in °K.

A mercury-in-glass thermometer calibrated against a NIST-traceable thermometer and a transfer standard barometer were used to take readings of ambient temperature and barometric pressure, which were required for the flow calculations. The appropriate flow units were used when comparing audit and site flow rates. Audit and site flow rates should agree within ±10%.

Whenever possible, additional flow measurements were made to check the sample system for leaks. In general, this involved measuring the flow at the sampler inlet or immediately above the leak-prone area, in addition to the flow at the collection media. Any noted difference between these upstream and downstream measurements indicated a leak within the system. After the accuracy and precision of the flow measuring devices had been taken into account, any difference between upstream and downstream flows of greater than 2% of the upstream flow indicated a leak.

In addition to the above measurements, flow rates of any other component vital for the operation of the sampler were also checked. These include bypass and inlet flow rates for samplers equipped with SSI inlets.

All results were entered into the AVARS, which performed the calculations for comparing the audit flows with the reported site flows.

The procedures for using the various auditing devices are summarized below.

4.6.5.1 Mass Flowmeters

The audit procedures for mass flow meters were as follows:

- The mass flow meter was turned on and allowed to warm up for at least 15 minutes.
- With the ends of the flow element capped, a zero reading was obtained and recorded.
- The flow meter was attached to the line being audited.
- A stable flow meter reading was obtained by waiting at least 3 minutes or until the flowmeter stopped showing any upward or downward trends.
- The corrected flow meter reading was calculated in standard l/min by using the following equation:

$$Q_{std} = a * (Q_o - (z_c - z)) + b \qquad (3)$$

where

Q_0 is the flowmeter reading,

z is the measured mass flowmeter zero reading,

z_c is the mass flowmeter zero reading at the time of the certification,

a is the certification slope,

b is the certification intercept.

4.6.5.2 Roots Meter

The audit procedures for the roots meter were as follows:

- The Roots meter was attached to the line being audited.
- The audit stopwatch was reset.
- At a convenient reference point on the Roots meter dial, the stopwatch was started and the exact initial Roots meter reading was recorded.
- At least 1 minute was allowed for the test to run.
- At a convenient reference point on the Roots meter dial, the stopwatch was stopped, and the exact final Roots meter reading was recorded.
- The above steps were repeated two times for the same volume as defined by the Roots meter.
- An average of the three times obtained from the stopwatch was calculated.
- The measured volumetric flow rate was calculated by using the following equation:

$$Q_{vol} = (R_1 - R_0) / t \qquad (4)$$

where

R_0 is the initial roots meter reading,

R_1 is the final roots meter reading,

t is the average stopwatch reading.

4.6.5.3 High-Volume Orifices

The audit procedures for high-volume orifices were as follows:

- If a traditional high-volume sampler was being audited, then a clean sample filter was installed in the orifice cassette.
- The orifice plate was clamped down to make an airtight seal. If the orifice had been clamped onto an adapter, then the adapter was attached to the line being audited.
- The water manometer was hooked to the port on the orifice.
- The system was allowed to run for at least 5 minutes to allow it to stabilize.
- At the end of the stabilization period, readings were obtained from the water manometer; the ambient air temperature and the barometric pressure readings were also obtained.
- The following equation was used to calculate the audit sampler flow rate in standard units:

$$Q_{td} = H * \frac{(P_a \times 298)}{(29.92 \times T_a)} * A + B \qquad (5)$$

where

H is the pressure differential across the orifice (H_2O),

A, B are calibration coefficients for the calibrated orifice,

P_a is the barometric pressure in inches of Hg,

T_a is the ambient temperature in °K.

4.6.6 Particulate Matter Samplers

Particulate matter samplers were audited with the same type of filter media used during ambient sampling. Unique audit requirements for specific samplers are summarized below.

4.6.6.1 SGS

This sampler has 12 channels for sampling. Flow rates through all 12 channels were measured during each audit. Particular emphasis was placed on checking for leaks in this sampler, because the sampler plenum is quite large and its proper seating is critical to minimize the chance of leaks.

4.6.6.2 SFS

Similar in construction to the SGS, this sampler has 12 sample channels, all of which were audited. In addition, there is a thirteenth channel for drawing the bypass flow that is required to bring the total flow to the inlet's design flow rate. This flow was also checked. Emphasis was placed on checking for leaks in this sampler.

4.6.6.3 TEOM

To check for leaks, the PM_{10} sample head was removed from the sample inlet. The sample inlet was then plugged, and the flow readings as displayed on the front panel of the instrument were noted and recorded. Any measured flow indicated a leak.

The mass flow meter was connected to the sample inlet to measure the total flow. The sampler bypass flow tube was then disconnected from the sampler inlet and plugged. The resulting flow was the sample flow.

4.6.6.4 MOUDI

The 0.05-µm stage of the MOUDI sampler can become plugged after loading, thus affecting the flow rate through the sampler. Emphasis was placed on verifying that the flow rates were not affected in this manner.

There were no special performance audit considerations for the remaining samplers.

4.6.7 Fog Samplers

Flows through the CASCC2 and SFCASCC fog samplers are produced by fans, with flow rates at approximately 5,800 l/m for the CASCC2 and 19,000 l/m for the SFCASCC. These flows could not be verified via existing flow meters. The flow rates for these samplers were estimated by directing the exhaust from the sample into a large plastic bag of known volume and recording the time required to fill the bag. An audit criterion of ± 20% was used for this approximate measurement.

There were no special performance audit considerations for the ETH and IESL impactors.

In addition to sample collection, the pH of the collected samples was measured before preparing them for shipping to the analytical laboratory. Operation of the pH meter was audited by analyzing an audit buffer solution with a pH of 6–7.

4.6.8 VOC Canister and Carbonyl Cartridge Samplers

The VOC and carbonyl samplers, in general, entailed no special performance audit considerations. For the VOC samplers, audit flow rates were also compared with the sample time and the sample container volume to verify that the containers would not overfill.

4.6.9 CSASP Optical Scatter Probe

The CSASP was audited by sprinkling 20-µm glass spheres within the optical path of the instrument during a fog-free period. The output from the instrument was then checked to verify that droplets were detected in the 20-µm bin range only.

4.6.10 Continuous Peroxide Analyzers

Solutions required to calibrate the peroxide analyzers are unstable and could not be prepared in advance of the audit, and therefore, considered to be outside the scope of the audit. Similarly, development of a generator capable of producing gaseous concentrations of peroxides is a major undertaking, and was considered outside the scope of the audit. Therefore, performance audits of the peroxide analyzers concentrated on measuring the various flow rates critical to its operation.

4.6.11 Continuous NH_3 Analyzer

The continuous $NH_3/NO/NO_2$ analyzer was audited in much the same manner as a traditional $NO/NO_x/NO_2$ analyzer. The audits of the air quality samplers required the technician to identify the appropriate data channel and take it offline so that ambient data would no longer be collected. Next, the technician disconnected the sample line of the corresponding analyzer from the sample manifold. After the open port of the sampler manifold was plugged, the sample line or inlet filter was connected to the dilution system via a vented glass manifold through which the audit span gas was introduced. This allowed the audit test atmosphere to travel through as much of the normal sampling train (such as filters and scrubbers) as possible. The analyzer was challenged with specific concentrations of span gas, as follows:

Audit Point	Concentration Range $NO/NO_x/NH_3$
1	0.0
2	0.03 to 0.08
3	0.15 to 0.20
4	0.35 to 0.45

NO/NO_x and NH_3 concentrations were generated by NIST-traceable cylinders and gas dilution.

NO_2 concentrations were introduced into the analyzer by gas phase titration (GPT) of NO with O_3.

NO reacts completely with O_3 to produce NO_2 and O_2.

The NO_2 input concentration was determined by the following equation:

$$[NO_2 \text{ input}] = \frac{[\text{NO input}] - [\text{NO reading}]}{\text{NO slope}} \qquad (6)$$

where

NO input is the analyzer's NO channel response to the NO span before the addition of O_3,

NO reading is the analyzer's NO response after the addition of O_3,

NO slope is the slope of the curve generated by linear regression of the NO concentrations versus the analyzer's response during the audit of the NO channel, where the *NO input* is the abscissa and the NO response is the ordinate.

The final stage of the analyzer audit was to determine the converter efficiency from the following equation:

$$[NO_2 \text{ converted}] = [NO_2 \text{ input}] \quad \frac{[NO_x \text{ initial}] - [NO_x \text{ final}]}{NO_x \text{ slope}} \qquad (7)$$

where

NO_x initial is the analyzer's NO_x channel response before the addition of O_3

NO_x final is the analyzer's NO_x response after the input sample of NO is titrated with O_3

NO_x slope is the slope obtained from the audit of the NO_x channel

The converter efficiency for each audit point will be:

$$\frac{[NO_2 \text{ converted}]}{[NO_2 \text{ input}]} * 100$$

The converter efficiency is defined as the linear regression using the NO_2 source versus the NO_2 converted multiplied by 100. The converter efficiency must be greater than or equal to 96% to pass the audit.

4.6.12 Nephelometer

The nephelometer was audited by performing a check of its 0 and 1 upscale span point. The 0 point was produced by introducing Ultra-Pure Air into the nephelometer's optical sampling chamber and noting the output readings after a period of approximately 20 minutes. The span point was produced in the same manner as the 0 point, but with the introduction of the Dupont SUVA-134A refrigerant in place of the Ultra-Pure air.

4.7 Resolving Problems and Verifying Corrections

The goal of the audits was to verify the function of each measurement system with respect to the DQOs. Given that the performance audits were comparisons between the audit standards and the individual measurement systems, discrepancies between the audit standards—or audit standard inputs—and the measurement outputs could be the result of a problem with the measurements, the audit standards, or both. The auditors made every effort to verify the audit results onsite. It was the auditor's practice not to leave the site until any discrepancy between the auditor's results and the site operator's results were within tolerance. It should be noted that the agreement between the auditor and site operator could be an agreement to disagree. If that was the case, then further investigation was needed to resolve the problem.

4.7.1 RWPs, RASSs, and Sodars

Each variable was audited by comparing its response to that of a collocated transfer standard. For the audit sodar, the standard was the AVR. For the radar profilers and measurement sodars, the standard was a sodar. For the RASS, the standard was the airsonde. For the orientation and level audits, the results were available immediately. For the radar profilers, RASSs, and sodars, the initial comparisons were qualitative and were performed by using Level 0 validated data. If the indicated deviation exceeded the study DQOs, then the auditor and site operator reviewed the audit equipment and measurement system setups. Once the Level 1 data were available, the comparison with transfer standards was made.

Before leaving each site, the auditor reported the audit results to the onsite technician and the monitoring supervisor (Bastion Schoell of STI, for the radar profilers and RASSs; Jeff Murata of PG&E, for the PG&E sodar; and David Pankratz of AeroVironment Inc., for the AeroVironment sodar). Problems noted were discussed, and an action plan for resolving them was developed. If there was a question about the validity of the audit standard, the auditor tested, corrected, or—if necessary—replaced the standard. If the problem was verified, then its disposition was documented. The auditor followed up on each problem within a week of the audit.

Measurement problems were communicated to David Bush of AeroVironment and Paul Solomon of PG&E within one day of identification.

4.7.2 Surface Meteorological Measurements

Each variable was audited by either comparing its response to that of a collocated transfer standard or by creating a simulated field against which the measurement system response was compared. A spreadsheet-based program was used to apply correction factors to the audit transfer standard readings, calculate the difference between the measurement systems and audit standard responses or simulated field values, and compare values with the corresponding DQOs at the completion of the audit of each observable. If the deviation exceeded the study DQOs, then the auditor and site operator reviewed the audit equipment and measurement system setups. If problems with either were noted, then they were corrected, and the variable was reaudited.

Before leaving each site, the auditor reported the audit results to the appropriate monitoring supervisor, Bastion Schoell of STI. Problems noted were discussed, and an action plan for resolving them was developed. If there was a question about the validity of the audit standard, then the auditor tested, corrected, or—if necessary—replaced the standard. If the problem was verified, then its disposition was documented. The auditor followed up on each problem within a week of the audit.

Measurement problems were communicated to David Bush of AeroVironment Inc. and Paul Solomon of PG&E within one day of identification.

4.7.3 Rawinsondes

The audits of the rawinsonde operations, except for the reference instruments, were systematic. At the end of the sonde preparation and flight and shutdown procedures, the auditor discussed the findings with the operators. Problems noted (i.e., noncompliance with the SOPs) were pointed out, discussed, and

documented. If it was found that the noncompliance enhanced the operations, then a recommendation was made that the change be discussed with other similar rawinsonde operations personnel; if the change was agreed upon, then the SOPs were amended.

Before leaving each site, the auditor reported the audit results to the appropriate monitoring supervisor, Don Lehrman of Technical and Business Systems, Inc. Problems noted were discussed, and an action plan for resolving them was developed. If there was a question about the validity of the audit standard, then the auditor tested, corrected, or—if necessary—replaced the standard. If the problem was verified, then its disposition was documented. The auditor followed up on each problem within a week of the audit.

Measurements problems were communicated to David Bush of AeroVironment Inc. and Paul Solomon of PG&E within one day of identification.

4.7.4 Core Site Samplers

Each audited flow was evaluated by comparing the audited flow rate with the flow rate that was used to calculate sampler measured concentrations, which was supplied by the site technician. A spreadsheet-based program was used to apply correction factors to the audit transfer standard readings, calculate the difference between the measurement systems and audit standard responses, and compare these differences with the corresponding DQOs at the completion of the audit of each observable. If the deviation exceeded the study DQOs, then the auditor and site operator reviewed the audit equipment and measurement system setups. If problems with either were noted, then they were corrected, and the variable was reaudited.

Before leaving each site, the auditor reported the audit results to the appropriate monitoring supervisor. Problems noted were discussed, and an action plan for resolving them was developed. If there was a question about the validity of the audit standard, then the auditor tested, corrected, or—if necessary—replaced the standard. If the problem was verified, then its disposition was documented. The auditor followed up on each problem within a week of the audit.

Measurements problems were communicated to David Bush of AeroVironment Inc. and Paul Solomon of PG&E within one day of identification.

4.8 Reporting

4.8.1 Audit Summaries

4.8.1.1 RWPs, RASSs, and Sodars

Fundamental to each audit was the debriefing of the site operator about the audit results at the completion of each audit. On basis of the observations made, any problems identified during the audit were discussed with the site operator before the auditor left the site. Additionally, a written summary was given to the site operator that consisted of the orientation results, the level and vista audits, and any comments about data handling. A qualitative assessment was made of the wind measurements through a comparison of the raw Level 0 data with the unvalidated audit sodar data. This immediately identified any "gross" differences between the sodar and radar profiler data, the audit and measurement sodar data, and the airsonde and RASS data. A comparison of the Level 1 radar profiler and validated audit sodar data with the validated audit and measurement sodar data was included in the audit report that followed.

4.8.1.2 Surface Meteorological Measurements

At the conclusion of each audit, the audit reports for the individual variables were printed out and given to the site operator. A 1-page summary listing the problems noted and the corresponding recommended actions was included with the audit reports. Suspected problems, comments and recommendations for improving site operations were included in the recommendations section. A copy of the summary was emailed or faxed to the project managers and field managers within one day of the audit.

4.8.1.3 Rawinsondes

At the conclusion of each audit, the Rawinsonde System Audit Form and the audit reports for the performance audits of the reference instruments were printed out and given to the site operator. A 1-page summary listing the problems noted and the corresponding recommended actions was included with the audit reports. Suspected problems, comments, and recommendations for improving site operations were included in the recommendations section. A copy of the summary was emailed or faxed to the project managers and field managers within one day of the audit.

4.8.2 Audit Reports

4.8.2.1 RWPs, RASSs, and Sodars

Audit reports on the RWPs, RASSs, and sodars were submitted to the project managers and field managers within five to seven days after the validated data from the measurements contractor were received. These reports included the system audit results originally reported to the site operator in the summary reports.

4.8.2.2 Surface Core Site Samplers, Meteorological Measurements, and Rawinsondes

Audit reports on the surface core site samples, meteorological measurements, and rawindsondes were emailed or faxed to the project manager within five days after the auditing was performed. The reports included the following content:

- Audit location
- Date
- Auditor's name
- Variables audited
- Problems noted and corrective actions needed
- Recommendations and comments
- Measurement system information tables
- Audit results summary tables
- Audit results forms for each variable
- System audit checklist form

Section 5

DATABASE MANAGEMENT GUIDELINES

This section describes the IMS95 database management process, including the objectives, basic procedures, guidelines for contractors, and data validation levels. This process was based on the study personnel's previous experience obtained in database management during the San Joaquin Valley Air Quality Study.

5.1 Objectives

The objective of the database management were to (1) minimize the effort required to combine numerous and diverse data sets from various sources into a single data archive, (2) maximize the quality of the final data archive by providing adequate and accurate data documentation, and (3) maximize accessibility to the final data archive to accomplish the overall objectives of IMS95.

To help accomplish these three objectives, guidelines on "project" reference standards (such as units of measure, time reference, naming conventions, and data format) and procedures (processing, QA, and data analysis) were specified, along with other requirements for the submittal of primary data by contractors. Contractors' conformance with these guidelines greatly streamlined the effort of producing a unified database. Acceptance criteria and guidelines for the collection, processing, and QA of supplemental data by the project sponsors and data manager were specified, to ensure compatibility between primary and supplemental ("in-kind" or existing) data. Specific procedures were developed for finalizing and providing a master database that contains both primary and supplemental data.

5.2 Basic Procedures

ARB staff were in charge of the database management process. Their past experience included developing the database archive for SJVAOS; a two-year process from 1991 to 1993. More recently, ARB assembled a 6-year database of existing air pollution measurements (including PM_{10} and its components) and meteorological measurements from 1988 to 1993. These data were used in planning the IMS95 field study.

Creating these two archives demonstrated that the following procedures are important:

- Always allow more time for data collection, documentation, validation, and organization than what is thought adequate.

- Identify each measurement site, ascertain its coordinates and elevation, assign it an alphanumeric site code, document the measurements made at the site, and transmit this information to all project participants. Verify the location and elevation with a global positioning system (GPS) device. Use a digital camera to photograph the immediate site and its surroundings. Videotape the site and the area around it up to a distance of 1.6 km. Inventory each instrument and include the make and model as well as information about its threshold, range, expected accuracy, and precision.
- For all variables, specify the naming conventions, averaging times, time conventions, data flagging codes, temperature and pressure adjustments, and preferred data formats. Before the study, give this information to all the study's participants. In previous work, data were received that used widely varying conventions, and much effort was required to provide consistency.
- Define data examination and validation procedures carried out by each data sponsor before data delivery. This facilitates creation of a uniform final data archive.
- Before designing the field study, fully document the locations, methods, and quality of the databases to be acquired from supplemental networks.
- Create data management and traceability systems that allow data discrepancies to be rapidly investigated and corrected.
- Develop a uniform and simple flag system for contractors to use when submitting data.

All the above procedures were incorporated in IMS95. Their purpose was to prevent major problems and to streamline the entire database management process.

5.3 Guidelines For Contractors

Below are the requirements that contractors had to fulfill when submitting data to the data manager. These requirements reduced the processing time for integrating the contractors' data into the final data archive and made the data available to analysts and modelers in a timely fashion.

5.3.1 Data Requirements

5.3.1.1 Data Format

The data must be submitted as comma-delimited text files in the following formats, with one data point per record:

- For continuous surface measurements: SSS, MM/DD/YY, HR,TIME, DURATION, INSTR, PARAM, RESULT, QCFLAG
- For surface particle measurements: SSS, MM/DD/YY, HR,TIME,DURATION, INSTR, PARAM, SIZE, RESULT, QCFLAG
- For surface fog measurements: SS, MM/DD/YY, HR,TIME,DURATION, INSTR, FRACTION,PARAM, RESULT, QCFLAG

- For upper air (tower) measurements: SSS, MM/DD/YY, HR, TIME, EV_MSL, INSTR, PARAM, RESULT, QCFLAG

All other upper air meteorological data from the sodars, rawindsondes, and radar profilers must be submitted to the data manager as ASCII text files in the contractor's original format, along with adequate documentation.

Any data that are not listed above, including VOC and hydrocarbon data, tracer measurements, and emissions inventories, must be submitted to the data manager in the contractor's original format, along with adequate documentation.

Below is a description of the file elements:

- SSS = 3-character project site code (SITE.DBF in Table 5-1)
- MM/DD/YY = date specification
- HR: PST "begin" hour (0–23); this is the nearest hour to the actual measurement time.
- TIME = HH:MM:SS
- DURATION = period of sampling in total minutes
- EV_MSL = elevation in m msl
- INSTR = 5-character project instrument type code (INSTR.DBF in Table 5-2)
- FRACTION = size fraction of the cloud droplet collector; S=small, M=medium, L= large. The actual diameter ranges vary by instrument and were included in a lookup table.
- PARAM = 5-character project parameter code (PARAM.DBF in Table 5-3)
- SIZE = 1-letter particle size category; 'T' = PM_{10} (0–10 μm), 'F' = fine (0–2.5 μm), 'C' = coarse (2.5–10 μm), 'S' = sum of fine + coarse – PM_{10}, 'P' = TSP (0–30 μm)
- RESULT = data value in specified significant digits; in Table 5-3, PARAM.DBF lists significant digits for reporting each parameter data value.
- QCFLAG = 1-character project QC code indicating the quality of the data point (QCFLAG.DBF in Table 5-4)

5.3.1.2 Parameter Names, Units, Significant Digits, and Averaging Times

All project parameter codes (PARAM), project units of measure, significant digits, and averaging times used in creating the data files for submission are in Table 5-3.

5.3.1.3 Time Reference

The project time reference was the PST "begin" hour. For example, hour 1 is the measurement from 0100 PST to 0200 PST.

Table 5-1

Supplemental Measurements in Place during the IMS95 Fall and Winter Field Programs
(November 1995 - January 1996)

SITE	SITE_NAME	NET CODE	PURPOSE	SITETYPE	LATITUDE	LONGITUDE	UTMX	UTMY	TV_MSL (m)	O3	NX	CO	S2	BC	CI	WD	ST	TT	RH	SR	PR	WE	CH	VS	MA	S4	N3	CL	N4	TC	OS
ARR	ARROYO GRANDE-RALCOA	ARB	Routine Ambient Monitoring for AQ	SRF/AQ	35_02 28.01" N	120_34' 18.60" W	723.7390	3880.1910	333				X																		
ARV	ARVIN	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_12 29.85" N	118_47 42.40" W	313.8650	3904.0960	136	X	X					X		X	X	X	X										
ATL	ATASCADERO-LEWIS AVENUE	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_29 30.12" N	120_40 04.80" W	713.3450	3929.8740	252	X	X					X	X	X		X											
BAT	BATTLES DETERRA VIA ROAD	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	34_57 20.01" N	120_24 00.00" W	737.5080	3867.4490	91	X	X			X		X	X	X													
BGS	BAKERSFIELD-1128 GOLDEN STATE	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_23 01.90" N	119_00 52.92" W	362.0440	3922.9010	131	X	X	X		X		X		X	X	X	X				X						
BKA	BAKERSFIELD-1125 CALIFORNIA AV	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_20 21.32" N	119_02 25.00" W	359.1630	3919.5590	117	X	X	X	X		X	X		X	X	X					X	X	X	X	X	X	X
CLK	CHINA LAKE	ARB	Routine Ambient Monitoring for PM	SRF/AQ	35_48 33.99" N	117_37 06.00" W	[illegible]	3962.3730	693																X	X	X	X	X	X	
CLO	CLOVIS-908 N VILLA AVENUE	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_49 30.00" N	119_42 59.40" W	793.0970	4080.2990	350	X	X	X		X		X		X	X	X	X				X	X	X	X	X		
COV	CORCORAN-VAN DORSTEN AVE	ARB	Routine Ambient Monitoring for PM	SRF/AQ	36_05 11.94" N	119_33 46.20" W	805.4930	3996.9030	61																X	X	X	X	X		X
EDI	EDISON	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_20 45.96" N	118_51 01.62" W	677.1850	3913.8540	128	X	X					X		X													
FNP	FRESNO-NORTH PERIMETER ROAD	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	37_05 36.07" N	119_53 03.63" W	831.6475	4116.5430	3719	X						X		X	X												
FSD	FRESNO-4706 E DRUMMOND	ARB	Routine Ambient Monitoring for AQ & PM	SRF/AQ	36_41 44.88" N	119_44 33.20" W	791.0873	4065.8740	663	X	X	X													X						
FSF	FRESNO-3425 FIRST STREET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_46 53.04" N	119_46 19.50" W	788.0358	4075.2880	96	X	X	X	X		X	X		X					X		X	X	X	X	X	X	X
FSS	FRESNO-SIERRA SKYPARK #2	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	36_50 30.13" N	119_52 36.40" W	778.7530	4081.6710	98	X	X	X				X															
GCL	GROVER CITY-LESAGE DRIVE	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_07 [illegible] N	120_37 58.80" W	720.2830	4111.3580	4	X	X		X			X	X	X													
HIR	HANFORD-S IRWIN STREET	ARB	Routine Ambient Monitoring for PM & Met	SRF/AQ	36_19 [illegible] N	119_38 34.80" W	800.5620	4015.4020	73	X	X														X	X	X	X	X		
IYA	INYOKERN AIRPORT	ARB	Routine Ambient Monitoring for PM	SRF/AQ	35_39 25.80" N	117_39 34.80" W	1090.1900	3950.1070	719																X						
KCC	KETTLEMAN CITY-CAL TRANS	ARB	Routine Ambient Monitoring for PM	SRF/AQ	36_00 24.84" N	119_57 32.40" W	774.8010	3988.7720	73																X	X	X	X	X		
MBP	MORRO BAY	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_18 24.00" N	120_50 36.00" W	726.8180	3907.3070	[illegible]	X			X			X															
MCS	MARICOPA SCHL-STANISLAUS	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	35_03 [illegible] N	119_24 11.40" W	620.0000	3884.7730	209	X						X		X													
MER	MERCED	ARB	Routine Ambient Monitoring for PM	SRF/AQ	37_18 35.18" N	120_28 53.90" W	723.1440	4131.0670	65																X	X	X	X	X		
MHD	MADERA-HEALTH DEPT	ARB	Routine Ambient Monitoring for AQ	SRF/AQ	36_57 [illegible] N	120_03 [illegible] W	768.9450	4093.8830	83	X																					
MLB	MADERA-LIBRARY	ARB	Routine Ambient Monitoring for PM	SRF/AQ	36_57 [illegible] N	120_03 [illegible] W	768.6730	4094.3510	82																X	X	X	X	X		X
MOP	MOJAVE-923 POOLE STREET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_03 48.72" N	118_09 09.00" W	941.5360	3881.2530	853	X	X					X		X							X	X	X	X	X		
MRA	MERCED-385 S COFFEE AVE	ARB	Routine Ambient Monitoring for AQ & Met	SRF/AQ/MET	37_16 [illegible] N	120_25 50.80" W	727.3800	4129.8970	55	X	X					X		X													
NGR	NIPOMO-1300 GUADALUPE RD	ARB	Routine Ambient Monitoring for AQ	SRF/AQ	35_01 [illegible] N	120_33 43.20" W	725.4430	3877.8490	[illegible]	X			X																		
NPP	NIPOMO	ARB	Routine Ambient Monitoring for AQ	SRF/AQ/MET	35_02 [illegible] N	120_30 00.30" W	728.0435	3880.3270	131	X	X		X				X														
OLD	OILDALE-3311 MANOR	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	35_26 [illegible] N	119_00 57.60" W	363.6990	3925.8170	[illegible]	X	X		X		X	X		X					X	X	X	X	X	X	X	X	
PLR	PARLIER	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_36 00.00" N	119_30 28.80" W	812.3890	4055.9780	[illegible]	X	X					X		X	X	X	X										
PRF	PASO ROBLES-711 SANTA FE	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	35_37 [illegible] N	120_41 34.00" W	709.8830	3943.3580	246	X						X		X					X								
SHA	SHAFTER	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	35_30 00.00" N	119_16 04.80" W	338.3330	3928.7070	[illegible]	X	X					X		X						X							
SLM	SAN LUIS OBISPO-MARSH	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	35_17 02.04" N	120_39 14.40" W	713.3590	3906.8530	64	X	X	X				X		X					X								
SMY	SANTA MARIA-BROADWAY	ARB	Routine Ambient Monitoring for AQ, Met & Vs	SRF/AQ/MET	34_56 55.14" N	120_26 02.40" W	734.3330	3870.0970	74	X	X		X			X		X					X								
TAC	TAFT COLLEGE	ARB	Routine Ambient Monitoring for PM	SRF/AQ	35_08 35.06" N	119_27 36.00" W	637.5470	3891.1390	342																X	X	X	X	X		X
TSM	TURLOCK-900 S MINARET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	37_29 [illegible] N	120_50 06.00" W	691.4100	4151.0730	51	X	X	X				X									X						
VIS	VISALIA-CHURCH STREET	ARB	Routine Ambient Monitoring for AQ, Met & PM	SRF/AQ/MET	36_19 [illegible] N	119_17 24.00" W	831.0130	4025.9000	93	X	X	X			X	X		X					X		X	X	X	X	X		X
ASV	ARVIN-EDISON	CIM	2 m tower/met variables in agricul. area	SRF/MET	35_12 [illegible] N	118_46 40.00" W	[illegible]	3903.9770	158							X	X	X	X	X											
BKC	BLACKWELLS CORNER	CIM	2 m tower/met variables in agricul. area	SRF/MET	35_36 [illegible] N	119_57 30.00" W	773.5940	3945.1620	213							X	X	X	X	X											
CUY	CUYAMA	CIM	2 m tower/met variables in agricul. area	SRF/MET	34_55 [illegible] N	119_36 13.00" W	810.1520	3874.3330	698							X	X	X	X	X											
SEO	ARROYO SECO	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_20 [illegible] N	121_17 23.00" W	655.4020	4024.9810	73							X	X	X	X	X											
FIV	FIVEPOINTS/WSFS USDA	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_21 11.00" N	120_06 47.00" W	759.1230	4024.9290	67							X	X	X	X	X											
FNS	FRESNO STATE	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_49 [illegible] N	119_44 31.00" W	790.6150	4079.3570	103							X	X	X	X	X											
FRB	FIREBAUGH/TELLES	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_51 [illegible] N	120_35 35.00" W	714.8400	4080.8640	56							X	X	X	X	X											
GUA	GUADALUPE	CIM	2 m tower/met variables in agricul. area	SRF/MET	34_57 [illegible] N	120_35 48.00" W	724.0040	3871.3440	24							X	X	X	X	X											
KCO	KING CITY-OASIS RD.	CIM	2 m tower/met variables in agricul. area	SRF/MET	36_07 17.00" N	121_03 22.00" W	631.4430	3998.9150	105							X	X	X	X	X											
KES	KESTERSON	CIM	2 m tower/met variables in agricul. area	SRF/MET	37_13 57.00" N	120_52 48.00" W	686.0700	4122.9470	33							X	X	X	X	X											

026.22-99.2

Table 5-1

Supplemental Measurements in Place during the IMS95 Fall and Winter Field Programs
(November 1995 - January 1996)

SITE	SITE_NAME	NET CODE	PURPOSE	SITETYPE	LATITUDE	LONGITUDE	UTMN	UTMEX	EV_MSL (m)	O3	NOX	CO	SO	HC	CH	WD	ST	TP	RH	SR	PR	WE	CH	VS	SIA	SI	NO	CL	N4	TC	DI
KET	KETTLEMAN	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	35_57'01.00" N	119_53'53.00" W	780.4140	3933.6639	104							X	X	X	X	X											
LCV	LINDCOVE	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	36_20'24.00" N	119_09'53.00" W	853.7110	4030.3886	146							X	X	X	X	X											
LOS	LOS BANOS	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	37_03'26.00" N	120_45'35.00" W	699.1100	4107.1950	29							X	X	X	X	X											
PRL	PARLIER	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	36_37'53.00" N	119_30'18.00" W	812.8100	4055.7886	101							X	X	X	X	X											
PIV	PIXLEY	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	36_17'23.00" N	119_45'55.00" W	702.1170	4000.9990	46							X	X	X	X	X											
SHC	SHAFTER/USDA	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	35_30'59.00" N	119_16'58.00" W	837.2250	3934.3250	100							X	X	X	X	X											
SLB	SAN LUIS OBISPO	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	35_15'22.00" N	120_19'57.00" W	712.7300	3909.3930	101							X	X	X	X	X											
STF	STRATFORD	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	36_05'25.00" N	119_51'00.00" W	783.3870	4001.8186	79							X	X	X	X	X											
STM	SANTA MARIA	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	34_57'04.00" N	120_29'03.00" W	738.6660	3830.9190	63							X	X	X	X	X											
VLA	VISALIA/CLAIR TOLL	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	36_18'03.00" N	119_19'23.00" W	859.1970	4023.7390	107							X	X	X	X	X											
WLC	WESTLANDS	CIM	2 m/lowe/met variables in agricult. area	SRF/MET	36_38'05.00" N	120_22'53.00" W	754.0870	4057.8880	53							X	X	X	X	X											
TEL	TELLOWS	ESC	10 m/lowe/met variables at Westside Operators	SRF/AQM/ET	35_18'18.00" N	119_22'12.00" W	818.4661	3899.8870	370	X	X		X			X															
KRG	KERN RIDGE	ESC	10 m/lowe/met variables at Westside Operators	SRF/AQM/ET	35_27'01.00" N	119_42'23.00" W	798.9970	3977.9900	177	X	X		X			X															
BAF	BAKERSFIELD/MEADOWS FIELD	NWS	10 m/lowe/met variables at airport	SRF/MET	35_27'00.12" N	119_03'07.00" W	838.7100	3938.2390	152							X		X	X			X		X							
FAT	FRESNO AIR TERMINAL	NWS	10 m/lowe/met variables at airport	SRF/MET	36_46'39.42" N	119_48'08.00" W	799.0190	4015.6610	100							X		X	X			X		X							
BKP	BAKERSFIELD	PGE	Temp & RH in Urban Area	SRF/MET	35_18'03.00" N	119_01'23.00" W	838.5070	3935.1850	94									X	X												
BUC	POINT BUCHON	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_37'30.00" N	120_51'43.00" W	698.4900	3963.3400	18							X	X	X													
DCC	DIABLO CANYON	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_11'43.00" N	120_42'00.00" W	709.5900	3896.9420	30							X	X	X													
DLO	DELANO	PGE	10 m/lowe/met variables for monitoring	SRF/MET	35_45'44.00" N	119_28'23.00" W	818.7220	3963.8410	61							X	X	X													
FRP	FRESNO	PGE	Temp & RH in Urban Area	SRF/MET	36_45'08.00" N	119_43'32.00" W	788.9030	4018.3310	91									X	X												
GRC	GROVER CITY	PGE	10 m/lowe/met variables for monitoring	SRF/MET	35_07'28.00" N	120_37'54.00" W	719.8000	3889.2300	6							X	X	X													
GRG	GREGG	PGE	10 m/lowe/met variables for monitoring	SRF/MET	36_38'03.00" N	119_55'13.00" W	774.9190	4032.4660	91							X	X	X													
HER	HERNDON	PGE	10 m/lowe/met variables for monitoring	SRF/MET	36_50'48.00" N	119_55'23.00" W	778.3730	4041.8950	73							X		X													
KTF	KETTLEMAN CITY	PGE	10 m/lowe/met variables for monitoring	SRF/MET	36_00'03.00" N	119_57'13.00" W	792.3590	3945.5540	0							X	X	X	X												
LRP	LOS PADRES	PGE	10 m/lowe/met variables for monitoring	SRF/MET	37_07'03.00" N	121_00'08.00" W	656.1600	4061.4300	96							X	X	X													
MAQ	MORRO BAY A Q	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_28'39.00" N	120_50'27.00" W	696.1900	3915.6300	43							X	X	X													
MBY	MORRO BAY POWER PLANT	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_27'27.00" N	120_51'13.00" W	698.9700	3916.4700	0							X	X	X													
MCA	MCCALL	PGE	10 m/lowe/met variables for monitoring	SRF/MET	36_30'39.00" N	119_38'13.00" W	801.4272	4056.8210	93							X	X	X													
MDD	MIDWAY	PGE	10 m/lowe/met variables for monitoring	SRF/MET	35_28'04.00" N	119_27'09.00" W	823.0400	3913.2000	84							X	X	X													
MRP	MERCED	PGE	Temp & RH in Urban Area	SRF/MET	37_17'43.00" N	120_31'40.00" W	755.9100	4030.8400	64									X	X												
PAR	PASO ROBLES	PGE	Temp & RH in Urban Area	SRF/MET	35_36'24.00" N	120_41'03.00" W	708.6300	3919.0500	326									X	X												
SKP	STOCKDALE	PGE	10 m/lowe/met variables for monitoring	SRF/MET	35_14'03.00" N	119_07'23.00" W	818.5670	3915.7100	84							X	X	X	X												
SLC	LOS OSOS CEMETERY	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_18'28.00" N	120_49'03.00" W	698.9900	3909.0000	27							X	X	X													
SLD	DAVIS PEAK	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_18'23.00" N	120_47'03.00" W	701.5000	3920.8000	549							X	X	X													
SLF	FOOTHILL ROAD	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_16'24.00" N	120_45'38.00" W	708.5900	3925.9000	43							X	X	X													
SLS	SERVICE CENTER	PGE	10 m/lowe/met variab near Power Plant	SRF/MET	35_18'32.00" N	120_49'38.00" W	703.3790	3901.5000	37							X	X	X													
SMR	SANTA MARIA	PGE	Temp & RH in Urban Area	SRF/MET	34_57'04.00" N	120_27'37.00" W	732.4950	3866.7200	67									X	X												
TEM	TEMPLETON	PGE	10 m/lowe/met variables for monitoring	SRF/MET	35_34'29.00" N	120_42'09.00" W	705.6900	3919.0000	329							X	X	X													

Table 5-2

Instrument Type Codes

INSTR	MANUFACTUR	MODEL	INSTR_DESC	INSTR_TYPE
SASS	ISierra Anderson		SSI HIVOL SAMPLER	CM_collection
RPTE	ORyprecht & Patachnik		TEOM (Tapered Element Oscillating Microbalance) SAMPLER	CM_collection
SADI	CSierra Anderson		DICHOT	CM_collection
GMTS	PGeneral Metals		TSP HI-VOL	CM_collection
XOTO	XXontech		TOXICS	CM_collection
APAN	AAir Prodects,		GAS ANALYZER	Field_meas
TEAN	ATECO		ANALYZER	Field_meas
DSAN	ADasibi		ANALYZER	Field_meas
AMPO	RAIRmetrics, Inc.		Minivol Portable Survey Sampler with PM_{10} inlet (battery powered)	CM_collection
WABA	MWedding & Assoc.	BAM-102	Beta Attenuation Monitor	CM_collection
CADM	ASierra Anderson	245	CADMP Sampler PM_{10}	CM_collection
SSI	UNKNOWN		HiVol SSI Sampler	CM_collection
WASS	IWedding & Assoc.		HiVol SSI Sampler	CM_collection
DICH	OUNKNOWN		Dichotomous Sampler	CM_collection
WADI	CWedding & Assoc.		Dichotomous Sampler	CM_collection
ANBA	MAnderson		Beta Attenuation Tape Sampler	CM_collection
TEOM	UNKNOWN		TEOM Continuous Sampler	CM_collection
CASC	2Caltech	CASCC2	Caltech Active Strand Cloudwater Collector Vers. 2	Fog_collection
CSAS	PPMS	CSASP-100 HV	Optical Scattering probe for measuring aerosols	Fog_collection
BEIM	PHauke Instruments	LPI 30/0.06/8	Berner Aerosol Impactor	Fog_collection
IEIM	PUniv. of Illinois I.E.S.		Cloud Impactor	Fog_collection
RPRA	SRadian Corporation		Radar WInd Profiler +RASS	Upper_air
SODA	RUNKNOWN		Sodar Wind Profiler	Upper_air
VZRW	SVIZ Manufacturing		Rawindsonde	Upper_air
SONI	CUNKNOWN		Sonic Anemometer	Field_meas
METI	Met One		Meteorological Measurement Package	Field_meas
CLIM	AClimatronics		Meteorological Measurement Package	Field_meas
RMYO	URM Young	5303-AQ	Combined wind speed/wind direction sensor	Field_meas
GFAA	SVarian	AA640Z	Graphite Furnace Atomic Absorption Spectrometer	Fog_analysis
DIOI	CDionex	DX-500	Ion Chromotograph	Fog_analysis
SHIF	SShimadzu	RF-1501	Spectrofluorophotometer	Fog_analysis
HITU	VHitachi	U-2000	UV/VIS Spectrophotometer	Fog_analysis
SHIO	CShimadzu	TOC-5000A	Total Organic Compound Analyzer	Fog_analysis
ETIM	PETII		Cloud Water Impactor	Fog_collection
SFCA	SCaltech	SF-CASCC	Size-Fractionating Active Strand Cloudwater Collec	Fog_collection

Table 5-2 (Continued)

Instrument Type Codes

INSTR	MANUFACTUR	MODEL	INSTR_DESC	INSTR_TYPE
SFSU	1Sierra Anderson	254I	Sequential Filter Sampler Unit 1 PM_{10} Inlet/Nitric Acid Denuder-TTD filter	CM_collection
SFSU	2Sierra Anderson	254I	Sequential Filter Sampler Unit 2 PM_{10} Inlet/Nitric Acid Denuder-TQN filter	CM_collection
SFSU	3Bendix	240 cyclone	Sequential Filter Sampler Unit 3 $PM_{2.5}$ Inlet/Nitric Acid Denuder-FTQ filter	CM_collection
SFSU	4Bendix	240 cyclone	Sequential Filter Sampler Unit 4 $PM_{2.5}$ Inlet/Nitric Acid Denuder-FQN filter	PM_collection
CSIT	HCSI	107	Thermistor-based temperature sensor	Field_meas
MLO3	AMonitor Labs	8410	Ozone analyzer	Field_meas
TESO	ATeco	43S	SO_2 Analyzer	Field_meas
TENO	ATeco	146	NO,NO_2,NO_X Analyzer	Field_meas
TECO	ATeco	48S	CO Analyzer	Field_meas
PORL	TUNKNOWN		Portable PM_{10} Light Transmission	Field_meas
MRNE	PMRI	1550B	Nephelometer	Field_meas
HVTS	PUNKNOWN		HiVol TSP Sampler	CM_collection
MOUD	IDRI		MOUDI Sampler	CM_collection
IMPR	AAIHL	Modifed Cyclon	eIMPROVE Sampler Module A ($PM_{2.5}$ Mass,BABS,ELEMENTS)	CM_collection
IMPR	BAIHL	Modifed Cyclon	eIMPROVE Sampler Module B ($PM_{2.5}$ IONS)	CM_collection
IMPR	CAIHL	Modifed Cyclon	eIMPROVE Sampler Module C ($PM_{2.5}$ OEC)	CM_collection
IMPR	DWedding	Low Volume	IMPROVE Sampler Module D (PM_{10} Mass & SO_2 gas)	CM_collection
CADM	BBendix	240	CADMP Sampler $PM_{2.5}$	CM_collection
DRIW	SDRI		Time of Wetness Sensor	Fog_collection
GAST	SGast		Tape Sampler	Field_meas
ARRW	SA.I.R.	3A-RT	Radio Theodolite Rawinsonde	Upper_air
PHME	TOrion/Microelectrodes, I	nMI-710	Orion Portable pH meter with combination PH microelectrodes	Fog_collection
VATR	HVaisala, Inc.	HMP-35	Temperature/Relative Humidity Sensor	Field_meas
QZTH	EUNKNOWN		Quartz Themometer	Field_meas(LWS)
MISO	DUNKNOWN		Mini SODAR Phased Array	Upper_air
RMYS	SRM Young	18810	Selectable Speed Anemometer	Field_meas(LWS)
AVSF	6AeroVironment	CTA 1000	SF6 Measurement Device	Tracer
LICS	RLicor	LI200SB	Solar Radation Pyranometer	Field_meas(LWS)
SF6A	NUNKNOWN		SF6 Analyzer	Tracer

Table 5-3

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
CA+	99	AD	Calcium Ions	mg/l	ARB
CL-	99	AD	Chloride Ions	mg/l	ARB
K+	99	AD	Potassium Ions	mg/l	ARB
MG+	99	AD	Magnesium Ions	mg/l	ARB
N3-	99	AD	Nitrate Ions	mg/l	ARB
NA+	99	AD	Sodium Ions	mg/l	ARB
NH+	99	AD	Ammonium Ions	mg/l	ARB
P3-	99	AD	Phosphate (Ortho) Ions	mg/l	ARB
PH	99	AD	pH	pH units	ARB
S4=	99	AD	Sulfate Ions	mg/l	ARB
SVO	99	AD	Sampler Volume	liters	ARB
XX	99	AD	Conductivity	umho/cm	ARB
H2S	99	GI	Hydrogen Sulfide	ppb	SAR
HP	99	GI	Hydrogen Peroxide	ppb	SAR
NO	99	GI	Nitric Oxide	ppb	SAR
NO_2	99	GI	Nitrogen Dioxide	ppb	SAR
NO_x	99	GI	Oxides of Nitrogen	ppb	SAR
O3	99	GI	Ozone	ppb	SAR
PAN	99	GI	Peroxyacetyl Nitrate	ppb	SAR
SO2	99	GI	Sulfur Dioxide (Pulsed Fluorescence)	ppb	SAR
TRS	99	GI	Total Reduced Sulfur	ppb	ARB
TSU	99	GI	Total Sulfur	pphm	ARB
CC2	99	GO	Cannister Carbon Dioxide (TO-12)	ppmV	SAR
CH4	99	GO	Methane (FID hourly)	pptmC	SAR
CO	99	GO	Carbon Monoxide (NDIR) (hourly)	ppm	SAR
CO2	99	GO	Carbon Dioxide (NDIR) (hourly)	ppm	SAR
NMC	99	GO	Non-methane Hydrocarbons(FID hourly)	pptmC	SAR
NMH	99	GO	Non_Methane Hydrocarbons (TO-12)	ug/m3	SAR
OGS	ACETA	GO	ACETALDEHYDE	ppbC	SAR
OGS	ACETO	GO	ACETONE	ppbV	SAR
OGS	ALKAN	GO	ALKANE (PARAFFINS)	ppbC	SAR
OGS	ALKEN	GO	ALKENE (OLEFINS)	ppbC	SAR
OGS	APINE	GO	a-PINENE	ppbC	SAR
OGS	AROMA	GO	AROMATICS	ppbC	SAR
OGS	BENZA	GO	BENZALDEHYDE	ppbV	SAR
OGS	BENZE	GO	BENZENE	ppbC	SAR
OGS	BPINE	GO	beta-PINENE	ppbC	SAR
OGS	BUTAN	GO	BUTANAL	ppbV	SAR
OGS	C10AR	GO	C10 AROMATIC	ppbC	SAR
OGS	C10PA	GO	C10 PARAFFIN	ppbC	SAR
OGS	C24MH	GO	2,4-DIMETHYLHEPTANE	ppbC	SAR
OGS	C2BUT	GO	c-2-BUTENE	ppbC	SAR
OGS	C2HEX	GO	cis-2-HEXENE	ppbC	SAR
OGS	C2OCT	GO	c-2-OCTENE	ppbC	SAR
OGS	C2PEN	GO	c-2-PENTENE	ppbC	SAR
OGS	C4MPN	GO	c-4-METHYL-2-PENTENE	ppbC	SAR
OGS	C4OLE	GO	2-METHYLPROPYLENE,BUTENE-1	ppbC	SAR

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
OGS	C5CAR	GO	C5 CARBONYL	ppbV	SAR
OGS	C6CAR	GO	C6 CARBONYL	ppbV	SAR
OGS	C6OLE	GO	C6 OLEFIN	ppbC	SAR
OGS	C7CAR	GO	C7 CARBONYL	ppbv	SAR
OGS	C7OLE	GO	C7 OLEFIN	ppbC	SAR
OGS	C7PAR	GO	C7 PARAFFIN	ppbC	SAR
OGS	C8OLE	GO	C8 OLEFIN	ppbC	SAR
OGS	C8PAR	GO	C8 PARAFFIN	ppbC	SAR
OGS	C9ARO	GO	C9 AROMATIC	ppbC	SAR
OGS	C9OLE	GO	C9 OLEFIN	ppbC	SAR
OGS	C9PAR	GO	C9 PARAFFIN	ppbC	SAR
OGS	CARBM	GO	Carbon Monoxide (TO-12)	ppbV	SAR
OGS	CH2CL	GO	CH2Cl2	ppbC	SAR
OGS	CYHEP	GO	CYCLOHEPTANE	ppbC	SAR
OGS	CYHEX	GO	CYCLOHEXANE	ppbC	SAR
OGS	CYHEX	GO	CYCLOHEXENE	ppbC	SAR
OGS	CYHX	GO	CYCLOHEXANAL	ppbV	SAR
OGS	CYPAN	GO	CYCLOPENTANE	ppbC	SAR
OGS	CYPEN	GO	CYCLOPENTENE	ppbC	SAR
OGS	DECAN	GO	n-DECANE	ppbC	SAR
OGS	ETBEN	GO	ETHYLBENZENE	ppbC	SAR
OGS	ETCYH	GO	ETHYLCYCLOHEXANE	ppbC	SAR
OGS	ETHAN	GO	ETHANE	ppbC	SAR
OGS	ETHEN	GO	ETHENE or ETHYLENE	ppbC	SAR
OGS	ETHYL	GO	ETHYLENE	ppbC	SAR
OGS	ACETY	GO	ACETYLENE	ppbC	SAR
OGS	FORMA	GO	FORMALDEHYDE	ppbV	SAR
OGS	FREON	GO	FREON 113	ppbC	SAR
OGS	HEPTA	GO	n-HEPTANE	ppbC	SAR
OGS	HEXAN	GO	n-HEXANE	ppbC	SAR
OGS	HEXHE	GO	HEXANONES+HEXANAL	ppbV	SAR
OGS	IBBEN	GO	i-BUTYLBENZENE	ppbC	SAR
OGS	IBUTA	GO	ISOBUTANE	ppbC	SAR
OGS	IBUTE	GO	i-BUTENE	ppbC	SAR
OGS	IPENT	GO	ISOPENTANE	ppbC	SAR
OGS	IPROB	GO	i-PROPYLBENZENE	ppbC	SAR
OGS	ISOPR	GO	ISOPRENE	ppbC	SAR
OGS	MCYHE	GO	METHYLCYCLOHEXANE	ppbC	SAR
OGS	MCYPE	GO	METHYLCYCLOPENTANE	ppbC	SAR
OGS	MEK	GO	MEK	ppbV	SAR
OGS	MEKBU	GO	MEK+BUTANOL	ppbV	SAR
OGS	METHA	GO	METHANE	ppbC	SAR
OGS	METHT	GO	Methane (TO-12)	ppbV	SAR
OGS	METOL	GO	m-ETHYLTOLUENE	ppbC	SAR
OGS	MPXYL	GO	m&p-XYLENE	ppbC	SAR
OGS	MSTYR	GO	METHYLSTYRENE	ppbC	SAR
OGS	NBUTA	GO	n-BUTANE	ppbC	SAR
OGS	NMHCS	GO	Non-methane Hydrocarbons (OGI)	ppbC	SAR
OGS	NONAN	GO	n-NONANE	ppbC	SAR

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
OGS	NONEN	GO	1-NONENE	ppbC	SAR
OGS	NPENT	GO	n-PENTANE	ppbC	SAR
OGS	NPRPB	GO	n-PROPYLBENZENE	ppbC	SAR
OGS	OCTAN	GO	n-OCTANE	ppbC	SAR
OGS	OCTEN	GO	1-OCTENE	ppbC	SAR
OGS	OETOL	GO	o-ETHYLTOLUENE	ppbC	SAR
OGS	OXYLE	GO	o-XYLENE	ppbC	SAR
OGS	PENPA	GO	PENTANONE+PANTONAL	ppbV	SAR
OGS	PENTA	GO	PENTANAL	ppbV	SAR
OGS	PENTE	GO	1-PENTENE	ppbC	SAR
OGS	PETOL	GO	p-ETHYLTOLUENE	ppbC	SAR
OGS	PROPA	GO	PROPANE	ppbC	SAR
OGS	PROPE	GO	PROPENE	ppbC	SAR
OGS	PROPL	GO	PROPANAL	ppbV	SAR
OGS	PXYLE	GO	p-xylene	ppbC	SAR
OGS	SBBEN	GO	sec-BUTYLBENZENE	ppbC	SAR
OGS	STYRE	GO	STYRENE	ppbC	SAR
OGS	T2BUT	GO	t-2-BUTENE	ppbC	SAR
OGS	T2HEX	GO	TRANS-2-HEXENE	ppbC	SAR
OGS	T2PEN	GO	t-2-PENTENE	ppbC	SAR
OGS	T4MPN	GO	t-4-METHYL-2-PENTENE	ppbC	SAR
OGS	TBBEN	GO	t-BUTYLBENZENE	ppbC	SAR
OGS	TCLET	GO	111HCL ETHANE	ppbC	SAR
OGS	TERPE	GO	TERPENES	ppbC	SAR
OGS	TIHC	GO	TOTAL IDENTIFIED HYDROCARBONS	ppbC	SAR
OGS	TOLUE	GO	TOLUENE	ppbC	SAR
OGS	TRICH	GO	TRICHLOROETHYLENE	ppbC	SAR
OGS	TUHC	GO	TOTAL UNIDENTIFIED HC	ppbC	SAR
OGS	UNC10	GO	UNIDENTIFIED C10+	ppbC	SAR
OGS	UNC29	GO	UNIDENTIFIED C2-C9	ppbC	SAR
OGS	X123T	GO	1,2,3-TRIMETHYLBENZENE	ppbC	SAR
OGS	X124B	GO	1,2,4-TRIMETHYLBENZEN sec-BUTYLBENZE	ppbC	SAR
OGS	X124T	GO	1,2,4-TRIMETHYLBENZENE	ppbC	SAR
OGS	X135T	GO	1,3,5-TRIMETHYLBENZENE	ppbC	SAR
OGS	X13BU	GO	1,3-BUTADIENE	ppbC	SAR
OGS	X13DB	GO	1,3-DIETHYLBENZENE	ppbC	SAR
OGS	X14DB	GO	1,4-DIETHYLBENZENE	ppbC	SAR
OGS	X1BUT	GO	1-BUTENE	ppbC	SAR
OGS	X1HEX	GO	1-HEXENE	ppbC	SAR
OGS	X2233	GO	2,2,3,3--TETRAMETHYLBUTAN	ppbC	SAR
OGS	X223M	GO	2,2,3-TRI-METHYLPENTANE	ppbC	SAR
OGS	X224A	GO	2,2,4-TRIMETHYLPENTANE	ppbC	SAR
OGS	X224M	GO	2,2,4--TRIMETHYLHEXANE	ppbC	SAR
OGS	X225M	GO	2,2,5-TRIMETHYLHEXANE	ppbC	SAR
OGS	X22DP	GO	2,2-DIMETHYLPROPANE	ppbC	SAR
OGS	X22MB	GO	2,2-DIMETHYLBUTANE	ppbC	SAR
OGS	X22MH	GO	2,2--DIMETHYLHEPTANE	ppbC	SAR
OGS	X234M	GO	2,3,4-TRIMETHYLPENTANE	ppbC	SAR

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
OGS	X23MA	GO	2,3-DIMETHYLHEPTANE	ppbC	SAR
OGS	X23MB	GO	2,3-DIMETHYLBUTANE	ppbC	SAR
OGS	X23MH	GO	2,3-DIMETHYLHEXANE	ppbC	SAR
OGS	X23MP	GO	2,3-DIMETHYLPENTANE	ppbC	SAR
OGS	X2441	GO	2,4,4--TRIMETHYL--1--PENTEN	ppbC	SAR
OGS	X2442	GO	2,4,4--TRIMETHYL--2--PENTEN	ppbC	SAR
OGS	X24MH	GO	2,4-DIMETHYLHEXANE	ppbC	SAR
OGS	X24MP	GO	2,4-DIMETHYLPENTANE	ppbC	SAR
OGS	X25MH	GO	2,5-DIMETHYLHEPTANE	ppbC	SAR
OGS	X25MX	GO	2,5-DIMETHYLHEXANE	ppbC	SAR
OGS	X2M1B	GO	2-METHYL-1-BUTENE	ppbC	SAR
OGS	X2M2B	GO	2-METHYL-2-BUTENE	ppbC	SAR
OGS	X2M2P	GO	2-METHYL-2-PENTENE	ppbC	SAR
OGS	X2MHE	GO	2-METHYLHEPTANE	ppbC	SAR
OGS	X2MHX	GO	2-METHYLHEXANE	ppbC	SAR
OGS	X2MPE	GO	2-METHYLPENTANE	ppbC	SAR
OGS	X2MPN	GO	2-METHYL-1-PENTENE	ppbC	SAR
OGS	X33MP	GO	3,3-DIMETHYLPENTANE	ppbC	SAR
OGS	X3ETH	GO	3-ETHYLHEXANE	ppbC	SAR
OGS	X3M2P	GO	c&t-3-METHYL-2-PENTENE	ppbC	SAR
OGS	X3MBU	GO	3-METHYL-1-BUTENE	ppbC	SAR
OGS	X3MCH	GO	3MECYCLOHEXENE	ppbC	SAR
OGS	X3MHE	GO	3-METHYLHEPTANE	ppbC	SAR
OGS	X3MHX	GO	3-METHYLHEXANE	ppbC	SAR
OGS	X3MOC	GO	3-METHYLOCTANE	ppbC	SAR
OGS	X3MPE	GO	3-METHYLPENTANE	ppbC	SAR
OGS	X4MOC	GO	4-METHYLOCTANE	ppbC	SAR
OGS	X4MPN	GO	4-METHYL-1-PENTENE	ppbC	SAR
OP	99	GO	Organoperoxide	?	SAR
THC	99	GO	Total Hydorcarbons(FID hourly)	pptmC	SAR
ALT	99	ME	Altimeter Setting	in of mercry	ARM
BSP	99	ME	Barometric Station Pressure	in of mercuy	ARM
CHT	99	ME	Cloud height	hundreds ft	NWS
CTY	99	ME	Lowest cloud layer or obscuring phenomena	description	NWS
DRZ	99	ME	Present weather (drizzle, freezing drizzle)	1 or 0	NWS
DS	99	ME	Direct Normal Insolation	watts/m2	SAR
DT	99	ME	Dew Point Temperature	degrees C	SAR
FOG	99	ME	Present weather (fog, blowing dust, blowings)	1 or 0	NWS
HVB	99	ME	Horizontal Visibility	100ths of mi	NWS
NS	99	ME	Net Solar Radiation	watts/m2	SAR
OBP	99	ME	Obscuring Phenomena	description	NWS
PR	99	ME	Atmospheric Pressure	mb	SAR
PRE	99	ME	precipitation	Inches	CIM
PWS	99	ME	peak wind speed	meters/sec	ARM
RAI	99	ME	Present weather (rain,rain showers & freezing)	1 or 0	NWS
RG	99	ME	Rain Gauge	inches	ARM
RH	99	ME	Relative Humidity	%	SAR
SLP	99	ME	Pressure, reduced to sea level	mb and tenth	NWS

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
SMK	99	ME	Present weather (smoke, haze, smoke & haze,du)	1 or 0	NWS
SP	99	ME	Sigma Phi	degrees wind	SAR
ST	99	ME	Sigma Theta	degrees wind	SAR
STB	99	ME	Stability Category (1='A',6='F')		BAQ
T	99	ME	Temperature	degrees C	SAR
TB	99	ME	Indicated Turbulence, e**1/3	(cm2/s3)**.3	SAR
TLT	99	ME	total light transmission	Watts/m2	ARM
TS	99	ME	Total Solar Radiation	watts/m2	SAR
TSC	99	ME	total sky cover		ARM
UD	99	ME	Unit Vector Wind Direction	deg N	SAR
US	99	ME	Ultraviolet Solar Radiation	watts/m2	SAR
VIS	99	ME	visibility	Miles	ARN
WBT	99	ME	wet bulb temperature	Deg C	ARM
WD	99	ME	Resultant Vector Wind Direction	deg N	SAR
WG	99	ME	Wind Gust	m/s	CIM
WS	99	ME	Scalar Horizontal Wind Speed	m/s	SAR
WV	99	ME	Vector Horizontal Wind Speed	m/s	SAR
WZ	99	ME	Vertical Wind Speed (PGE Dopplers)	m/s	SAR
ABC	99	PM	Aethelometer Black Carbon	ng/m3	SAR
BDS	99	PM	Dry Particle Light Scattering	1/Mm	SAR
BFS	99	PM	Fine Particle Light Scattering	1/Mm	SAR
BOA	99	PM	Optical absorption	10-8 m-1	IMP
BS4	99	PM	Particle Light Scattering @400 nm	1/Mm	SAR
BS5	99	PM	Particle Light Scattering @550 nm	1/Mm	SAR
BS7	99	PM	Particle Light Scattering @ 700nm	1/Mm	SAR
BSO	99	PM	Benzene Soluble Organics (0-10 um)	ug/m3	ARB
BTA	99	PM	Total Particle Light Absorption	1/Mm	SAR
BTS	99	PM	Total Particle Light Scattering	1/Mm	SAR
COH	99	PM	Coefficient of Haze	1/(1000 ft)	SAR
PMC	AL	PM	Aluminum (2.5-10 um)	ug/m3	ARB
PMC	AS	PM	Arsenic (2.5-10 um)	ug/m3	ARB
PMC	BA	PM	Barium (2.5-10 um)	ug/m3	ARB
PMC	BR	PM	Bromine (2.5-10 um)	ug/m3	ARB
PMC	CA	PM	Calcium (2.5-10 um)	ug/m3	ARB
PMC	CD	PM	Cadmium (2.5-10 um)	ug/m3	ARB
PMC	CL	PM	Chlorine (2.5-10 um)	ug/m3	ARB
PMC	CL-	PM	Soluble Chloride (2.5-10 um)	ug/m3	IMP
PMC	CO	PM	Cobalt (2.5-10 um)	ug/m3	ARB
PMC	CR	PM	Chromium (2.5-10 um)	ug/m3	ARB
PMC	CU	PM	Copper (2.5-10 um)	ug/m3	ARB
PMC	ECHT	PM	Elemental Carbon, high temp (2.5-10 um)	ug/m3	IMP
PMC	ECLT	PM	Elemental Carbon, low temp (2.5-10 um)	ug/m3	IMP
PMC	FE	PM	Iron (2.5-10 um)	ug/m3	ARB
PMC	H	PM	Hydrogen (2.5-10 um)	ug/m3	IMP
PMC	HG	PM	Mercury (2.5-10 um)	ug/m3	ARB
PMC	K	PM	Potassium (2.5-10 um)	ug/m3	ARB
PMC	K+	PM	Soluble Potassium (0 -2.5 um)	ug/m3	SAR
PMC	TMASS	PM	PM Coarse (2.5-10 um) mass	ug/m3	ARB

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
PMC	MG	PM	Magnesium (2.5-10 um)	ug/m3	IMP
PMC	MN	PM	Manganese (2.5-10 um)	ug/m3	ARB
PMC	MO	PM	Molybdenum (2.5-10 um)	ug/m3	ARB
PMC	NA+	PM	Soluble Sodium (2.5-10 um)	ug/m3	SAR
PMC	NH_{4+}	PM	Soluble Ammonium (2.5-10 um)	ug/m3	ARB
PMC	NI	PM	Nickel (2.5-10 um)	ug/m3	ARB
PMC	NO_2-	PM	Soluble Nitrite (2.5-10 um)	ug/m3	IMP
PMC	NO_3-	PM	Soluble Nitrate (2.5-10 um)	ug/m3	IMP
PMC	OCHT	PM	Organic Carbon, high temp (2.5-10 um)	ug/m3	IMP
PMC	OCLT	PM	Organic Carbon, low temp (2.5-10 um)	ug/m3	IMP
PMC	P	PM	Phosphorus (2.5-10 um)	ug/m3	ARB
PMC	PB	PM	Lead (2.5-10 um)	ug/m3	ARB
PMC	RB	PM	Rubidium (2.5-10 um)	ug/m3	ARB
PMC	S	PM	Sulfur (2.5-10 um)	ug/m3	ARB
PMC	SE	PM	Selenium (2.5-10 um)	ug/m3	ARB
PMC	SI	PM	Silicon (2.5-10 um)	ug/m3	ARB
PMC	SO4=	PM	Soluble Sulfate (2.5-10 um)	ug/m3	SAR
PMC	SR	PM	Strontium (2.5-10 um)	ug/m3	ARB
PMC	TI	PM	Titanium (2.5-10 um)	ug/m3	ARB
PMC	U	PM	Uranium (2.5-10 um)	ug/m3	ARB
PMC	V	PM	Vanadium (2.5-10 um)	ug/m3	ARB
PMC	Y	PM	Yttrium (2.5-10 um)	ug/m3	ARB
PMC	ZN	PM	Zinc (2.5-10 um)	ug/m3	ARB
PMC	ZR	PM	Zirconium (2.5-10 um)	ug/m3	ARB
PMC	TC	PM	Total Carbon (2.5-10 um)	ug/m3	ARB
PMC	OC	PM	Organic Carbon (2.5-10 um)	ug/m3	SAR
PMC	EC	PM	Elemental Carbon (2.5-10 um)	ug/m3	SAR
PMC	GA	PM	Gallium (2.5-10 um)	ug/m3	SAR
PMC	PD	PM	Palladium (2.5-10 um)	ug/m3	SAR
PMC	AG	PM	Silver (2.5-10 um)	ug/m3	SAR
PMC	IN	PM	Indium (2.5-10 um)	ug/m3	SAR
PMC	SN	PM	Tin (2.5-10 um)	ug/m3	SAR
PMC	SB	PM	Antimony (2.5-10 um)	ug/m3	SAR
PMC	LA	PM	Lanthanum (2.5-10 um)	ug/m3	SAR
PMC	AU	PM	Gold (2.5-10 um)	ug/m3	SAR
PMC	TL	PM	Thallium (2.5-10 um)	ug/m3	SAR
PMF	AL	PM	Aluminum (0-2.5 um)	ug/m3	ARB
PMF	AS	PM	Arsenic (0-2.5 um)	ug/m3	ARB
PMF	BA	PM	Barium (0-2.5 um)	ug/m3	ARB
PMF	BR	PM	Bromine (0-2.5 um)	ug/m3	ARB
PMF	CA	PM	Calcium (0-2.5 um)	ug/m3	ARB
PMF	CD	PM	Cadmium (0-2.5 um)	ug/m3	ARB
PMF	CL	PM	Chlorine (0-2.5 um)	ug/m3	ARB
PMF	CL-	PM	Chloride (0-2.5 um)	ug/m3	IMP
PMF	CO	PM	Cobalt (0-2.5 um)	ug/m3	ARB
PMF	CR	PM	Chromium (0-2.5 um)	ug/m3	ARB
PMF	CU	PM	Copper (0-2.5 um)	ug/m3	ARB
PMF	ECHT	PM	Elemental Carbon, high temp (0-2.5 um)	ug/m3	IMP
PMF	ECLT	PM	Elemental Carbon, low temp (0-2.5 um)	ug/m3	IMP

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
PMF	FE	PM	Iron (0-2.5 um)	ug/m3	ARB
PMF	H	PM	Hydrogen (0-2.5 um)	ug/m3	IMP
PMF	HG	PM	Mercury (0-2.5 um)	ug/m3	ARB
PMF	K	PM	Potassium (0-2.5 um)	ug/m3	ARB
PMF	K+	PM	Soluble Potassium (0 -2.5 um)	ug/m3	SAR
PMF	TMASS	PM	PM Fine (0-2.5 um) mass	ug/m3	ARB
PMF	MG	PM	Magnesium (0-2.5 um)	ug/m3	IMP
PMF	MN	PM	Manganese (0-2.5 um)	ug/m3	ARB
PMF	MO	PM	Molybdenum (0-2.5 um)	ug/m3	ARB
PMF	NA+	PM	Soluble Sodium (0 -2.5 um)	ug/m3	SAR
PMF	NH_4+	PM	Soluble Ammonium (0- 2.5 um)	ug/m3	ARB
PMF	NI	PM	Nickel (0-2.5 um)	ug/m3	ARB
PMF	NO_2-	PM	Soluble Nitrite (0-2.5 um)	ug/m3	IMP
PMF	NO_3-	PM	Soluble Nitrate (0-2.5 um)	ug/m3	IMP
PMF	OCHT	PM	Organic Carbon, high temp (0-2.5 um)	ug/m3	IMP
PMF	OCLT	PM	Organic Carbon, low temp (0-2.5 um)	ug/m3	IMP
PMF	P	PM	Phosphorus (0-2.5 um)	ug/m3	ARB
PMF	PB	PM	Lead (0-2.5 um)	ug/m3	ARB
PMF	RB	PM	Rubidium (0-2.5 um)	ug/m3	SAR
PMF	S	PM	Sulfur (0-2.5 um)	ug/m3	ARB
PMF	SE	PM	Selenium (0-2.5 um)	ug/m3	ARB
PMF	SI	PM	Silicon (0-2.5 um)	ug/m3	ARB
PMF	SO4=	PM	Soluble Sulfate (0-2.5 um)	ug/m3	SAR
PMF	SR	PM	Strontium (0-2.5 um)	ug/m3	ARB
PMF	TI	PM	Titanium (0-2.5 um)	ug/m3	ARB
PMF	U	PM	Uranium (0-2.5 um)	ug/m3	ARB
PMF	V	PM	Vanadium (0-2.5 um)	ug/m3	ARB
PMF	Y	PM	Yttrium (0-2.5 um)	ug/m3	ARB
PMF	ZN	PM	Zinc (0-2.5 um)	ug/m3	ARB
PMF	ZR	PM	Zirconium (0-2.5 um)	ug/m3	ARB
PMF	TC	PM	Total Carbon (0-2.5 um)	ug/m3	ARB
PMF	OC	PM	Organic Carbon (0-2.5 um)	ug/m3	SAR
PMF	EC	PM	Elemental Carbon (0-2.5 um)	ug/m3	SAR
PMF	GA	PM	Gallium (0-2.5 um)	ug/m3	SAR
PMF	PD	PM	Palladium (0-2.5 um)	ug/m3	SAR
PMF	AG	PM	Silver (0-2.5 um)	ug/m3	SAR
PMF	IN	PM	Indium (0-2.5 um)	ug/m3	SAR
PMF	SN	PM	Tin (0-2.5 um)	ug/m3	SAR
PMF	SB	PM	Antimony (0-2.5 um)	ug/m3	SAR
PMF	LA	PM	Lanthanum (0-2.5 um)	ug/m3	SAR
PMF	AU	PM	Gold (0-2.5 um)	ug/m3	SAR
PMF	TL	PM	Thallium (0-2.5 um)	ug/m3	SAR
PMT	AL	PM	Aluminum (0-10 um)	ug/m3	ARB
PMT	AS	PM	Arsenic (0-10 um)	ug/m3	ARB
PMT	BA	PM	Barium (0-10 um)	ug/m3	ARB
PMT	BR	PM	Bromine (0-10 um)	ug/m3	ARB
PMT	CA	PM	Calcium (0-10 um)	ug/m3	ARB
PMT	CD	PM	Cadmium (0-10 um)	ug/m3	ARB
PMT	CL	PM	Chlorine (0-10 um)	ug/m3	ARB

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
PMT	CL-	PM	Soluble Chloride (0-10 um)	ug/m3	IMP
PMT	CO	PM	Cobalt (0-10 um)	ug/m3	ARB
PMT	CR	PM	Chromium (0-10 um)	ug/m3	ARB
PMT	CU	PM	Copper (0-10 um)	ug/m3	ARB
PMT	ECHT	PM	Elemental Carbon, high temp (0-10 um)	ug/m3	IMP
PMT	ECLT	PM	Elemental Carbon, low temp (0-10 um)	ug/m3	IMP
PMT	FE	PM	Iron (0-10 um)	ug/m3	ARB
PMT	H	PM	Hydrogen (0-10 um)	ug/m3	IMP
PMT	HG	PM	Mercury (0-10 um)	ug/m3	ARB
PMT	K	PM	Potassium (0-10 um)	ug/m3	ARB
PMT	K+	PM	Soluble Potassium (0 -2.5 um)	ug/m3	SAR
PMT	TMASS	PM	PM_{10} (0-10 um) mass	ug/m3	SAR
PMT	MG	PM	Magnesium (0-10 um)	ug/m3	IMP
PMT	MN	PM	Manganese (0-10 um)	ug/m3	ARB
PMT	MO	PM	Molybdenum (0-10 um)	ug/m3	ARB
PMT	NA+	PM	Soluble Sodium (0 -10 um)	ug/m3	SAR
PMT	NH_4+	PM	Soluble Ammonium (0-10 um)	ug/m3	ARB
PMT	NI	PM	Nickel (0-10 um)	ug/m3	ARB
PMT	NO_2-	PM	Soluble Nitrite (0-10 um)	ug/m3	IMP
PMT	NO_3-	PM	Soluble Nitrate (0-10 um)	ug/m3	IMP
PMT	OCHT	PM	Organic Carbon, high temp (0-10 um)	ug/m3	IMP
PMT	OCLT	PM	Organic Carbon, low temp (0-10 um)	ug/m3	IMP
PMT	P	PM	Phosphorus (0-10 um)	ug/m3	ARB
PMT	PB	PM	Lead (0-10 um)	ug/m3	ARB
PMT	RB	PM	Rubidium (0-10 um)	ug/m3	ARB
PMT	S	PM	Sulfur (0-10 um)	ug/m3	ARB
PMT	SE	PM	Selenium (0-10 um)	ug/m3	ARB
PMT	SI	PM	Silicon (0-10 um)	ug/m3	ARB
PMT	SO_4=	PM	Soluble Sulfate (0-10 um)	ug/m3	SAR
PMT	SR	PM	Strontium (0-10 um)	ug/m3	ARB
PMT	TI	PM	Titanium (0-10 um)	ug/m3	ARB
PMT	U	PM	Uranium (0-10 um)	ug/m3	ARB
PMT	V	PM	Vanadium (0-10 um)	ug/m3	ARB
PMT	Y	PM	Yttrium (0-10 um)	ug/m3	ARB
PMT	ZN	PM	Zinc (0-10 um)	ug/m3	ARB
PMT	ZR	PM	Zirconium (0-10 um)	ug/m3	ARB
PMT	TC	PM	Total Carbon (0-10 um)	ug/m3	ARB
PMT	OC	PM	Organic Carbon (0-10 um)	ug/m3	SAR
PMT	EC	PM	Elemental Carbon (0-10 um)	ug/m3	SAR
PMT	GA	PM	Gallium (0-10 um)	ug/m3	SAR
PMT	PD	PM	Palladium (0-10 um)	ug/m3	SAR
PMT	AG	PM	Silver (0-10 um)	ug/m3	SAR
PMT	IN	PM	Indium (0-10 um)	ug/m3	SAR
PMT	SN	PM	Tin (0-10 um)	ug/m3	SAR
PMT	SB	PM	Antimony (0-10 um)	ug/m3	SAR
PMT	LA	PM	Lanthanum (0-10 um)	ug/m3	SAR
PMT	AU	PM	Gold (0-10 um)	ug/m3	SAR
PMT	TL	PM	Thallium (0-10 um)	ug/m3	SAR
S4N	99	PM	Sulfate on Nylon	ng/m3	IMP

Table 5-3 (Continued)

Project Parameter Codes

PARAMETER CODE	ANALYTE	GENRE	PARAMETER DESCRIPTION	PROJECT UNITS	ORIGIN
LS	99	TS	Light Scatter	1/Mm	ARB
PL	99	TS	Particulate Lead	ug/m3	ARB
S4T	99	TS	TSP Sulfate (>10 um)	ug/m3	CHE
SI	99	TS	Soiling Index	COH/1000	ARB
SN3	99	TS	Suspended Nitrates	ug/m3	ARB
SS3	99	TS	Suspended Sulfates	ug/m3	ARB
TOF	99	TS	Total Organic Fraction	ug/m3	ARB
TSP	99	TS	Total Suspended Particulates	ug/m3	ARB
TD	99	ME	Temperature Difference	degrees C	ARB
PMT	NA	PM	Sodium (0-10 um)	ug/m3	IMP
PMC	NA	PM	Solium (2.5-10 um)	ug/m3	IMP
PMF	NA	PM	Sodium (0-2.5 um)	ug/m3	IMP
PMF	CL-	PM	Soluble Chloride (0-2.5 um)	ug/m3	IMP
ACP	99	ME	Accumulated Precipitation	inches	RAW

Table 5-4

Data Point Quality Codes

QCFLAG	FLAG DESCRIPTION
0	Valid data
1	Estimated Value
2	Calibration or instrument check
3	Instrument failure
4	Off-scale reading
5	Interpolated
6	Below detection limit
7	Suspect
8	Invalid
9	Missing
a	Hourly average (45 min <= avg period < 60 min)
b	Hourly average (avg period < 45 min)
d	Averaged data
e	Zero mode
f	Blank sample
g	Out of Range
h	Recalculated or reprocessed
q	Questionable (filter affected by something)

5.3.1.4 File Naming Conventions

The convention CDDMMYYA.PLL was used for creating file names. The elements in this name are as follows:

- C = 1-character contractor code (D = DRI, S = STI, U = UCO)
- DD = 2-character data category:
  - CM = particulate chemistry and mass
  - ME = meteorological
  - GS = gaseous
  - HC = hydrocarbon and VOC
  - FG = fog
  - VS = visibility
  - TR = tracer
  - EM = emissions
  - SS = special studies and miscellaneous
- MM = 2-letter month code (JA, FE, MR, AP, MY, JN, JL, AU, SE, OC, NO, DE)
- YY = year
- A = averaging interval codes:
  - A = 3-hour samples
  - B = 6-hour samples
  - C = 12-hour samples
  - D = 24-hour samples
  - H = hourly
  - J = jumps (every other hour)
  - V = hourly but varies, possibly fewer than 24 measurements per day
  - I = instantaneous (<1 min)
  - M = 15-minute samples
  - P = partial hour samples (<60 min)
- P = measurement platform code (S = surface, U = upper air)
- LL = 2-character data validation level code (0A, 0B, 1A, 1B, 2A, 2B, 3A; for explanation, see Section 5.4 and VALIDLEV.DBF)

5.3.1.5 Data Processing Routines

Standard data processing routines were available to each contractor to ensure processing consistency. Codes were written in Microsoft Fox Pro 2.6 programming language. In particular, this included

transforming RH to dew point data and averaging wind speed and wind direction. These programs were on the ARB project server and were available through file transfer protocol (FTP), as discussed in Section 5.3.5.1. In addition, all data processing routines from each contractor were expected to be submitted as part of the data for documentation purposes.

5.3.1.6 QC Flags

The project QC flags for creating data files for submission are listed in Table 5-4 and in QCFLAGS.DBF.

5.3.1.7 Instrument Codes

Table 5-2 lists the defined project instrument codes in INSTR.DBF that were required in the data files. The instrument codes could range from general to fairly specific, depending on how much was known about the instrument. Upon being notified, the data manager added missing instrument codes to the file or corrected incorrectly entered code.

5.3.1.8 Site Naming Conventions

The 3-letter site codes for the data files are defined in Table 5-1 (from SITE.DBF).

5.3.1.9 Missing Values

Missing data points were designated by -99.0.

5.3.2 Supporting Documentation and QA

For integration into a final database system, each data point had to be well documented with easy access to related important information about the measurement site, instrumentation, QC, and so on. The required empty DBF files were provided to each contractor. Each contractor was then required to fill the database files with pertinent information and upload these files back to the data manager along with the data files.

Contractors were asked to provide a written QA plan whose procedures fulfill minimum ARB and/or EPA requirements. Such a plan was expected to detail how data would be invalidated. Also, reports containing information about any instrument were valuable and were required if the instrument was state-of-the-art. All this documentation was to be uploaded as a Microsoft Word for Windows or WordPerfect document.

The following minimum information was required from the contractor who completed the site documentation:

1. The site location (as determined by a GPS device and confirmed by a USGS 7.5-minute quadrangle map), elevation (from GPS), and exactly what parameters were measured at each site.
2. Several maps, including a quadrangle identifying the site and a detailed site map describing the equipment, shelters, roads, and so on.
3. Photographs taken at the site while facing outward in the 8 cardinal directions, as well as photographs taken while facing toward the site from the same vantage points.
4. Videotape that shows all instrumentation as well as potential pollution sources in the surrounding area.

5.3.3 Reports

A report describing all the above elements was prepared after the study ended. Required content included a description and log of all problems encountered during the study. The report was to be produced in WordPerfect or Microsoft Word for Windows and submitted on disk as well as on paper. After review by ARB and project personnel, the contractor responded to any comments by those reviewers and issued a final report.

5.3.4 Data Plotting

The data were plotted on a time-series basis for review by the ARB database manager. All plots had to be submitted in electronic format. The plotting program, a macro or program in Excel, was provided to each contractor to obtain the time-series plots.

5.3.5 Access to Project Files

5.3.5.1 Internet Server

All IMS95 files were available on the Internet server **themis.arb.ca.gov**. The server was a UNIX workstation at ARB that could be accessed through the Internet and through telephone dialup at (916) 323-9715. The server supported FTP, which allowed rapid transfer of data files between the user and the server.

In addition, the server supported "telnet," which allowed the use of the server from remote sites; email, which allowed study participants to communicate with each other; and a "finger" participant locator, which provided basic information (such as name, affiliation, address, phone number, fax number, and email address) about each study participant.

All current study participants were identified by the alias "TC," and mail and announcements were sent to them at the address **TC@themis.arb.ca.gov**. Other aliases were created for smaller communication groups, as needed.

5.3.5.2 Directory Structures

Data and communications files were organized into several subdirectories within the IMS95 directory on **themis.arb.ca.gov**. Each contained additional subdirectories to further organize the information.

Except for the TEMP directory, all directories had read-only privileges for most users, to avoid the inadvertent erasure of information. Files could be uploaded to the TEMP directory for later placement in the appropriate read-only directory by the data manager. These directories were as follows:

- INFO: This directory contains information about the study, including the "readme" file, important databases described in the present report's tables, and other important information available to the study participants.
- SOFTWARE: This directory contains software available for processing, plotting, and so on. The subdirectories are GRAPHICS and PROCESSG.
- TEMP: This was a temporary location where study participants uploaded files before transferring files to their designated parent directory. An email message was sent to the data manager indicating the uploaded file name and its desired directory location. The TEMP directory also allows the transfer of nonarchived scratch files among study participants.
- REPORTS: This directory contains files related to project reports, memoranda, and minutes. The subdirectories are as follows:
  - PROGPLN for the latest draft of the program and management plans
  - MEMO for project memoranda
  - MINUTES for minutes of discussions
  - PRGREP for progress reports
  - ANALYSIS for data analysis reports
  - RFP for final versions of RFPs
- DATA: This directory contains data files in the form in which they were received from the data source.
- DBASE: This directory contains validated project and supplemental data in xBase (*.DBF) formats. The files are stored in four different data structures: surface continuous, particle, fog, and upper air. These files are organized into the following subdirectories according to their source:
  - STI for data measured and validated by STI
  - DRI for data measured and validated by DRI
  - CSU for data measured and validated by CSU

- ARB for data measured and validated by ARB
- CIM for data obtained and validated by DRI
- PGE for data obtained from the PG&E meteorological data network
- IMP for data obtained from the IMPROVE network
- NWS for data obtained from NWS
- WSO for data obtained from the WSO Network (Chevron and Texaco)
- MISC for miscellaneous database files

- MODELS: This directory includes input and output files for different modeling applications.

Other directories and subdirectories were created as needed to organize the information produced by IMS95.

The contractor submitted the data and all other documentation database files to ARB at **themis.arb.ca.gov** via FTP in the TEMP directory by using the ANONYMOUS login. The data were in the normalized format (that is, one record for each site, date, time, and type of measurement; however, upper air data were in the defined contractor format), in the defined structures, and in a comma-delimited ASCII text file format. The contractor used the file naming convention described above.

5.4 Data Validation Process

Mueller (1980), Mueller et al. (1983), and Watson et al. (1983, 1989, 1995) defined a three-level data validation process for environmental measurements. In this process, data records that pass these levels are designated by entries in the VAL column of each data file. These levels, and the validation codes that designate them, are defined below.

5.4.1 Level 0

This level presents collection of raw data and is the first of four data validation levels. These data are obtained directly from the data loggers that acquire data in the field. Averaging times represent the minimum intervals recorded by the data logger, which do not necessarily correspond to the averaging periods specified for the database files. Level 0 data have not been edited for instrument downtime, nor have procedural adjustments for baseline and span changes been applied. Level 0 data are not contained in the IMS95 database, although they are consulted regularly to ascertain instrument functionality and identify potential episodes before receipt of Level 1A data.

5.4.2 Level 1A

These data have passed several validation tests applied by the network operator that are specific to the network. These tests are applied before acquisition of data by the data manager. The data quality indicator in the SITE.DBF file is a qualitative judgment of how stringent these Level 1A tests are when data from different networks are compared. The general features of Level 1A are (1) removal of data values and the replacement with the characters -99.0 when monitoring instruments did not function within procedural tolerances, (2) flagging of measurements when significant deviations from measurement assumptions have occurred, (3) verification of computer file entries against data sheets, (4) replacement of data from a backup data acquisition system in case the primary system fails, (5) adjustment of measurement values for quantifiable baseline and span or interference biases, and (6) identification, investigation, and flagging of data that are beyond reasonable bounds or are unrepresentative of the variable being measured (e.g., high light scattering associated with adverse weather).

5.4.3 Level 1B

After data are received by the data manager, converted, and incorporated into the database, validation at Level 1B is performed. This is accomplished by software filters that flag (1) data that are below a specified lower bound, (2) data that are above a specified upper bound, (3) data that change by more than a specified amount from one hour to the next, and (4) data values that do not change over a specified period—i.e., flat data. Data identified by these filters are individually examined and verified with the data supplier. Obvious outliers (such as high solar radiation at midnight or 300° C temperatures) are invalidated. Other data may be invalidated or flagged according to the results of the investigation. The bounds used in these tests are determined by agreement between the project manager and the measurement investigators. If a datum fails one or more of the above tests, then it is flagged, and corrective action is taken. Such action may require resubmission of the data. The tests are performed in the order cited above.

5.4.4 Level 2A

Level 2A data validation takes place after data from various measurement methods have been assembled in the master database. Level 2 validation is the first step in data analysis. Level 2A tests involve the testing of measurement assumptions (such as assuming that internal nephelometer temperatures do not significantly exceed ambient temperatures), comparisons of collocated measurements (such as filter and continuous sulfate and absorption), and internal consistency tests (such as determining that the sum of measured aerosol species does not exceed measured mass concentrations).

Section 6

MODELING AND EMISSIONS ASSESSMENT

Various modeling and data analysis activities were planned for interpreting the IMS95 data and several had specific requirements for emissions-related data. In addition, the adequacy of the emissions estimates must be determined, or the emissions estimates must be validated. Adequacy can be determined from the bottom up, by starting with emission factors and activities on a source-by-source, species-by-species basis, or the emissions can be reconciled with the ambient data—i.e., the reasonableness of the emissions estimates is assessed with respect to the ambient concentration data. This section provides an overview of emissions modeling and validation. Data analysis needs are similar to modeling needs with respect to emissions – that is, gridded, hourly, and speciated emissions data are needed and are used to better understand the spatial and temporal nature of the emissions relative to receptors, rather than using the emissions estimates as input files. This section also outlines the baseline emissions inventory and emissions surveys. Receptor-oriented models cannot be used directly for estimating the impact of emissions reductions associated with future emissions control strategy designs. They are most useful for directly emitted particles. On the other hand, emissions-oriented models can be used to estimate the effect emissions control strategies in the future. They are most useful for secondary species (i.e., those formed in the atmosphere), as they typically lack the spastical resolution needed for modeling primary particles.

6.1 Modeling

Two types of air quality models can be evaluated and/or applied by using the IMS95 aerometric data set: source-oriented models and receptor-oriented models. Source-oriented models describe the physical and chemical dynamics of the atmosphere and attempt to estimate ambient concentrations of pollutants at a receptor on the basis of source emissions, atmospheric processes, and meteorology. On the other hand, receptor-oriented models estimate source contributions at a receptor, on the basis of ambient concentrations measured at the receptor and known chemical profiles of emissions sources; however, emissions rates are not needed.

6.1.1 Source-Oriented Models

Source-oriented models are sophisticated eulerian models that use three-dimensional representations of meteorology, atmospheric chemistry and physics, and emissions to estimate ambient air quality concentrations. Currently, such models simulate both gaseous and secondary aerosol formation and

chemistry, and they include highly parameterized treatments for fog dynamics and fog water chemistry (Lurmann et al. 1996). A gridded, temporally, spatially, chemically speciated, and particle-size-resolved database of emissions estimates is required to support such modeling. The pollutants to be addressed for emissions are VOCs, NO_x, CO, SO_x, NH_3, and PM.

The VOC and PM emissions data must be chemically resolved into the classes of compounds included in the models (Table 6-1). The PM emissions must be further resolved by particle size (Table 6-2). A temporal resolution of 1 hour is required, and day-specific emissions estimates are highly desirable. A gridded inventory with 4-km resolution is needed for the modeling domain, which for IMS95 covers the full width of the SJV and extends from about 110 km north of Fresno to about 60 km south of Bakersfield. For PM_{10}, gridded inventories with much higher resolution may be required, if modeling of particles greater than 2.5 μm is needed or desired because of the short transport distances for coarse particles. Project parameter codes and data point quality codes are shown in Tables 5-3 and 5-4, respectively.

6.1.2 Receptor-Oriented Models

Receptor-oriented models, such as the CMB model, use the chemical and physical characteristics of particles measured at a source and receptor to identify and quantify the source contributions at the receptor. The CMB model requires that (1) the proportions of the chemicals that compose the particles from one source differ from the proportions within particles from other sources, (2) these proportions remain relatively constant for each source type, and (3) changes in these proportions between source and receptor are negligible or can be accounted for.

Emissions data required for CMB modeling include chemically speciated source profiles – that is, the fractional amount of each chemical species present in each source type. Size-resolved source profiles are desired to allow separate application of the CMB model to the fine (0 to 2.5 μm), coarse (2.5 to 10 μm), and PM_{10} size fractions.

6.2 Validating Emissions Estimates

During the last 10 years, the validation of emissions estimates has become critical for successfully modeling source-receptor relationships, especially with emissions-based eulerian models and with primary PM (where little effort has been applied, as compared to the effort for O_3 emissions inventories). Currently, emissions estimates or emissions inventories, which are a critical part of emissions-based modeling, account for the greatest uncertainty associated with model inputs or measurements. Thus, top-down validation of emissions estimates is an important step in reducing the overall uncertainty in model

outputs. Various top-down methods exist for assessing the adequacy of emissions estimates through comparison with ambient data. Methods that can be pursued with the IMS95 data are summarized below.

Table 6-1

Chemical Speciation Classes for SAPRC-90 to Be Used with IMS95 Modeling

No.	Model Species Nomenclature	Chemical Name or Category
1	NO	Nitrogen Oxide
2	NO_2	Nitrogen Dioxide
3	HONO	Nitrous Acid (HNO_2)
4	CO	Carbon Monoxide
5	PAN	Peroxyacetyl Nitrate
6	PPN	Peroxypropionaly Nitrate
7	RNO_3	Organic Nitrates
8	ETHE	Ethane
9	HCHO	Formaldehyde
10	CCHO	Acetaldehyde
11	RCHO	Propionaldehyde
12	CRES	Cresols
13	MGLY	Methyl Glyoxyl
14	MEK	Methyl Ethyl Keytone
15-16	ALK1 - ALK2	Less and More Reactive Alkanes
17	ARO1	Less Reactive Aromatics
18	ARO2	More Reactive Aromatics
19-22	OLE1 - OLE4	Teminal Alkenes, Internal Alkenes, Isoprene, C10 Monoterpines
23	AFG2	Aromatic Ring Opening Products
24	SO_2	Sulfur Dioxide
25	NH3	Ammonia
26	NA+1	Aerosol Sodium
27	CL-1	Aerosol Chloride
28	SO_4=1	Aerosol Sulfate
29	EC.1	Aerosol Elemental Carbon
30	OC.1	Aerosol Organic Material
31	OTR.1	Aerosol Other

Table 6-2

PM Size-fractionation Profile for Mass, Sulfate, Elemental Carbon, Organic Carbon, and Other Species

PM_{10} Size Cuts (:m)	
1	0.03906
2	0.07812
3	0.1562
4	0.3125
5	0.625
6	1.25
7	2.5
8	5

6.2.1 Ambient versus Emissions Pollutant Ratios

Pollutant ratios derived from ambient data can be compared with ratios of the same pollutants derived from emissions data. This method assumes that the pollutants are relatively inert and well mixed, and that the ambient concentrations are representative of emissions within a set number of grid cells surrounding the site or along a back trajectory from the site. This method has traditionally been used to examine NMOC/NO_x and CO/NO_x ratios (e.g., as in SCAQS and SARMAP), but it could be applied to PM and its precursors. Previous applications have been useful in highlighting underestimation in the NMOC and CO inventories (Ingalls 1989, Gertler 1993).

Emissions requirements are equivalent to those required for the source-oriented grid model described in Section 6.1.1. Day-specific emissions are desirable, although a seasonally stratified inventory could be used. County-level emissions can be used if a few sources are dominant and spatially homogeneous, but this is unlikely to occur in the SJV, particularly for PM.

6.2.2 CMB Source Contributions versus Emissions Estimates

Source contributions developed from CMB modeling can be compared with emissions estimates for the region surrounding the site. As with the pollutant ratio method, the pollutants modeled must be relatively inert and well mixed. This method has been applied to both VOC species and particulate

species and has proven useful in diagnosing underestimates in the NMOC inventory, as well as diagnosing the presence of previously unknown sources.

The emissions requirements are equivalent to those for the pollutant ratio comparison method. Source profiles are also required.

6.2.3 Factor Analysis

Factor analysis includes methods such as principal components analysis (PCA) and empirical orthogonal functions (EOFs). These methods examine the degree to which groups of variables covary in space or time. PCA, for example, can determine groupings of species that explain the greatest amount of variance in a data set. These groupings can then be attributed to specific source categories, given the chemical characteristics of the source emissions. Whereas previous applications of these methods have merely tended to confirm the presence of known sources (such as fugitive dust), the method does have potential for evaluating chemical profiles as well as highlighting the existence of potentially unknown sources.

No direct emissions data are required for this method; however, source profiles are necessary to interpret the results.

6.2.4 Ambient versus Emissions Speciation Profiles

Emissions-based speciation profiles can be compared with speciated ambient data to assess the adequacy of existing speciation emissions profiles. Relative abundances of species may also highlight unknown sources. This method assumes that the pollutants are relatively inert and well mixed, and that the ambient concentrations are representative of emissions within a set number of grid cells surrounding the site or along a back trajectory from the site. This method can be applied to both NMOC and PM profiles. It may be particularly useful in assessing the adequacy of current speciation profiles for both NMOC and PM, given recent changes in fuel usage and formulation.

The emissions requirements are equivalent to those for the pollutant ratio comparison method. Source profiles are also required.

6.2.5 Pollutant Fluxes/Mass Balance

This method uses measurements of a pollutant at the upwind and downwind boundaries of a region to determine the net amount of emissions in the region. This method requires a known and consistent flow regime and assumes that the pollutants are relatively inert over the distance between the upwind and downwind flux planes. It is assumed that deposition is small or that estimates of the deposition of the

pollutants of interest are known. This method may not be appropriate for primary PM emissions if the scale of the emissions may be less than the scale of the flux plane measurements.

Temporally resolved total emissions for the region are needed for this method.

6.3 Emissions Inventory and Source-Oriented Modeling

The emissions estimates and data collection tasks supporting IMS95 consisted of two main components: developing a baseline gridded inventory and surveying day-specific emissions activity data. The latter described in Section 3.3.5.1.2.3, consisted of a one-time micro land use survey around each air quality monitoring site and a survey of day-specific activity data around the core and saturation sampling sites. To a lesser extent, activity at boundary and flux plane sites was surveyed.

6.3.1 Baseline Inventory

The initial IMS95 baseline emissions inventory developed for application of eulerian models, consisted of a spatially and temporally resolved anthropogenic emissions inventory developed by the ARB (Hughes 1997) and included emissions estimates of CO, NH_3, NO_x, TOG, SO_x, and PM. The emissions data have a spatial resolution of 4 km over the study domain and a temporal resolution of 1 hour. Spatially and temporally resolved emissions estimates of NO_x, TOG, SO_x, and PM were speciated into SAPRC-90 "lumped" model species, and PM emissions were size-resolved by EMS95 via standard ARB speciation and fractionation profiles (Tables 6-1 and 6-2).

Emissions inputs for CO, NO_x, TOG, SO_x, and PM consisted of BURDEN-generated, average-day motor vehicle emissions (Version 7G 1.0A, county-specific emissions using day-specific temperatures) and annual average point and area source emissions from the 1994 California Emissions Inventory, extracted from the ARB California Emissions Inventory Data Reporting System (CEIDARS). The NH_3 emissions data were from TSS 15, which was a CRPAQS planning study on how to evaluate and improve methods for determining ammonia emissions in the SJV (Chinkin 1996). The spatial and temporal disaggregation of annual average point and average-day motor vehicle emissions inputs for CO, NO_x, TOG, SO_x, and PM were based on scalars generated from the SARMAP 1990 point and motor vehicle emissions inventory. That inventory was developed by using GEMAP (the predecessor to EMS95). Spatial surrogates and temporal profiles generated by EMS95 from raw inputs were used to disaggregate the annual average area source emissions for CO, NO_x, TOG, SO_x, and PM.

This baseline emissions inventory served as the main source of gridded emissions estimates for the IMS95 modeling domain. The initial gridded emissions inventory for this domain was completed by August 1997. The ARB Technical Support Division will continue making improvements through the CRPAQS.

6.3.2 Source-Oriented Modeling via UAM-AERO

The objectives of this modeling study were as follows:

- Gain a better understanding of the origin of high 24-hour PM concentrations during winter episodic conditions
- Use the IMS95 database to evaluate the performance of air quality models with aerosol routines
- Identify the quality and quantity of emissions data and ambient measurements of meteorology and air quality required to improve model performance
- Assist in designing the Fall and Winter studies

UAM-AERO (the aerosol version of Urban Airshed Model IV) (Lurmann et al. 1996) was selected as the primary tool for grid-based 3-dimensional modeling of IMS95. This decision was based on the availability of the model and the ease of preparing input files for it. Another model that became available after that decision was made, SAQM-AERO, requires prognostic meteorological data simulated via The Mesoscale Meteorological Model V.5 (MM5). Because of the effort required to generate such data, SAQM-AERO will be applied to IMS95 only after all preliminary work is completed via UAM-AERO.

The first episode selected for modeling was January 4–6, 1996. Of all three winter episodes in the IMS95 database, this is the best-characterized episode. The modeling run began at midnight on January 3, 1996 to allow for a spinup day, and it ended at midnight on January 6, 1996. The modeling domain is approximately 215 km east to west and 290 km north to south, extending from the Coastal Range to the crest of the Sierra Nevada and from the Tehachapi Mountains to Merced. The model has four vertical layers below the diffusion break and three layers above it.

The wind fields were generated via a diagnostic wind model. First, the 2-dimensional surface wind fields were developed on the basis of data from 35 surface meteorology stations. These wind fields were then extended into the third dimension by using the data from 6 upper air sites (profilers at MTL, COR, MKR, and ELN, and balloons at BFK and FEI). The 3-dimensional temperature and water vapor fields were also constructed in a similar manner. The hourly inversion layer heights were inferred from the T_v profiles at these sites.

As outlined in Section 6.3.1, EMS95 (GEMAP) was used to generate a gridded inventory for UAM-AERO (Hughes 1997). This inventory contains all the emitted model species listed in Table 6-1. The PM emissions are further resolved into the size cuts listed in Table 6-2.

The initial and boundary PM conditions used for modeling were derived from the 24-hour observations at boundary sites. The top of the modeling domain, which is at a constant height of 2 km, was assumed to be clean. For preliminary studies, the initial and boundary conditions for gases were assumed to be comparable to summer conditions. The O_3 concentrations in both initial and boundary conditions were kept at the clean air value of 40 ppb. These concentrations may be too low because of the stagnant winter conditions, but the model results' sensitivity to these conditions will be investigated in the near future. The final set of initial and boundary conditions for modeling will be based on the outcome of further data analysis.

Finally, the simulated air quality and aerosol concentrations for this winter episode will be compared with the measurements made during this period. The emphasis here will be on the formation of secondary aerosols. The sensitivity of modeled results to input data such as initial/boundary conditions, emissions, and meteorology will also be studied.

Section 7

INTEGRATED DATA ANALYSIS

This section outlines IMS95 data analysis activities that help to answer specific questions that are of interest to scientists and decision makers. These questions are a subset of questions from Watson et al. (1996) that more generally address the causes of high PM throughout the year in the SJV. Appendix A presents the major questions that Watson et al. (1996) posed in the overall CRPAQS data analysis plan and the reasons why they are important. Appendix A thus helps to show how the IMS95 data analysis effort fits into the overall CRPAQS plan.

7.1 Overview

Because air quality questions have few definitive answers, data analysis examines the preponderance of evidence, testing how quantitatively and confidently each question can be answered. Where data or analytical tools may be lacking, new data collection and analysis activities are specified for subsequent phases. The IMS95 data analysis was divided into three phases that correspond to major data collection efforts, as described below.

Phase 1 examined existing data that had been compiled from long-term and special study measurements in Central California during 1988–95 and were posted on the Internet via the ARB network server at **engine.arb.ca.gov.** This database includes information from nearly 30 data sets, which are listed in detail in the introductory section of the overall CRPAQS data analysis plan.

Phase 2 analyzed IMS95 data (Solomon et al. 1996a). The results of that analysis are being disseminated in a series of presentations, journal articles, and reports. The initial presentations were given at the AWMA Measurements of Toxic and Related Pollutants Conference in May 1996, and the next presentations were given at the AAAR Annual Meeting in October 1996. The TSS databases, TSS data analysis, and IMS95 final reports were completed by December 1996. The extended data analysis activities described in the present report were completed by December 1998. A special issue is being published in Atmospheric Environment, 1999.

Phase 3 will analyze data from future studies that are designed to fill knowledge gaps revealed by Phases 1 and 2. Such gaps were indicated by the inability to answer specific questions via the existing data sets.

The IMS95 data analysis plan specifies only activities that can be performed, at least partially, by using IMS95 data. This plan does not incorporate or rely on historical analysis; that information is available in separate reports.

7.2 Objectives And Activities

The Topics of Sections 7.2.1 through 7.2.8 correspond to 8 of the 10 CRPAQS questions that appear in Appendix A (CRPAQS questions 8 and 9 cannot be addressed by IMS95). The IMS95 data analysis activities were intended to provide information about these topics and their subtopics. The subtopics are presented below in the form of objectives; each objective is followed by the activities that were needed to accomplish it.

Because the IMS95 data analysis plan was ambitious, the study data were unlikely to fully satisfy most of these objectives or fully answer any of the CRPAQS questions. Instead, the plan's intent was to: (1) take well-defined incremental steps toward those two ends, (2) indicate remaining knowledge gaps, and (3) recommend ways to fill such gaps.

7.2.1 Measurement Methods Validation

7.2.1.1 Collocated Aerosol Sampling

The objectives were to determine the comparability and equivalence among collocated aerosol sampling methods, the biases of one instrument with respect to others, and how these biases can be minimized.

The activities needed to accomplish these objectives were as follows. Review IMS95 QA/QC methods, procedures, and results to ensure that they provide valid measurements and acceptable estimates of precision and accuracy for each monitor employed during IMS95 and supplemental measurement from the existing routine networks. For PM measurement methods, create a table of collocated particle mass measurements at each site for which they are available, indicating time periods of measurement overlap and the availability of chemical composition. Include the following sampling instruments: (1) Graseby-Andersen SSI; (2) Graseby-Andersen dichotomous sampler; (3) R&P TEOM; (4) Graseby-Andersen BAM; (5) SFS (CADMP, ERT, Oregon); (6) MRI 1590 heated nephelometer; (7) Graseby-Andersen paper tape sampler (COH); (8) OPTEC unheated nephelometer; (9) MRI 1590 heated nephelometer; and (10) Aerometrics portable saturation sampler. Create scatterplots of PM_{10} and $PM_{2.5}$ mass concentrations and calculate linear regression slopes, intercepts, and correlations; average ratios; ratios of averages; propagated precisions; collocated precisions; and distributions of differences for instruments

that measure these parameters (e.g., Mathai et al. 1990). Note where reasonable comparability exists and where it does not. Identify outliers, especially those at high concentrations. Estimate biases between different types of samplers, and explain those biases in terms of known differences in sampling and analysis methods. Identify methods for minimizing these biases in future measurements. Where chemical compositions are available, calculate the weighted sum of species and compare these with mass concentrations. Average the hourly surrogate measure (COH, B_{SCAT}) over time periods corresponding to collocated $PM_{2.5}$ measurements and calculate the same statistics versus $PM_{2.5}$ measurements. Compare other measurements of the same component (e.g., continuous versus filter ammonia SO_2, sulfate, and EC), following the same procedures. Determine at which sites and under what environmental conditions reliable relationships can be assumed between continuous and integrated measurements—specifically, the surrogates of $PM_{2.5}$ as well as continuous measurements of mass and chemical species versus integrated filter-based measurements.

State and justify conclusions and assumptions about (1) the accuracy, precision, and equivalence of different PM measurement methods, and likely causes of differences; (2) the utility of hourly surrogates for representing diurnal PM_{10} and $PM_{2.5}$ variations; and (3) the validity of continuous or short-term integrated species-specific methods employed during IMS95.

7.2.1.2 Surface and Aloft Meteorological Measurements

The objective was to determine how adequate and valid the current methods are for measuring meteorological variables at the surface and aloft.

The needed activities were as follows. Review studies in which surface and upper air measurement systems were evaluated or attempts were made to perform thorough external QA (e.g., SARMAP, NOAA [Boulder tower], NARSTO Northeast and IMS95). Where additional analysis of IMS95 data can provide improved estimates of accuracy, precision, validity, and equivalency, perform those analyses. For example, evaluate the use of sonic anemometers, RASSs associated with the profilers, and any improvements that may have occurred with the radar profilers themselves since the evaluation of the 1990 SJVAQS data by Thuillier (1994). Consideration should also be given to how well these measurement systems perform under stable and stable-and-foggy conditions.

State and justify conclusions and assumptions about accuracy, precision, validity, and equivalence among methods.

7.2.1.3 Ammonium Nitrate Loss

The objective was to determine how much ammonium nitrate is lost in the sampling and analysis.

The needed activities were as follows. Determine anion/cation balances and compare ammonium and nitrate concentrations on front and backup filters. Calculate expected ammonium ion concentrations on the basis of assumptions of different mixtures of sodium chloride, sodium nitrate, sulfuric acid, ammonium bisulfate, ammonium sulfate, and ammonium nitrate (Chow et al. 1994c) and plot these against actual ammonium measurements of 3-hour data collected at the IMS95 core sites and 24-hour average data collected at saturation and boundary sites. Identify and investigate data pairs that are outside of expected ranges. On the basis of ratios for neutralized sulfate and nitrate compounds, determine which samples appear to be neutralized and which appear to contain acidic components. From measurements using denuder difference sampling and absorbing filter packs, for each site prepare time-series plots of (1) denuder nitrate (gas phase nitrate), (2) front filter nitrate (nonvolatilized particulate nitrate), (3) backup nylon filter nitrate (volatilized particle nitrate), (4) the ratio of backup nitrate to the sum of front and backup nitrate (the proportion of volatilized particulate), and (5) temperature for humidifies below 62% and above 62%. Perform the same analysis for the ammonium/ammonia pair, although limited IMS95 data are available. Verify that these values are physically reasonable by comparing them with literature values for ammonium nitrate equilibrium as a function of temperature and RH. Estimate the amount of particulate nitrate and ammonium that is expected to evaporate during sampling as a function of the temperature and of the sampling site. Where collocated with routine (existing) monitors, compare nitrate and ammonium collected via compliance monitors with nitrate and ammonium concentrations measured by instruments specifically designed to measure these compounds accurately. Quantify nitrate and ammonium loses from routine samples and determine the effects on PM_{10} concentrations as a function of observed environmental variables (temperature and RH). Put results from IMS95 data into perspective with those found in laboratory tests (e.g., Fitz et al. 1996) and other field monitoring programs (e.g., the Nitrogen Species Intercomparison Study by Hering et al. 1988).

State and justify conclusions and assumptions about (1) the accuracy and validity of ammonium and nitrate sampling methods, and (2) the extent to which acidic species have been neutralized in the atmosphere.

7.2.1.4 OC Volatilization and Adsorption

The objectives were to determine how much OC is lost from samples because of volatilization and how much OC is really due to adsorption of vapors on filters.

The needed activities were as follows. Create scatterplots of front filter OC versus backup filter carbon. Compare sums of chemical species with mass with and without backup carbon subtraction. From detailed organic compound analysis of backup filters, summarize the fractions of what constituents are adsorbed by the quartz fiber filter media. From detailed organic compound analysis of front filters and organic equilibrium models, determine how much semivolatile OC is likely to volatilize during sampling and storage. Identify methods, such as using denuders and alternative sampling media, that might minimize adsorption and volatilization of OC. Where these denuders and media are collocated with compliance monitors where OC is measured, compare the OC collected via compliance monitors with OC concentrations measured by instruments specifically designed to measure OC accurately. Estimate OC losses from compliance samples and determine the effects on PM_{10} concentrations as a function of observed environmental variables (temperature and RH). Place the results from Central California measurements in perspective with those found in other areas (e.g., McDow and Huntzicker 1990, Turpin et al. 1994). Determine whether the results are consistent with those observed during the Carbon Species Intercomparison Study (Lawson et al. 1990).

State and justify conclusions and assumptions about bias in particulate carbon results that are due to adsorption of gaseous organic species and due to volatilization of organic particles during sampling.

7.2.1.5 Analysis of Gas and Aerosol Species

The objective was to determine whether the analytical methods used to chemically analyze IMS95 samples (inorganic and organic species in the gas and aerosol phases) are sufficiently selective and sensitive, or whether more recently developed analytical methods can provide improved measurement capabilities and/or additional species information that might be important to understanding PM in the SJV.

The needed activities were as follows. Review the literature and the IMS95 measurement methods and databases, then provide a detailed listing by method and species of the analytical capabilities of the inorganic and organic chemical analysis methods for aerosol, gas phase, and aqueous samples collected during IMS95. Review the analytical capabilities in terms of selectivity, sensitivity, precision, and

accuracy and evaluate emerging methodologies that may offer improved capabilities. For emerging methods, determine whether the interferences really are known, the methods are sensitive enough, the precision and accuracy have been adequately defined, the proper QA/QC procedures are being used, and whether some investigators have modified the methods and achieved improvements over standard methods. Review current literature and contact experts in the field, then provide a summary of emerging methods and their capabilities and indicate how the new methodologies will add to the existing base of knowledge. On the basis of the review, recommend the most cost-effective methods that provide data of the highest quality and whose uncertainty is known. Suggest new methods that, if applied to samples collected via existing methods, may improve the understanding of atmospheric process related to PM buildup in the SJV.

State and justify conclusions and assumptions about accuracy, precision, limits of detection, interferences, and equivalence of different analytical methods and procedures, and likely causes of differences. Provide recommendations about the suitability of methods used during IMS95. Provide recommendations about any new methodologies that may yield improved species-specific information.

7.2.1.6 PM and Meteorological Data

The objective was to determine whether collection and analysis methods or monitoring systems exist for obtaining improved measurements of PM, PM components, PM precursors, and meteorological variables over what was used during IMS95.

The needed activities were as follows. Identify and evaluate the suitability of collection and analysis methods for obtaining PM components of PM precursors, especially continuous species-specific methods, or meteorological variables that were measured during IMS95, as well as methods that were not used. Review recent literature and interview experts in the field to identify important or unique species and methods. For example, organic aerosol species have been measured recently in a number of source samples, resulting in organic aerosol source profiles for the sources tested (Rogge 1996). The profiles were used in receptor modeling to identify the impact of sources on ambient organic aerosols. Polycyclic aromatic hydrocarbons (PAHs) have also been recently identified as being able to differentiate between diesel- and gasoline-burning automobiles (Fujita et al. 1996, personal communication). The feasibility of applying these methods to ambient samples in urban and nonurban areas must be evaluated. The evaluation should also include estimates of the accuracy and precision of these methods and a thorough review of QA/QC procedures. Determine whether the inclusion of other

methods, such as measurement of PAH species, would improve the understanding of source-receptor relationships.

This activity should not be limited to organic species, but should include inorganic trace species (e.g., species-specific continuous monitors and single-particle analysis) or other properties of particles that might provide insight into the causes of high PM through the development of source-receptor relationships. QA/QC procedures should also be evaluated to provide reasonable estimates of uncertainty bounds and confidence in the estimates.

Meteorological variables for improved measurements of wind speed and direction (especially under stable conditions) and integrated and continuous measurements of temperature, RH, and solar radiation as a function of wavelength should also be evaluated. Special emphasis should be paid to meteorological methods that allow continuous measurements (with less than 5-minute integration times) of these variables at the surface and aloft. QA/QC procedures should also be evaluated to provide reasonable estimates of uncertainty bounds and provide confidence in the estimates. If it is warranted on the basis of the review, expert interviews, and critical evaluation, then recommend other approaches that should be considered in future field programs for measuring air quality or meteorological variables at the surface and aloft. Clearly state how the measurement should improve the understanding of the causes of high PM concentrations in the SJV, list analytical capabilities of the methods, and state all assumptions associated with the conclusions.

State and justify conclusions and assumptions about the use of additional or alternate methods and indicate how these measurements will improve the understanding of the PM problem in the SJV if used in future field studies.

7.2.2 Optimizing Network Design

7.2.2.1 Representativeness of Sites

The objectives were to (1) determine the spatial representativeness of a receptor site under various meteorological conditions and during peak and nonpeak periods, and (2) given such conditions and periods, determine how well IMS95 sites represent their designated site type, and how well the existing PM monitoring sites within the IMS95 saturation site networks represent human exposure, maximum PM concentrations, and maximum source impacts.

The needed activities were as follows. For IMS95 sites, obtain tables of site codes, coordinates, site classifications, and descriptions of surroundings. Such descriptions include site drawings, photographs, videotapes, and electronic maps of the areas around the sampling site that have been prepared at several scales showing residences, restaurants, major roads, and industrial or agricultural operations. Obtain similar information, as available, for routine monitors operated by the ARB and District and within the IMS95 study domain. After reviewing the site descriptions, verify siting criteria and site classifications (e.g., neighborhood, urban, upwind and downwind urban, suburban, boundary, regional, and flows into and out of the valley) and site types (residential, industrial, agricultural, and motor vehicle) that were designated a priori in planning IMS95 (Solomon et al. 1996). Use statistical analysis—such as spatial correlation analysis, cluster analysis, empirical orthogonal functions, and analysis of variance—and emissions activities as a function of distance from the receptor to obtain a better understanding of the relationships between and among sites and their surroundings. Examine the spatial representativeness of IMS95 and existing routine monitoring sites. Evaluate the appropriateness of site classifications as a function of spatial representativeness and as a function of peak and nonpeak periods for both the fall and winter seasons and different meteorological conditions. Determine whether the site classifications, spatial representativeness, and spatial scales of influence change during the sampling period (fall versus winter studies), between the different sampling periods, under different meteorological conditions, or with variations in source strength. Plot the existing and IMS95 networks and overlay them with the spatial scale that each site represents. Compare the result with population distributions and locations of major source types or land use types. Evaluate the adequacy of site coverage and make recommendations on (1) the adequacy of IMS95 sites, (2) how sites may have been better located during IMS95, (3) changes in site classification for IMS95 sites, and (4) where changes in routine ARB and District site locations and/or site classifications may be beneficial.

State and justify conclusions and assumptions about the adequacy of the IMS95 and existing monitoring sites for representing designated site types, human exposure, maximum PM concentrations, source influences, and spatial gradients for primary and secondary species.

7.2.2.2 Representativeness of Meteorological Measurements

The objective was to determine how well the IMS95 meteorological measurements represent (1) representativeness with respect to its surroundings (i.e., whether measurement is influenced by local effects; (2) transport and dispersion under low wind speed/stagnation conditions; (3) frequency, spatial extent, and intensity of fogs; (4) temperatures at 850 mbar; (5) downvalley and crossvalley flows; and (6)

mixed layer depths, vertical distributions of winds, temperature, and RH. Also of interest was what changes might be needed in routine and research-oriented meteorological monitoring.

The needed activities were as follows. For IMS95 sites, obtain tables of site codes, coordinates, site classifications, and descriptions of surroundings. Such descriptions include site drawings, photographs, videotapes, and electronic maps of the areas around the sampling site that have been prepared at several scales showing residences, restaurants, major roads, and industrial or agricultural operations. Obtain similar information, as available, for routine monitors operated by ARB and the District and within the IMS95 study domain. Examine sampling site surroundings, documenting (1) possible obstructions to both surface and upper air wind speed and wind direction measurements, and (2) items that might influence temperature, RH, or solar radiation measurements (e.g., a site on a roof near heat or moisture vents). Plot time-height cross sections of wind vectors, temperatures, and RH from rawinsonde and continuous upper air measurements from radar profilers (with or without RASSs) and DAS measurements (as appropriate), spatial and time-series vector plots of surface winds, and spatial and time-series plots of surface temperatures, RH, and solar radiation for periods of elevated PM concentrations. Examine these plots to evaluate the 3-dimensional spatial coverage of surface and upper air wind, temperature, RH, and solar radiation measurements. Determine when and where (horizontally and vertically) actual wind speeds are lower than those achievable by standard instruments with wind speed thresholds above 0.5 to 1 m/s. Evaluate the occurrence of wind speeds above 0.05 m/s for locations and times where sonic anemometers are operated. Examine site descriptions and describe the meteorological phenomena that are represented by the upper air and surface meteorological measurements in terms of measurement location, elevation, and surrounding terrain. Examine similarities and differences within and above the local boundary layer. Examine the wind, temperature, and RH at the highest altitudes, generally above the tops of the terrain where synoptic forcing should dominate, and compare the results obtained by the different measurement systems and locations. For peak days, examine synoptic flow patterns by using upper air meteorological maps and hourly satellite images (as available) to identify periods of consistency and inconsistency with surface and upper air measurements. Evaluate each upper air station with respect to its representation of regional flow patterns. Determine the vertical elevations of measurements that distinguish regional from local transport. Identify which measurement locations are suitable for representing transport phenomena on different scales for each conceptual model. Evaluate the utility of each existing network for elucidating each conceptual model and recommend measurement locations, sampling frequencies, sampling periods, observables, and monitoring equipment to supplement current networks.

State and justify conclusions and assumptions about the suitability or adequacy of surface and upper air meteorological data collected during the winter and fall studies at routine and IMS95 sites to describe important meteorological phenomena when high PM concentrations occur. Recommend additional measurements that are needed to characterize these meteorological fields.

7.2.2.3 Characterization of Fog and Stratus Clouds

The objectives were to determine how extensive the three-dimensional coverage of fogs in the valley is and how well the existing measurements characterize the presence of fogs and/or stratus clouds.

The needed activities were as follows. Plot the locations of existing fog measurement systems in operation during IMS95, including NWS observations, satellite photos, RH measurements, the California Department of Transportation (CALTRANS) visibility sensor network, and other surrogates. Review the adequacy of these systems on the basis of the historical data analysis evaluation (Smith and Lehrman 1996). Plot the hours of fog and low-lying stratus cloud observations for each winter day by using existing data from measurement approaches that were deemed adequate in the historical analysis; determine differences and similarities between measurement sites. Evaluate the frequency, spatial extent, and intensity of fogs and low-lying stratus clouds observed during IMS95 by using measurements that are deemed adequate on the basis of the above review. Examine the spatial distributions of RH data and relate these to fog observations. Determine whether measurement methods exist that can provide the elevation and spatial coverage of the bottom of the fog layer when it has lifted from the surface. Evaluate the utility of each existing network for elucidating the winter fog conceptual model and recommend measurement locations, sampling frequencies, sampling periods, observables, and monitoring equipment to supplement routine and future research networks.

State and justify conclusions and assumptions about the ability to determine the 2-dimensional and 3-dimensional spatial extent of fogs and low-lying stratus clouds, including the mixing heights or depth of the fog or stratus layer, as these conditions occurred during IMS95.

7.2.2.4 PM, Aerosol Precursor, and Meteorological Sampling Frequency

The objective was to determine the optimum sampling frequency for PM, aerosol precursors, and meteorological variables.

The needed activities were as follows. Examine the shortest time-averaged data available from continuous PM measurements, PM filter measurements from periods shorter than 24 hours, continuous and filter-based

precursor species measurements, and/or PM surrogates (e.g., B_{scat} and COH) and evaluate the diurnal variations of PM. Examine high-frequency (< 5 minutes) meteorological data and evaluate them against understanding meteorological phenomena, modeling needs, and vector versus scalar wind speed averages. Using time-series analysis, frequency distributions, and an understanding of data needs—both for modeling and data analysis—examine the winter study data for the need to sample more frequently than usual. Consider source attributes and meteorological changes in the decision process, such as development and breakup of the boundary layer, traffic patterns, and so on. Evaluate the short-term (3-hour, 1-hour, or less) average sampling for PM and PM precursors and the higher-than-1-hour average sampling frequency for IMS95 meteorological variables. Create a table indicating optimal sampling frequencies for each of these variables (PM mass, specific PM chemical components, organic and inorganic precursor species, fog-related species and measurements, and surface and aloft meteorological variables, including fog-related variables). In the table, indicate the species of interest and the optimal sampling frequency under IMS95 winter conditions. Suggest one or several available methods for obtaining the measurement, give limits of detection at the stated integration time, and estimate the accuracy and precision of the measurement at the given sampling frequency. If no available method meets the higher sampling frequency needs, then examine possible research methods, or, last, determine whether the measurement is limited by the lack of measurement methods. Under IMS95 environmental conditions, determine whether longer sampling frequencies are needed than are optimally desired (because of measurement limitations), and what the impact is on understanding atmospheric processes and developing control strategies. Make recommendations as to optimal sampling frequencies for each species or group of related species and measurement methods. Indicate whether the measurement can be obtained at reasonable cost or is limited by the lack of a measurement method at the frequency needed. If research methods exist, then indicate their level with respect to routine use in the field or use during special studies.

State and justify conclusions and assumptions about the need for a shorter-than-24-hour sampling frequency for PM (PM_{10}, $PM_{2.5}$, and PM_{coarse}), primary and secondary precursor species and a shorter-than-1-hour average sampling frequency for wind speed and direction, as well as for other meteorological variables.

7.2.3 Descriptive Analysis

7.2.3.1 PM_{10} and $PM_{2.5}$ Components

The objectives were to determine (1) how much of PM_{10} is composed of $PM_{2.5}$, and how this relationship changes by measurement site, fall versus winter sampling periods, peak and nonpeak

periods, and environmental conditions (such as temperature and RH); (2) how accurately $PM_{2.5}$ concentrations can be deduced from PM_{10} measurements; (3) what the major chemical components of PM_{10}, $PM_{2.5}$, and PM coarse are and how these differ by site, season, time of day, and emissions activity; and (4) how important the crustal component in $PM_{2.5}$ is and how much of it is real or a possible artifact caused by sampling inlet efficiencies.

The needed activities were as follows. Using winter study data collected at core and boundary sites, create $PM_{2.5}/PM_{10}$, PM_{coarse}/PM_{10}, and $PM_{2.5}/PM_{coarse}$ scatterplots and stacked time-series plots of mass concentrations, silicon or aluminum, sulfur or sulfate, nitrate, ammonium, OC, and EC where data are available. Assess these ratios for peak and nonpeak periods and calculate comparability measures, including slopes, intercepts, correlation coefficients, average ratios, and ratios of averages for and between the different periods. List specific outliers from these measures, and compare the occurrence of these outliers with exceptional meteorological and emissions events that might be indicated in the daily emissions activity survey. Using the detailed chemistry and the comparability factors, determine the extent, accuracy, and precision with which $PM_{2.5}$ concentrations might be estimated from PM_{10} concentrations at sites where $PM_{2.5}$ is not measured. Quantify the proportion of each major chemical component that is in the $PM_{2.5}$ fraction, as opposed to its abundances in the PM_{10}, and identify conditions under which these proportions will be similar. Of the abundant crustal species aluminum, silicon, iron, manganese, and calcium, apply multiplication factors representing the oxide forms of these species (1.89 for Al_2O_3, 2.14 for SiO_2, 1.43 for Fe_2O_3, 1.66 for MgO, and 1.40 for CaO) and calculate the fraction of $PM_{2.5}$ that might be attributed to crustal material. Estimate incremental amounts of crustal material in $PM_{2.5}$ relative to amounts of crustal material in PM_{10}. For each site at which data are available, estimate the crustal contribution to the highest $PM_{2.5}$ concentrations and the samples in which the crustal contribution is largest. Examine meteorological and emissions conditions when the crustal contribution is high and determine when this is due to emissions activities. Compare the crustal contributions to $PM_{2.5}$ with the levels or proposed $PM_{2.5}$ standards. Review the literature and CRPAQS historical analysis to determine what fraction of the $PM_{2.5}$ crustal component is an artifact caused by sampling inlet efficiencies.

State and justify conclusions and assumptions about (1) the ratios of $PM_{2.5}$, PM_{10}, and PM_{coarse} and how these vary among sites and seasons; (2) the chemical components that are most abundant in the $PM_{2.5}$ fraction and the coarse fraction; (3) potential artifacts of crustal-related species in the $PM_{2.5}$ fraction caused by sampling inlet efficiencies; and (4) implications for attainment or nonattainment of future $PM_{2.5}$ standards.

7.2.3.2 Variations in PM Mass, Components, and Precursors

The objective was to determine the day-to-day and diurnal variations in PM mass and chemical components and in PM precursor species concentrations observed during IMS95.

The needed activities were as follows. For the IMS95 fall and winter sites, plot PM_{10} and $PM_{2.5}$ mass and chemical composition and PM precursor species concentrations as a function of time for sites collecting less-than-24-hour-average data (i.e., IMS95 core sites) and for sites collecting 24-hour data. Note similarities and differences between (1) diurnal patterns for PM_{10} and $PM_{2.5}$ and their chemical components, and (2) peak and nonpeak days for PM_{10} and $PM_{2.5}$ and their chemical components and assess dominant species in each size fraction by time of day (peak values versus lower values). Plot spatial pie charts and describe spatial patterns as a function of time of day and over a 24-hour average period (midnight to midnight). Compare peak periods with periods of lower PM concentrations as a function of the time of day and location by site type or site environment.

State and justify conclusions and assumptions about (1) differences between sites, (2) chemical composition as a function of time of day, (3) chemical composition on peak versus nonpeak days and during the buildup and decline of a peak period, and (4) differences between PM_{10} and $PM_{2.5}$ and precursor species as a function of the time of day and of peak versus nonpeak days.

7.2.3.3 Boundary and Background Variations in PM

The objectives were to determine (1) the PM concentrations at the boundaries, and how they varied temporally and spatially during IMS95; (2) for the IMS95 study domain, the natural background conditions (not influenced by anthropogenic sources), regional background conditions (possibly influenced by anthropogenic sources), and boundary conditions; and (3) the characteristics of a background site and a boundary site with respect to IMS95 modeling and data analysis needs.

The needed activities were as follows. Provide a clear definition of what a boundary site is and what a background site is (natural and regional), for use by IMS95 data analysts and modelers. The definition may change according to the season (fall versus winter) and area (local versus regional considerations). All assumptions associated with the definitions must be clearly defined. Plot PM mass and composition and precursor species concentrations at boundary sites—including the IMS95 core boundary site (SWC), where 3-hour samples were obtained. Evaluate differences between sites and compare them with the concentrations and chemical composition at source-oriented and receptor-oriented sites. Determine what fraction, as a function of location, the background contributes to receptor sites within the valley.

Determine how the concentration at the boundary (the northern boundary for IMS95) varies during the day. Determine how boundary concentrations vary as a function of fall and winter and as a function of peak versus nonpeak days during IMS95. Using the definitions specified above, indicate which sites act as boundary sites and which act as background sites. Where data apply, perform this analysis for both the fall and winter studies.

State and justify conclusions and assumptions about (1) the concentrations and chemical composition of background and boundary sites and how these vary during the monitoring period and, in particular, during peak and nonpeak periods; (2) the ability to detect background contributions versus those from local sources at boundary and receptor sites at different temporal scales; and (3) the appropriate use of background concentrations for various data analysis and modeling activities.

7.2.4 Meteorology

7.2.4.1 Relationship of PM Peaks to Synoptic and Regional Weather

The objectives were to determine (1) the relationships between peak fall and winter PM concentrations and regional and synoptic meteorological variables, and (2) whether peak PM periods can be forecast.

The needed activities were as follows. Fully describe the meteorological situation for both the fall and winter studies, using synoptic weather maps; hourly maps of winds, temperature, RH, and fog; and available PM measurements. Include a description of synoptic weather patterns, local and regional wind speeds and directions, changes in mixed layer depth, changes in RH, and fog characteristics. Examine meteorology during the study period and how key meteorological variables change as peak PM periods build and decline. Create spatial plots of surface and upper air layers of wind speed, wind direction, temperature, and RH and examine in detail the surface and upper air meteorological data during each study period to better understand the flow above and within the mixed layer. Modify the surface and upper air meteorological description of each of the two conceptual models that relate to IMS95, to make them more descriptive of actual situations. Note exceptions to the model and explain why they occur. Determine the probability of forecasting PM peak periods for either conceptual model scenario. Validate current forecast criteria (Hackney and Solomon 1996, Smith 1994) to determine the success of forecasting IMS95 fall and winter peak periods.

State and justify conclusions and assumptions about (1) which variables are most relevant to the highest PM values, (2) meteorological indicators on days before a high PM event, (3) the degree to which

meteorological conditions conducive to the fall and winter PM episodes might be forecast, and (4) how the meteorological variables are likely to affect high PM levels during the fall and winter.

7.2.4.2 Dispersion and Mixing of Pollutants

The objectives were to determine (1) how emissions disperse and dilute under low wind conditions, and (2) the role of diffusion versus organized flow patterns during stagnant, low wind speed situations as potential mechanisms for pollutants to mix.

The needed activities were as follows. Characterize vertical and horizontal mixing and dispersion of pollutants during low wind speed conditions by using data from the fall study. Develop a conceptual model for dispersion and mixing under low wind speeds. On the basis of this model, develop or modify existing models or modules for mixing and dispersion during calm conditions. Validate the models or modules by using tracer data. Set uncertainty bounds on the measurements and modeling results. On the basis of data analysis and modeling, if suitable models exist, use meteorological data from the existing network, if adequate, to estimate the role of diffusion versus organized flow patterns during stagnant, low wind speed situations as potential mechanisms for the mixing of pollutants. Evaluate the representativeness of the TSS5A core site by using data collected from sonic anemometers located throughout the study domain. Apply spatial correlation statistics to evaluate the representativeness of the TSS5A core site and of each of the five sonic anemometer sites deployed throughout the study domain Apply spatial correlation statistics to evaluate the representativeness of the TSS5A core site and of each of the five sonic anemometer sites deployed throughout the study domain. Perform time-series analysis, plot frequency distributions, and determine by location in the valley the fraction of time that wind speeds are below 1 m/s, 0.5 m/s, and 0.1 m/s. On the basis of the analysis, use data from all sonic anemometer sites to indicate how low the wind speeds are as a function of time of day, location in the valley, and PM_{10} and $PM_{2.5}$ concentrations. Indicate the need, if any, for very-low-threshold, but more expensive, wind monitoring equipment.

State and justify conclusions and assumptions about (1) the ability to model pollutant transport under calm conditions, including the influence on the choice of meteorological model (diagnostic, prognostic, or statistical); (2) the spatial distribution of very low winds during and between PM peak periods; (3) what specified threshold values are needed for wind speed and direction (u, v, and w) measurements; and (4) the need to use very-low-threshold wind speed and direction sensors or less expensive standard sensors that are of high quality and are highly maintained.

7.2.5 Emissions

7.2.5.1 Reconciling Emissions And Ambient Data

The objective was to determine how well emissions data can be reconciled with ambient data.

The needed activities were as follows. Compile and summarize emissions and ambient data. Prepare tables of day-specific and period average primary particle, SO_2, NO_X, and reactive organic gas emissions by county or study domain and by major source type for IMS95. Identify similarities and differences between sites for peak and nonpeak periods. Compile gridded emissions with as fine a resolution as possible for areas surrounding ambient routine and IMS95 monitoring sites. Compare ratios of ambient VOC/NO_X, PM/NO_X, CO/NO_X, and related PM components (e.g., aluminum/silicon, iron/silicon, CO/lead, and CO/EC) with ratios derived from emissions data. Assess the comparability of ambient and emissions VOCs and particulate speciation profiles. Apply principal components analysis and/or empirical orthogonal functions to ambient data to elucidate primary contributing sources. Identify discrepancies between ambient and emissions data. Assess the degree to which the reconciliation methods are valid and where differences suggest inaccurately characterized or missing sources.

State and justify conclusions and assumptions about the comparability of the data and the reasons for any discrepancies.

7.2.5.2 Contributions Calculated via CMB Source Apportionment

The objective was to determine which source contributions are most likely, on the basis of CMB source apportionment for the fall and winter studies.

The needed activities were as follows. Use the CMB receptor model, or other receptor methods, and measured source profiles to calculate source contributions and their uncertainties with respect to measured PM concentrations for 3-hour and 24-hour samples collected at routine monitoring sites and at core, saturation, and boundary/flux plane sites operated during IMS95. Examine the temporal and spatial variation of source contribution estimates with respect to known spatial and temporal distributions of emissions and determine consistencies and inconsistencies. Plot these contributions for each sample as stacked bar charts and compare the apportionments among sampling sites and sampling periods and for peak and nonpeak days. Summarize the magnitudes of source contributions at each sampling site in frequency tables. Conduct sensitivity and randomized data tests to evaluate the magnitudes of uncertainties in apportionments. Compare source contributions among nearby sites for consistencies and

inconsistencies. Classify each available sample by its major contributors and determine how many cases of peak PM concentrations are dominated by a single source type versus cases that represent a superposition of sources. On the basis of previous experience, indicate how adequately the existing source profiles can account for sources impacting receptor sites during the fall and winter studies; also indicate the adequacy of the individual source profiles for calculating source-receptor relationships.

State and justify conclusions and assumptions about how much of the measured PM is contributed by (1) crustal material (agricultural, road, construction, and windblown dust), (2) motor vehicles (pre-1991 diesel, post-1991 diesel, well-maintained gasoline, poorly maintained gasoline) and cold-start vehicle exhaust, (3) vegetative burning (fireplace, wood stove, agricultural, prescribed, and wildfires), (4) other industrial sources (engines, steam generators, food processing, and resource recovery), and (5) secondary aerosols (ammonium nitrate, ammonium sulfate, and organic species).

7.2.5.3 Relating Source Activities to Source Influences

The objective was to determine whether specific source activities can be detected at given sites to confirm source influences.

The needed activities were as follows. For IMS95 saturation networks—including core sites—where daily activities were monitored, document day-by-day changes in activities, especially those within sight of the monitoring site and those occurring on days when PM concentrations largely exceeded those measured at neighboring sites. Examine the incremental chemical compositions and source contribution estimates derived from CMB or other receptor analyses for samples that correspond to nearby activities and relate these increments in PM mass levels to those activities. Evaluate whether the day-specific database can be used to infer the impact of specific sources that cannot be deduced from receptor analysis alone (e.g., differentiation of specific sources of fugitive dust on the basis of an activity near a receptor). Document, if possible, specific evidence that indicates where dust comes from when winds are low and the ground is wet (i.e., during winter PM peak periods when secondary species are high and moisture is abundant).

State and justify conclusions and assumptions about when and where certain activities take place and about the evidence for these activities in ambient data sets.

7.2.5.4 Ammonia

The objectives were to determine (1) where the ammonia sources are, how much they emit, and when they emit it; and (2) how well emissions data and ambient data compare.

The needed activities were as follows. From the best available ammonia emissions inventory, plot locations and relative magnitudes of suspected ammonia sources (e.g., dairies, feedlots, chicken coops, and sewage plants). If necessary, augment the inventory to fill gaps. Examine ammonia concentrations and their proximity to large ammonia sources. For the fall and winter studies, where NH_4NO_3 is a significant portion of the collected mass, superimpose on emissions maps the indicators of ammonia concentrations (circles or bars) and wind roses as developed from ambient data. Determine the extent to extent to which ammonia levels are elevated downwind of different ammonia sources. Stratify samples by temperature, RH, and activity levels that are conducive to high and low ammonia emissions and identify the degree to which these changes are confirmed by ambient measurements. Identify other locations in the study domain where ambient sampling has not yet taken place and where similar situations might be found. Determine whether ambient ammonia concentrations in some areas are unexpectedly high, as compared with the ammonia emissions database.

State and justify conclusions and assumptions about how these nearby activities and meteorological variables influence the ammonia concentrations.

7.2.5.5 Composition of Precursors to Secondary Organic Aerosols

The objective was to determine the gaseous and particulate chemical compositions of source emissions that provide precursors for secondary organic formation and permit source subcategories to be distinguished from each other. Of specific interest were (1) wood smoke, prescribed burning, and agricultural burning; (2) well-maintained and poorly maintained engines; (3) diesel and gasoline engines; (4) cooking; (5) biogenic emissions; (6) agricultural processes, such as pesticides; and (7) secondary organic aerosols.

The needed activities were as follows. Review current source profiles (Rogge 1966, Rogge et al. 1991, 19931993a, 1993b, 1993c, 1993d, 1993e, 1993f, 1994) in conjunction with known sources of primary and secondary precursors for organic aerosols. Identify sources that might significantly impact secondary aerosol formation and recommend approaches for obtaining source profiles. Review ambient data sets for which organic aerosols have been collected and compare those sets with VOC (C_2–C_{20}) data that were collected simultaneously, to determine whether specific precursors can be identified and

related to sources. Reconcile sources with ambient data and perform organic aerosol species CMB analysis or more sophisticated analysis to apportion primary and secondary organic aerosols to sources. Evaluate uncertainties in both the ambient and analytical measurement methods for precursor and organic aerosol species determinations.

State and justify conclusions and assumptions about sources of organic aerosol species and the fraction of OC that is secondary. Identify, if possible, precursor species of secondary organic aerosols and attempt to relate these to their sources.

7.2.5.6 Source Component Zone of Influence

The objective was to determine the zone of influence of components of interest from sources (e.g., PM_{10} versus $PM_{2.5}$, or primary particles versus primary precursor gases).

The needed activities were as follows. Compare source contribution estimates from identifiable source categories on the basis of CMB or other receptor analyses by using data collected at fall and winter study saturation monitoring sites and from 3-hour measurements at core sites. Plot the locations of major emissions sources and compare them with calculated source contributions. Examine changes in source contributions with time and compare them with expected diurnal profiles of emissions sources. Plot hourly wind roses for each day of sampling, and, in conjunction with daily emissions activity data, attempt to verify source influences at one or more receptor sites. Identify gradients between monitors in the downwind direction from the source and determine dilutions with downwind transport. Estimate the mass emissions needed to provide incremental concentrations over background and compare this estimate with actual emissions.

State and justify conclusions and assumptions about the zone of influence of each source type with respect to the components that compose ambient PM concentrations.

7.2.6 Atmospheric Chemistry

7.2.6.1 Dynamic Atmospheric Processes and Secondary Aerosol Formation

The objective was to determine the degree of current understanding of dynamic atmospheric processes and the formation of secondary aerosols from primary and secondary aerosol precursors and their relationship to phase properties (liquid, solid, and gas).

The needed activities were as follows. Examine gas, aerosol, and aqueous phase data collected during the winter study and calculate the fraction of nitrogen, sulfur, and carbon and their individual compounds in each phase relative to the total in all phases. Plot these data as a function of the time of day and environmental parameters (e.g., temperature and RH). Statistically describe the data and use comparability statistics (e.g., ratios, multiple regression, frequency distributions, and cluster analysis) to obtain an understanding of the distribution of species among the phases. Use theory to calculate the phase distribution expected under equilibrium conditions and determine the situations in which the atmosphere might be in equilibrium and indicate what chemical and physical mechanisms might be important for obtaining the phase distribution. State assumptions and indicate the importance of these mechanisms for improving mathematical models.

State and justify conclusions and assumptions about (1) the distribution of nitrogenous, sulfur, and organic species among the solid, liquid, and gaseous phases and how these vary by time of day and environmental conditions; and (2) whether the atmosphere is in chemical equilibrium under stable stagnant conditions and the impact of that equilibrium on the understanding of chemical processes.

7.2.6.2 Ammonia and NO_X Limitations on Nitrate

The objectives were to determine (1) whether the nitrate is ammonia-limited or NO_X- limited in urban areas; (2) whether it is less ammonia-limited, or ammonia-saturated in rural areas near ammonia sources; and (3) how much any further SO_2 reductions will free up ammonia to create ammonium nitrate.

The needed activities were as follows. Apply equilibrium models to total ammonia and total nitrate values available over periods of constant temperature and RH. Calculate the partition between ammonia gas, nitric acid gas, and ammonium nitrate particles. Compare these with measurements and evaluate how well the equilibrium models apply to the SJV situation during the winter study. Examine the models' sensitivities to changes in temperature and RH over available sampling intervals. Determine whether shorter measurement intervals are needed or whether longer intervals can be tolerated. Use the chemical equilibrium portion of these models to plot isopleths of constant ammonium nitrate concentrations as functions of total ammonia and nitrate. Identify the location of typical measurements on these plots and determine the amounts of ammonia or nitrate precursors that must be reduced before significant changes in ammonium nitrate concentrations would be observed. Classify each sample as ammonia-limited or nitrate-limited. For each sample, reduce the ammonium sulfate concentration by half, and then to zero, examining the changes in ammonium nitrate with these reductions. Determine the extent to which further sulfate reductions might result in increases in ammonium nitrate concentrations.

Apply the aerosol evolution model to the gas and particle source profiles by using aging times determined by trajectory modeling. Create "aged" source profiles to represent the changes that are due to gas-to-particle conversion and deposition. Plot contours of aged apparent emissions on maps and compare them with ambient data. Determine whether aged source profiles improve comparisons between ambient data and sources of precursor species.

State and justify conclusions and assumptions about where and when ammonium nitrate concentrations are limited by ammonia levels and by nitrate levels.

7.2.6.3 Regional Causes of Secondary Pollutants

The objective was to determine whether the regional nature of secondary pollutants (e.g., ammonium nitrate and ammonium sulfate) is due to (1) well-defined transport between upwind and downwind regions, (2) slow diffusion over multiday stagnation periods, or (3) replication of analogous local processes throughout the domain. Also of interest was how the ammonia generated in rural areas mixes, under low wind and stagnant conditions, with the NO_x and sulfur generated along roadways and in urban areas.

The needed activities were as follows. Compare IMS95 micrometeorological measurements with those acquired from the study's existing networks. Determine whether the IMS95 meteorological network adequately represents flows from rural to urban areas. Determine transport patterns from standard and micrometeorological measurements and calculate transport times from rural to urban areas during peak periods; estimate the distance between urban receptors and the rural locations where ammonia has potentially originated. Examine land use and emissions maps to identify potential ammonia and NO_x sources. Examine saturation measurements for ammonia/ammonium and NO_x/HNO_3/nitrate to determine gradients in ammonia, ammonium, HNO_3, and nitrate with distance from urban and source-oriented measurement locations. Apply theory to estimate the oxidation rates of NO_x under different environmental conditions and compare these rates with ambient data from the winter study. Compare deposition and oxidation rates with transport times to determine the ability of oxidized nitrogen (e.g., HNO_3) to mix with ammonia and form ammonium nitrate. Estimate the potential for interaction of ammonia and oxidized NO_x on the basis of flow patterns.

State and justify conclusions and assumptions about how far emissions can be transported during stagnation periods relative to the time for deposition, oxidation, and neutralization of secondary aerosol

precursors. Examine the role of diffusion versus organized flow patterns during stagnant, low wind speed situations as potential mechanisms for pollutants to mix.

7.2.6.4 Mixing and Oxidation

The objectives were to determine (1) how NO_x emitted above the stable mixed layer gets into the shallow mixed layer when fog or stratus clouds are present; (2) what the important oxidants are, how much oxidant (such as O_3 and peroxides) is above the shallow mixed layer, and how much of it is within the mixed layer; (3) how NO_x is oxidized to nitric acid in a stagnant, cloudy environment with little photochemistry; and (4) how variations in concentrations of oxidants and SO_2 (and NO_x) in space and time influence aerosol formation in fog droplets.

The needed activities were as follows. For IMS95 data, apply the objective analysis technique to the radar refractive index parameter and the RASS vertical T_V measurements to determine hourly mixing depths. Examine selected corresponding T_V plots from radiosonde sites, estimate the mixed layer depths, and compare these with the mixing depths estimated from the radar profilers for hours with corresponding measurements. Determine how mixed layer depths change during the course of the day. Describe the correspondence between the mixing depths estimated from T_V and the diurnal evolution and apparent elevation of mixed layers seen in color slides and time-lapse videos. Use chemical data taken at the surface and aloft to determine which oxidants are found above the mixed layer and determine their profiles within the mixed layer and the boundary layer. Identify dominant pathways for aerosol formation in the aqueous phase from observations of IMS95 fog chemistry and measurements of oxidants (O_3 and peroxides) and catalysts (iron and manganese). Variations in these parameters in space (north versus south, urban versus rural, ground versus aloft) should be evaluated to determine when and where aqueous phase aerosol formation is most important and what factors limit its rate of formation. Examine the change in oxidant formation and distribution during the day as the mixed layer builds in the morning and lowers in the evening. Determine the role of light versus nighttime reactions and of oxidants at the surface versus oxidants aloft above the fog layer. Determine what role these oxidants play in the formation of HNO_3 and sulfuric acid under clear and foggy conditions. For sulfur, this analysis should also consider the formation of S(IV)-aldehyde complexes like hydroxymethanesulfonate, which may limit aqueous phase sulfate production.

State and justify conclusions and assumptions about (1) the depth of the mixed layer into and above which pollutants are emitted and can interact with each other, (2) diurnal boundary layer development, (3) where and when elevated emissions and pollutants carried over from prior days mix with those at the

surface or are decoupled from surface phenomena, (4) the fraction and depth to which oxidants are mixed into the mixed layer, and (5) the role of such oxidants in the oxidation of nitrogen and sulfur oxides.

7.2.6.5 Secondary Organic Aerosol Formation with and without Fog

The objectives were to determine, in the absence of photochemistry under stagnant foggy conditions, (1) to what extent secondary organic aerosol formation is a contributor in this situation, especially considering the significant amount of nitric acid/nitrate formation; and (2) to what extent secondary organic aerosol formation is a contributor under non-foggy/stratus cloud winter conditions.

The needed activities were as follows. Review IMS95 ambient speciated organic gas phase (C_2–C_{20}) and speciated organic aerosol data for primary (anthropogenic and natural) and secondary organic species. If possible, relate secondary species to their primary precursor species, on the basis of known atmospheric chemical processes. To better understand secondary organic gas phase and aerosol phase formation, examine speciated organic aerosol data, TC/OC and TC/EC ratios, and oxidant formation potential as a function of photochemical activity, atmospheric stability and mixing depth, presence or absence of fogs, and distance from a source area. Examine the relationship between primary and secondary aerosols as a function of meteorological variables (e.g., temperature, RH, and solar radiation) and evaluate differences in spatial and temporal patterns. Also use the more abundant OC, EC, and TC data to support the analysis and provide a wider spatial estimate of the fraction of secondary aerosols.

State and justify conclusions and assumptions about the fraction of secondary organic aerosols present in ambient samples during foggy and clear stable winter conditions. Suggest sources for organic aerosol precursors on the basis of species observed and describe mechanisms for the formation of secondary organic aerosols.

7.2.6.6 PM Chemical Composition and Fog

The objective was to determine how PM chemical composition and concentration change before, during, and after fogs.

The needed activities were as follows. Calculate a nitrogen, sulfur, crustal material, and organic species balance by using winter study data. Plot changes in the distribution of species as a function of time, noting whether fog was present at the site or within reasonable transport times to the site. Determine the chemical composition of PM samples before, during, and after fog events. Evaluate how fog alters the chemical composition of PM species as well as the distribution of aerosol precursors species. Identify

chemical and/or physical mechanisms attributable to fog that alter the size distribution and chemical composition of the aerosol from the time before the fog occurs until after it dissipates. Confirm that the physical and chemical mechanisms are appropriately represented in mathematical models, and if not, then recommend changes in the mathematical models and additional experiments to verify these mechanisms.

State and justify conclusions and assumptions about the effect of fog on PM concentrations and composition. State assumptions and indicate the importance of these mechanisms for improving mathematical models.

7.2.6.7 Fog Droplet Size and Secondary Aerosol Formation

The objectives were to determine (1) how deposition, owing to fog droplet growth, balances the creation of secondary aerosols in fog droplets; and (2) how significantly the drop-size dependence of the fog chemistry influences aerosol formation and deposition in fogs.

The needed activities were as follows. Examine fog chemistry as a function of fog droplet size. Compare 2- and 3-stage cloud collector data with bulk data to determine the added value of the size-fractionated fog droplet chemistry measurements. Evaluate enhancements of aqueous phase oxidation rates in the chemically heterogeneous fog drop population (represented by the multistage collectors) versus the rates predicted from the average fog composition (represented by the bulk fog collector samples). Using measurements of fog droplet size taken as the fog forms and dissipates, plot quantities of major species (crustal material, nitrate, sulfate, ammonium, OC, and EC) in fog droplets deposited as a function of time throughout a peak period. Examine the nonuniform distribution of sulfate, nitrate, and organic species across the drop size distribution on estimates of removal by fog drop deposition. Include in the analysis the spatial variability (north to south, urban versus "rural") as well as determining whether the size-dependent nature of the chemistry is more important in one environment versus another. Compare the deposition rates with rates of formation determined by the aerosol evolution model. The magnitude of errors in deposition and oxidation that result from examining only average (bulk) fog chemistry should be quantified to evaluate what resources should be expended in future work to obtain size-dependent fog drop composition information (instead of, e.g., augmenting spatial coverage in a bulk-only fog network).

State and justify conclusions and assumptions about how fast the droplets are removed by deposition, how this balances the rates at which secondary particles are created, and how deposition changes the size

distribution of the aerosol because of the presence of fog. Make recommendations as to whether size-fractionated fog droplet measurements are needed.

7.2.6.8 Acidification and Aerosol Formation in Fog Droplets

The objective was to determine how acidification of droplets caused by aqueous phase acid production (e.g., $SO_2 \rightarrow H_2SO_4$) limits aerosol formation in fog droplets.

The needed activities were as follows. Quantify the extent of buffering in size-fractionated and bulk fog samples. Also quantify the buffering capacity, relative to NH_3 uptake, to prevent fog drop acidification and thereby promote aqueous phase particle production. Titrate additional fog samples collected during IMS95 and other SJV fog studies to quantify the buffering, review compounds (probably organic buffering agents) likely to be present that would provide buffering in the pH regime observed (pH 6–7), and develop a simple model of the effect of the buffering on rates of sulfate production.

State and justify conclusions and assumptions about the species responsible for the high buffering capacity of fog in the valley and provide theoretical justification of the effect of buffering on the formation of sulfate in fog droplets.

7.2.7 Visibility

7.2.7.1 Biases in Light Scattering Measurements

The objective was to determine the accuracy, precision, validity, and equivalence of light scattering measurements.

The needed activities were as follows. Extending the historical analysis, use winter study data to evaluate potential nephelometer interferences. Estimate the effects of sample heating by (1) plotting differences between ambient and detection chamber humidities as a function of time and ambient temperature; (2) calculating RH reductions that are due to temperature changes as a function of time, ambient temperature, and ambient RH; and (3) using existing relations between light scattering and RH and typical particle compositions to determine the resulting biases caused by sample heating as a function of RH. Plot nephelometer zero and span values versus temperature to determine the effects of temperature variations on instrument response. Estimate the amount of measured scattering caused by coarse particles and the biases introduced by the angular truncation of the scattering geometry from prior studies with total and $PM_{2.5}$ nephelometer size fractions. Determine which samples might be significantly affected by coarse particle scattering from $PM_{2.5}$ measures of crustal species (aluminum,

silicon, iron, calcium, and titanium). Generate tables for each nephelometer, indicating the number of hours per month that the data are flagged as being influenced by meteorological effects. Acquire airport visibility data for the SJV, Class I areas, and the Mojave Desert. Convert airport human observer visual range data to extinction coefficient values using Koschmieder's formula along with an appropriate choice of threshold value for human visual perception. Compare extinction coefficient data derived from airport observations with extinction coefficient values obtained from instrumental methods at locations where nephelometers are sited near controlled airports. Attempt to describe causes of any systematic differences between human observation and instrumental methods.

State and justify conclusions and assumptions that quantify biases in light scattering measurements caused by the heating of the aerosol sample, changes in nephelometer response caused by ambient temperature fluctuations, and the partial response of coarse particles to light scattering caused by the angular truncation in the light scattering geometry.

7.2.7.2 Spatial and Temporal Characteristics

The objectives were to determine (1) the spatial and temporal characteristics of visibility (total extinction and its components) during IMS95, and (2) where, how much, how long, and how often visibility reduction occurs in the SJV, Class I areas, and in the Mojave Desert.

The needed activities were as follows. Determine diurnal variations in visual range, light scattering and absorption, and total extinction. Create monthly box-and-whisker plots of hourly light scattering and light absorption. Also plot total extinction for IMS95 core sites and sites in the SJV, Mojave Desert, and Class I areas where data are available from either nephelometers or human observers. Compare statistical deviations in diurnal patterns among the measurement sites and for peak and nonpeak PM_{10} and $PM_{2.5}$ periods. Identify consistencies and inconsistencies with the current understanding of diurnal variations in emissions, transport, and vertical mixing. Identify difference's in diurnal patterns with time of year. Tabulate the times and locations of hourly maxima and examine daily time-series plots of these situations to advance hypotheses for their causes. Quantify the degree to which the time-averaged aerosol sampling periods represent a constant level of light scattering and absorption in data sets corresponding to visibility measurements. Briefly describe each haze event and specify its beginning and ending dates, its visual character, and its apparent spatial extent. Include events that available monitoring data, color slides, or time-lapse photos show to be uniform and regional as well as events that appear local and layered. Identify those events when sources in the SJV may have made a perceptible contribution to haze in or above the Mojave Desert or Class I areas.

State and justify conclusions and assumptions about the pattern of diurnal changes in visibility during the winter study and the times when deviations from that pattern occur.

7.2.7.3 Chemical Concentrations and Visibility Reduction

The objective was to determine where, how much, how long, and how often different chemical constituents contribute to different levels of visibility reduction in the SJV during IMS95 and in the Mojave Desert.

The needed activities were as follows. Using chemically speciated and size-segregated aerosol concentrations measured during IMS95, apply a size-inversion model in the SJV and in the Mojave Desert and examine the aerosol size modes. Submit these distributions to a Mie-formulated extinction efficiency model and calculate extinction efficiencies as a function of RH. Evaluate changes in efficiencies for different assumptions, including (1) each chemical compound present as pure particles (external mixture), (2) soluble species mixed together in each particle (internal mixture), (3) ammonium sulfate around a carbon core, and (4) different formulations for changes in particle size with RH. Compare the efficiencies used to reproduce measured extinction (constant shape of size distribution) with those used to estimate the effects of emissions reductions (constant number distribution). Calculate empirical extinction efficiencies by the multiple linear regression (MLR) method, using different formulations of RH dependence. Include collinear measures, such as singular value decomposition, to evaluate the validity of the MLR efficiencies. Compare the derived extinction efficiencies with those found in prior studies and with each other. Attach uncertainty intervals to uncertainties that can be propagated through calculations of chemical extinction. Compare predicted scattering coefficient values to measured light scattering and compare predicted light extinction values to light extinction inferred from human observer records.

State and justify conclusions and assumptions about the efficiency factors and their uncertainties that relate chemical concentrations to light extinction, especially as the submodes of $PM_{2.5}$ vary.

7.2.7.4 Chemical Concentrations and Light Extinction

The objective was to determine how chemical constituents contribute to the light extinction budget.

The needed activities were as follows. Apply extinction efficiencies that account for RH effects on aerosol chemical concentrations to each major chemical component of EC, OC, ammonium nitrate, ammonium sulfate, and crustal material. Compare measured scattering with the sum of fine-particle scattering

contributions calculated from chemical concentrations and identify the differences that exceed propagated uncertainty intervals. Determine the cause of these differences. If discrepancies can be attributed to inadequate estimates of size distributions, then evaluate the need to include measurements of such size distributions in subsequent measurements. Plot chemical contributions to extinction, including Rayleigh scattering, as a time series of stacked bars. Compare and contrast the relative contributions to extinction as a function of sampling site and time of day. Identify where and when contributions differ significantly between sites in the northern SJV, the southern SJV, the Mojave Desert, and Class I areas in the Sierra Nevada. Note differences in RH between sampling locations during peak periods and determine the extent to which differences in extinction are due to chemical composition differences or differences in the liquid water content of the aerosol. Create frequency distributions that show the fractional contributions to extinction from Rayleigh scattering, sulfates, nitrates, OC, EC, and crustal material.

State and justify conclusions and assumptions about the contribution from each major chemical compound to light extinction at different locations and times, where IMS95 data permit.

7.2.7.5 Emissions Sources and Light Extinction

The objective was to determine how emissions sources contribute to the light extinction budget.

The needed activities were as follows. Use source apportionment results from Section 7.2.5.2 that relate source emissions to the concentrations of chemical constituents in the airborne particles to determine how the emissions from the major source types create the light extinction budgets computed in Section 7.2.7.4. Plot source contributions to extinction as a time series of stacked bars. Compare and contrast the relative contributions to extinction as a function of sampling site and time of day. Identify where and when contributions differ significantly between sites in the northern SJV, the southern SJV, the Mojave Desert, and Class I areas in the Sierra Nevada.

State and justify conclusions and assumptions about the contribution to light extinction from major emissions sources.

7.2.8 Overall Integration

7.2.8.1 Relating Current Data To Conceptual Models

The objective was to determine the following information:

- The causes of excessive PM_{10} concentrations in the SJV
- The influence of meteorology, emissions, chemistry, and deposition on PM concentrations

- The differences observed for PM, PM components, and precursor species among urban, rural, and industrial areas
- The chemical processes for the formation of secondary aerosols, especially during foggy conditions when the photochemical process may be limited
- The influence of fog on PM concentrations
- The spatial influence of primary emissions and secondary aerosol precursors during each conceptual model scenario
- Whether peak 24-hour values or moderate-range PM concentrations control the annual average PM concentrations
- What chemical species are most important for controlling the annual average, and whether the average varies with the time of year
- Needed modifications to conceptual models
- What knowledge gaps still exist, and what data are needed to fill those gaps
- Recommendations for future field, modeling, and data analysis studies
- What statements can be made about priority for emissions controls for primary aerosol and secondary precursor aerosol species
- If a new PM standard is promulgated, where and when it might be exceeded, what are the major chemical components, and what is its relationship to the existing PM standard from a chemical, spatial, and temporal standpoint

The needed activities were as follows. Synthesize data from other analyses. Update the understanding of conceptual models. Provide detailed descriptions of case studies for each conceptual model.

State and justify conclusions and assumptions about the ability of current data to adequately describe each conceptual model and the need for new data or studies to provide an improved understanding. Develop new conceptual models if needed.

7.2.8.2 Instruments and Analysis for Research and Routine Monitoring

The objective was to determine which combinations of instrumentation and analysis are most practical for research and routine monitoring.

The needed activities were as follows. Synthesize the results from the previous data analysis activities and the current literature to justify the continued use of the current routine monitoring methods or justify replacing them with more accurate or practical methods. Consider the following sampling frequencies in the analysis: continuous with a 1-hour average objective, a 3-hour average and 24-hour average every day, a 24-hour average every 3 days, and a 24-hour average every 6 days. Review literature and contact researchers who are expert in measuring different aerosol chemical components, aerosol precursors,

meteorological variables, and chemical and physical properties of fog. Use information gained from previous work elements, which focus strictly on the methods, in the overall integrated analysis for network design for compliance and research networks. Identify promising new methods worthy of future development and identify methods that have been shown to be feasible and could be made practical for special studies and long-term monitoring. Include an evaluation of how practical the method is (the ease of use, staffing to implement the method at suggested time scales, preparation of substrates, and requirements for chemical analysis) for such purposes as compliance monitoring, use in episodic-type field programs, and extended field programs for up to a year. Evaluate the cost of use for each of these purposes. Evaluate EPA proposals for compliance monitoring in light of the knowledge gained from performing the above steps and the steps described in the previous aerosol measurement sections.

State and justify conclusions and assumptions, on the basis of the IMS95 data and results from earlier activities, about the most cost-effective and practical air quality and meteorological instrumentation for gaining future data sets with sufficient accuracy, precision, and validity to meet future needs. Note that monitoring will be used for source and receptor modeling, understanding of PM formation, determining the actual effectiveness of rules, and compliance with and maintenance of standards. Consider less-than-24-hour average sampling times for PM and related species and less-than-1-hour averaging times for meteorological variables. Also consider surface and aloft measurements.

7.2.8.3 Effect of Emissions Reductions on Visibility

The objective was to determine how emissions reductions will affect visibility in the SJV, nearby Class I areas, and the Mojave Desert.

The needed activities were as follows. Examine current and proposed emissions reductions associated with the 1995 O_3 and the 1997 PM_{10} SIPS and estimate the effect of these controls on visibility in the SJV.

State and justify conclusions and assumptions about the effect of pollutant reductions on visibility in the SJV, nearby Class I areas, and the Mojave Desert, if pollutants are transported out of the valley.

7.2.8.4 Sources of Imprecision in Source Contribution Estimates

The objectives were to determine the major sources of imprecision in source contribution estimates determined by different types of models and which improvements would most reduce those imprecisions.

The needed activities were as follows. Critically evaluate the data analysis methods, including simple models, with respect to their formulations, their assumptions, and the adequacy of their input data. Tabulate the different methods used for analysis, including their needed inputs, the availability and uncertainty of those inputs, their assumptions, and compliance with those assumptions. Assign levels of confidence to conclusions and identify needed development efforts for future studies.

State and justify conclusions and assumptions about needed developments in model and input data sets.

7.2.8.5 Relating Emissions to PM Concentrations

The objectives were to determine (1) which contributions to PM are proportional to emissions rates, and which are not; (2) for contributions that are not proportional to emissions, what the limiting precursor is and how limiting it is; and (3) over what distance, and at what times, reductions in a specific emissions source will be detectable as PM reductions at receptors.

The needed activities were as follows. Synthesize data from other analyses. Evaluate where precursor emissions are concentrated and estimate how reductions in one part of the valley will affect concentrations in other parts of the valley. Provide a rationale for local as well as valleywide emissions reductions.

State and justify conclusions and assumptions about ammonia, NO_x, organic species, and SO_2 precursor effects on PM concentrations.

7.2.8.6 Performing Other Measurements

The objectives were to determine (1) whether other PM components, PM precursors, or other meteorological variables should be measured and based on earlier work elements; and (2) whether suitable collection and analysis methods or monitoring systems exist for those measurements.

The needed activities were as follows. Synthesize information from earlier work elements.

State and justify conclusions and assumptions about the use of additional or alternate methods and indicate how the measurement should improve the understanding of aerosol formation.

Section 8

REFERENCES

ARB. 1995. California Air Quality Data, Summary of 1995 Air Quality Data Gaseous, and Particulate Pollutants. Volume XXVII, Annual Summary. California Air Resources Board, Technical Support Division, Sacramento, CA.

ARB. 1995b. Performance Audit Procedures for Manual Gaseous Audits, Appendix Y; Audit Procedures Manual for Air Quality Monitoring, Volume V; State of California Air Resources Board, Monitoring, and Laboratory Division, Quality Assurance Section, Sacramento, CA.

Ashbaugh, L.L., J.C. Chow, and J.G. Watson. 1991. *Atmospheric Acidity Data Quality and Measurement Characteristics for California's Acid Deposition Monitoring Program.* Article No. 91-89.7, Air & Waste Management Association, 84th Annual Meeting, Vancouver, B.C. pp. 16.

AeroVironment. 1995. *Integrated Measurements Study*—1995, audit Program Work Plan, AV. 95-07-207A, AeroVironment, Inc., Monrovia, CA.

Blanchard, C.L. 1994. Regional Estimates of Acid Deposition Fluxes in California. Final Report, Contract No. A132-149, California Air Resources Board, Sacramento, CA.

Bush, D.H., A.N. Barnett, M. Miguel, K. Magliano, and P.A. Solomon. 1996. *1995 Integrated Monitoring Study: Quality Assurance Methods and Results.* In the Proceedings of the 1996 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants; Air & Waste Management Association, Pittsburgh, PA.

Chinkin, L.R. 1996. CRPAQS TSS No. 15: Task 3, Initial Ammonia Inventory for the San Joaquin Valley. Technical Memorandum, STI Ref. No. 95310, September 26, to Karen Magliano. Prepared by Sonoma Technology, Inc., Santa Rosa, CA for the California Air Resources Board, Technical Support Division, Sacramento, CA.

Chow, J.C., J.G. Watson, D.H. Lowenthal, P.A. Solomon, K.L. Magliano, S. Ziman, and L.W. Richards. 1993. PM_{10} and $PM_{2.5}$ Compositions in California's San Joaquin Valley. *Aerosol Sci. Technol.* **18**:105–128.

Chow, J.C., J.G. Watson, L.C. Pritchett, W.R. Pierson, C.A. Frazier, and R.G. Purcell. 1993b. "The DRI Thermal/Optical Reflectance Carbon Anaysis System: Description, Evaluation and Applications in U.S. Air Quality Studies." *Atmos. Environ.*, **27A**:1185–1201.

Chow, J.C. and J.G. Watson. 1994a. Guidelines for PM_{10} Sampling and Analysis Applicable to Receptor Modeling. Final Report. EPA-452/R-94-009. DRI Document No. 2625. 1F. Prepared by the Desert Research Institute, Reno, NV for OAQPS, US EPA, Research Triangle Park, NC.

Chow, J.C., and J.G. Watson, E.M. Fuita, Z. Lu, and D.R. Lawson. 1994b. Temporal and Spatial Variations of $PM_{2.5}$ and PM_{10} Aerosol in the Southern California Air Quality Study. *Atmos. Environ*, **28**, 2061-2080.

Chow, J.C. 1995. Critical Review: Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles. *J. Air & Waste Manage. Assoc.* **45**:320-382.

Chow, J.C., J.G. Watson, Z. Lu, D.H. Lowenthal, C.A. Frazier, P.A. Solomon, R.H. Thuillier, and K. Magliano. 1996. Descriptive Analysis of $PM_{2.5}$ and PM_{10} at Regionally Representative Locations during SJVAQS/AUSPEX. *Atmospheric Environment*: Special Issue for the Regional Photochemical Measurement and Modeling Studies Specialty Conference, 30(12): 2079–2112.

Chow, J.C. and D. Egami. 1997. San Joaquin Valley 1995 Integrated Monitoring Study: Documentation, Evaluation, and Descriptive Data Analysis of PM_{10}, $PM_{2.5}$, and Precursor Gas Measurements. Prepared by the Desert Research Institute, Reno, NV for the California Air Resources Board, Sacramento, CA.

Coe, D., L. Chinkin, C. Jones, K. Magliano, P.A. Solomon, and L. Ashbaugh. 1996. *Emissions Activity Measurements during the Fall and Winter IMS95 Components—Preliminary Results*. In the Proceedings of the 1996 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants; Air & Waste Management Association, Pittsburgh, PA.

Coe, D.L. and L.R. Chinkin. 1996. IMS95 Daily Activity Surveys. Final Draft Report, STI-95274-1616-FR. Prepared by Sonoma Technology, Inc., Santa Rosa, CA for the California Air Resources Board, Sacramento, CA.

Collett, J.L. Jr., A. Bator, D.E. Sherman, K. Hoag, G. Oliver, X. Rao, L.W. Richards, K. Magliano, and P.A. Solomon. 1996a. 1995 Integrated Monitoring Study: Fog Measurements in the Southern San Joaquin Valley—preliminary results. *In Proceedings of the Air & Waste Management Association and U.S. Environmental Protection Agency 11th International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC*, May 7–9, Air & Waste Management Association, Pittsburgh, PA, (VIP-64), p. 413.

Collett, J.L. Jr., A. Bator, D.E. Sherman, K. Hoag, L.W. Richards, S. Pandis, K. Magliano, and P.A. Solomon, 1996b. 1995 Integrated Monitoring Study: Fog Measurements in the Northern San Joaquin Valley—Preliminary Results. In *Proceedings of the Air & Waste Management Association and U.S. Environmental Protection Agency 11th International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 7–9*, Air & Waste Management Association, Pittsburg, PA, (VIP-64), p. 424.

Collett, J.L. Jr., K.J. Hoag, D.E. Sherman, and A. Bator. 1997. Technical Support Study 11: Investigating the Dynamics and Chemistry of Fog Formation and Dissipation. Final Report. Prepared by Colorado State University, Ft. Collins, CO, for the California Air Resources Board, Sacramento, CA.

Collett, J.L. Jr., A. Bator, X. Rao, and B. Demoz. 1994. Acidity variations across the cloud drop size spectrum and their influence on rates of atmospheric sulfate production. *Geophys. Res. Lett.* **21**, 2393–2396.

Collett, J.L. Jr., R. Iovinelli, and B. Demoz. 1995. A three-stage cloud impactor for size-resolved measurements of cloud drop chemistry. *Atmos. Environ.*, **29**, 1145–1154.

Collett, J.L. Jr., B. Oberholzer, and J. Staehelin. 1993. Cloud chemistry at Mt. Rigi Switzerland: Dependence on drop size and relationship to precipitation chemistry. *Atmos. Environ.* **27A**, 33–42.

Demoz, B., J.L. Collett Jr., and B.C. Daube Jr. 1996. On the Caltech Active Strand Cloudwater Collectors, *Atmos. Res.*, [41, 47-62].

Dzubay, T.G. et al. 1988. A Composite Receptor Model Applied to Philadelphia Aerosol. *Environ. Sci Technol.*, **22**, 46–52.

Dzubay, T.G. 1977. *X-Ray Fluorescence Analysis of Environmental Samples, 2nd Edition.* Ann Arbor Science, Ann Arbor, MI, pp. 289-306.

Eatough, D.J., N. Aghdaie, M. Cottam, T. Gammon, L.D. Hansen, E.A. Lewis, and R.J. Farber. 1990. "Loss of Semi-volatile Organic Compounds from Particles during Sampling on Filters." In *Transactions, Visibility and Fine Particles*, C.V. Mathai, ed. Air & Waste Management Association, Pittsburg, PA, pp. 146–156.

Federal Register. 1988. Ambient Air Monitoring Reference and Equivalent Methods; Equivalent Method Designation. *Federal Register* **53**:215, 44947.

Fung, K. and B. Wright. 1990. Measurement of Formaldehyde and Acetaldehyde Using 2,4-Dinitrophenylhdrazine-Impregnated Cartridges during the Carbonaceous Species Methods Comparison Study. *Aero. Sci. Technol.* 12:44.

Fung, K. and D. Grosjean. 1981. Determination of Nanogram Amounts of Carbonyls as 2,4-Dinitrophenylhydrazones by High-Performance Liquid Chromatography. *Anal. Chem.* **53**:168.

Gertler, A.W., D.H. Lowenthal, J.C. Chow, and J.G. Watson. 1993. Receptor Modeling of SCAQS Volatile Organic Compounds. In the Proceedings of the Southern California Air Quality Study, Data Analysis. Air & Waste Management Association, Pittsburgh, PA.

Gertler, A.W., W.G. Coulombe, and D. DeWitt. 1993. Quality Assurance Report, SJAQS/AUSPEX. DRI 8403.4fl. Prepared for Pacific Gas and Electric Company and the San Joaquin Valley Air Pollution Study Agency, by the Desrt Research Institute.

Gray, H.A., G.R. Cass, J.J. Huntzicker, E.K. Heyerdahl, J.A. Rau. 1986. Characteristics of Atmospheric Organic and Elemental Carbon Particle Concentrations in Los Angeles. *Environ. Sci. Technol.* **20**(6):580-589.

Gray, H.A., I.L. Carr, D. Pankratz, C. Biltoft, and J. Pederson. 1996. *1995 Integrated Monitoring Study: Low Wind Speed Study — Preliminary Results.* In the Proceedings of the 1996 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants; Air & Waste Management Association, Pittsburgh, PA.

Gundel, L.A., R.L. Dod, H. Rosen, and T. Novakov. 1984. The Relationship between Optical Attenuation and Black Carbon Concentration for Ambient and Source Particles. *Sci. Total Environ.* **36**, 197–202.

Hansen, A.D.A., H. Rosen, and T. Novakov. 1984. The Aethalometer — an Instrument for the Real-time Measurement of Optical Absorption by Aerosol Particles. *Sci. Total Environ.*, **36**, 191–194.

Hansen. 1995. Magee Scientific, Berkeley, CA. Private communication.

Hering, S.V., D.R. Lawson, I. Allegrini, A. Febo, C. Perrino, M. Possanzini, J.E. Sickles, II, K.G. Anlauf, A. Wiebe, B.R. Appel, W. John, Jo. Ondo, S. Wall, R.S. Braman, R. Sutton. G.R. Cass, P.A. Solomon, D.J. Eatough, N.L. Eatough, E.C. Ellis, D. Grosjean., B.B. Hicks, J.D. Womack, J. Horrocks, K.T. Knapp, T.G. Ellstad, R.J. Paur, W.J. Mitchell, M. Pleasant, E. Peak, A. MacLean, W.R. Pierson, W. Brachaczek, H.I. Schiff, G.I. Mackay, C.W. Spicer, D.H. Stedman, A.M. Winer, H.W. Biermann, and E.C. Tuazon. 1988. "The Nitric Acid Shootout: Field Comparison of Measurement Methods." *Atmos. Environ.*, **22**:1519–1539.

Hoag, K., A. Bator, E. Sherman, X. Rao, J.L. Collett Jr., and L.W. Richards. 1996. Sulfate production in fogs in California's Central Valley. In *AAAR '96 Abstracts: Fifteenth Annual Conference, Orlando, FL, October 14–18* American Association for Aerosol Research, Cincinnati, OH, p. 34.

Hoffmann, M.R., J.L. Collett Jr., and B.C. Daube. 1989. Characterization of cloud chemistry and frequency of canopy exposure to clouds in the Sierra Nevada. Final report prepared for the California Air Resources Board, Sacramento, CA.

Hughes, V. 1997. IMS95 Baseline Emissions Inventory. Prepared for the San Joaquin Valleywide Air Pollution Study Agency, California Air Resources Board, Sacramento, CA by the California Air Resources Board, Technical Support Division, Sacramento, CA.

Husar, R.B. 1974. "Atmospheric Particulate Mass Monitoring with a Beta Radiation Detector." *Atmos. Environ.*, **8**:183–188.

Ingalls, M.N. 1989. On-Road Vehicle Emission Factors from Measurements in a Los Angeles Area Tunnel. Proceedings of the 82nd A&WMA Annual Meeting & Exhibition, Anaheim, CA 25–30 June, 1989. Air & Waste Management Association, Pittsburgh, PA.

John, W., S.M. Wall, and J.L. Ondo. 1988. "A New Method for Nitric Acid and Nitrate Aerosol Measurement Using the Dichotomous Sampler." *Atmos. Environ.*, **22**:1627–1635.

Lawson, et al. 1990. Carbon Species Methods Comparison Study Overview Paper. *Aerosol Sci. And Tech.* Vol. **12**(20).

Lawson, D.R., A.M. Winer, H.W. Biermann, E.C. Tuazon, G.J. Mackay, H.I. Schiff, G.L. Kok, P.K. Dasgupta, and K. Fung. 1990. Formaldehyde Measurement Methods Evaluation during the Carbonaceous Species Methods Comparison Study. *Aero. Sci. Technol.* **12**:20.

Lazrus, A.L., G.L. Kok, J.A. Lind, S.N. Gitlin, B.G. Heikes, and R.E. Shetter. 1986. Automated fluorometric method for hydrogen peroxide in air. *Anal. Chem.* **58**, 594–597.

Lee, K.W. and M. Ramamurthi. 1993. "Filter Collection." In Aerosol Measurement: Principles, Techniques and Applications, K. Willeke and P.A. Baron, eds. Van Nostrand, Reinhold, New York, NY, pp. 179–205.

Lehrman. 1995. Personal communication, T&B Systems, Santa Rosa, CA.

Lindsey, C.G., S.E. Ray, B.M. Schoell, T.S. Dye, and M. Arthur. 1996. Data collected by a network of radar profilers, rawinsonde sounding stations, and surface meteorological monitoring sites during IMS95. Final data report prepared for California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Santa Rosa, CA, STI-95080-1622-FDR, December.

Lindsey, C.G., S.E. Ray, B.M. Schoell, T.S. Dye, and M. Arthur. 1997. Letter report to be prepared for California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Santa Rosa, CA, May.

Lippmann, M. 1989. "Sampling Aerosols by Filtration." In Air Sampling Instruments for Evaluation of Atmospheric Contaminants, S.V. Hering, ed. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 7th ed. pp. 305–336.

Lurmann, F.W., N. Kumar, C. Loomis, G.R. Cass, J.H. Seinfeld, D, Lowenthal, and S.D. Reynolds. 1996. PM_{10} Air Quality Models for Application in the San Joaquin Valley PM_{10} SIP. Prepared by Sonoma Technology, Inc. Santa Rosa, CA for the California Air Resources Board, Sacramento, CA.

Macias, E.S. and R.D. Husar. 1976. "Atmospheric Particulate Mass Measurement with Beta Attenuation Mass Monitor." *Environ. Sci. Technol.*, **10**:904–907.

Marple, V.A., B.Y.H. Liu, and G.A. Kuhlmey. 1981. "A Uniform Deposit Impactor." *J. Aerosol Sci.*, **12**:333–337.

McDow, S.R. and J.J. Huntzicker. 1990. "Vapor Adsorption Artifact in the Sampling of Organic Aerosol: Face Velocity Effects." *Atmos. Environ.*, **24A**:2563–2572.

Miguel, M. 1996. Final Audit Results for the Integrated Monitoring Study. Technical Memo prepared by the California Air Resources Board, Quality Assurance Section for the California Air Resources Board, Modeling Support Section, February.

McMurry, P.H. and X.Q. Zang. 1988. The Carbonaceous Species Methods Comparison Study: University of Minnesota Results. Final report No. 668, Dept. of Mechanical Engineering, University of Minnesota, Minneapolis, MN.

Mulik, J., R. Puckett, D. Williams, and E. Sawicki. 1976. "Ion Chromatographic Analysis of Sulfate and Nitrate in Ambient Aerosols." *Environ. Sci. Technol.*, **9**(7):653–663.

Munger, J.W., J.L. Collett Jr., B. Daube Jr., and M.R. Hoffmann. 1989. Chemical composition of coastal stratus clouds: dependence on droplet size and distance from the coast. *Atmos. Environ.* **23**, 2305–2320.

Oberholzer, B., J.L. Collett Jr., J. Staehelin, and A. Waldvogel. 1992. In-cloud Scavenging of Gases and Aerosols at a Mountain Site in Central Switzerland. *J. Atmos. Chem.* **14**, 61–71.

Pandis, S.N., J.L. Collett, and L.W. Richards. 1995. Technical Support Study II: Investigating the Dynamics and Chemistry of Fog Formation and Dissipation; Literature Review. STI-95090-1539-LR, prepared by Sonoma Technology, Inc., Santa Rosa, CA.

Patashnick, H. and E.G. Rupprecht. 1991. "Continuous PM_{10} Measurements Using the Tapered Element Oscillating Microbalance." *J. Air Waste Manage. Assoc.*, 41:1079–1083.

Peters, J.M. 1995. Epidemiologic Investigation to Identify Chronic Health Effects of Ambient Air Pollutants in Southern California, Phase II Draft Final Report, Appendix B. University of Southern California. Prepared for the California Air Resources Board on Contract No. A033-186.

Rasmussen, R.A. 1989. Standard Operating Procedures, VOC Collection-Analysis Systems. Adopted from EPA Compendium TO-14. Draft, Oregon Graduate Institute, Beaverton, OR.

Richards, L.W., S.N. Pandis, and T. Campos. 1997. Technical Support Study 11: Investigating the dynamics and chemistry of fog formation and dissipation; Phase II Report, Measurement at the Candelabra Tower. Report STI-95090-1727. Sonoma Technology, Santa Rosa, CA. Prepared for the California Air Resources Board, Sacramento, CA.

Rogge, W.F. 1993. Molecular tracers for sources of atmospheric carbon particles: measurements and model predictions. Ph.D. Thesis. California Institute of Technology, Pasadena, CA.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit. 1993a-f. Sources of fine organic aerosol. 5. Natural gas home appliances. *Environmental Science and Technology* **27**, 2736–2744.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit. 1994. Sources of fine organic aerosol. 6. Cigarette smoke in the urban atmosphere. *Environmental Science and Technology* **28**, 1375–1388.

Rogge, W.F. 1996. Feasibility of Using Organic Tracers for Tracking the Fate of Primary and Secondary Aerosols from Combustion Sources. Draft final report prepared for the San Joaquin Valleywide Air Pollution Study Agency by Florida International University, University Park, Miami, FL.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, B.R.T. Simoneit, and G.R. Cass. 1993b. Determination of Key Organic Compounds Present in the Particulate Matter Emissions from Air Pollution Sources. Final report prepared for the California Air Resources Board, Sacramento, CA by Environmental Quality Laboratory, California Institute of Technology, Pasadena, CA.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit. 1991. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. *Environmental Science and Technology* **25**, 1112–1125.

Rogge, W.F., L.M. Hildemann, A. Mazurek, G.R. Cass, and B.R.T. Simoneit. 1993c. Sources of fine organic aerosol. 4. Particulate abrasion products from surfaces of urban plants. *Environmental Science and Technology* **27**, 2700–2711.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit. 1993d. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environmental Science and Technology* **27**, 1892–1904.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit. 1993e. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science and Technology* **27**, 636–651.

Rogge, W.F., M.A. Mazurek, L.M. Hildemann, G.R. Cass, and B.R.T. Simoneit. 1993a. Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation. *Atmospheric Environment* **27**, 1309–1330.

Rodes, S.R., V.P. Guinn, and R.J. Thompson. 1989. General Atomic Absorption Procedure for Trace Metals in Airborne Material Collected on Filters. In *Methods of Air Sampling and Analysis*, J.P. Lodge, ed. Lewis Publishers, Chelsea, NY, pp. 608-618.

Roth, P.M. and J.G. Watson. 1993. A proposed PM_{10} Program for the San Joaquin Valley. Prepared for the San Joaquin Valleywide Air Pollution Study Agency. April 1993.

Rupprecht, E., M. Meyer, and H. Patashnick. 1992. The Tapered Element Oscillating Microbalance as a Tool for Measuring Ambient Particulate Concentrations in Real Time. Presented at European Aerosol Conference, Oxford, UK.

Schauer, J.J., W.F. Rogge, L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit. 1996. Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers. *Atmos. Environ.* 30. 3837–3855.

Smith, T.B. 1994. Ozone Episode Forecasting in the San Joaquin Valley. In Planning and Managing Regional Air Quality Modeling and Measurement Studies: perspective through the San Joaquin Valley Air Quality Study and AUSPEX, P.A. Solomon, ed. Lewis Publishers, Chelsea, MI, in conjunction with Pacific Gas and Electric Company, San Ramon, CA, pp 737-767.

Smith and Lehrman. 1996. SARMAP II Design: Analysis of the San Joaquin Valley Meteorological Environment During High PM_{10} Loadings. Prepared by Technical and Business Systems, Santa Rosa, CA.

Solomon, P.A., J.L. Moyers, and R.A. Fletcher. 1983. High-volume dichotomous virtual impactor for the fractionation and collection of particles according to aerodynamic size. *Aerosol. Sci. Technol.* 2, 455–464.

Solomon, P.A., R.H. Thuillier, K.L. Magliano, A.J. Ranzieri, R. Hackney, E. Niccum, J.G. Watson, D. Lehrman, P.M. Roth, S.D. Ziman, F. Lurmann, and G.R. Cass. 1996a. 1995 Integrated Monitoring Study: Study Objectives and Design. Proceedings of the 1996 U.S. EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants. Air & Waste Management Association.

Solomon, P.A. and R.H. Thuillier. 1995. SJVAQS/AUSPEX/SARMAP Air Quality Field Measurement Project, 1990; Volume II: Field Measurement Characterization; Volume III: Appendices. PG&E Environmental, Health and Safety Report Number 009.9-94.1. Pacific Gas and Electric Company, Department of Research and Development, San Ramon, CA.

Solomon, P.A. 1994. The Measurement of NO, NO_2, NO_x, and NO_y in the Atmosphere: Recommendations for SJVAQS/AUSPEX. In *Planning and Managing Regional Air Quality Modeling and Measurement Studies: Perspective through the San Joaquin Valley Air Quality Study and AUSPEX*, P.A. Solomon, ed. Lewis Publishers, Chelsea, MI in conjunction with Pacific Gas and Electric Company, San Ramon, CA, pp. 737–767.

Solomon, P.A., J.C. Chow, J.G. Watson, J. Gillies, D. Egami, K.L. Magliano, P. Roberts, D. Wright, D. Crow, J. Newman, and C. Berkowitz. 1996b. *1995 Integrated Monitoring Study: Spatial and Temporal Variability of* PM_{10} *during the Fall Saturation Study —Preliminary Results.* In the

Proceedings of the 1996 U.S. EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, Air & Waste Management Association, Pittsburgh, PA.

Solomon, P.A., T. Fall, L. Salmon, G.R. Cass, H.A. Gray, and A.J. Davidson. 1989. Air pollution Control Association. 1989 **39**(2) 154–163.

Solomon, P.A., K.L. Magliano, E. Niccum, K.J. Parsons, and K. Finn. 1997. Measurement Site Descriptions for the 1995 Integrated Monitoring Study of the California Regional PM_{10} Air Quality Study. Prepared by Pacific Gas and Electric Company, San Ramon, CA, for the California Air Resources Board, Sacramento, CA.

Stevens, R.K. 1985. "Sampling and Analysis Methods for Use in Source Apportionment Studies." *Eviron. International*, **18**, 271–283, (1985).

Tang, H., E.A. Lewis, D.J. Eatough, R.M. Burton, and R.J. Farber. 1994. Determination of the Particle Size Distribution and Chemical Composition of Semi-Volatile Organic Compounds in Atmospheric Fine Particles with a Diffusion Denuder System. *Atmos. Environ.* 28(5):939-950.

Thuillier, R.H. 1995. The Influence of Instrumentation, Siting, Exposure Height, and Temporal Averaging Methodology on Meteorological Measurements from SJVAQS/AUSPEX. *J. Applied Meteorology*, **34**(8), 1815–1823.

Thuillier, R.H. and N. Seaman. 1995. Thuillier from Pacific Gas and Electric Company, San Ramon, CA, and Seaman from Pennsylvania State University, University Park, PA. Private communications.

Thuillier, R.H., D.L. Blumenthal, and A.W. Gertler. 1994. Meteorological Field Measurement Program for SJVAQS/AUSPEX. Prepared for Pacific Gas and Electric Company, February 1994.

Turpin,, B.J., J.J. Huntzicker, and S.V. Hering. 1994. Investigation of Organic Aerosol Sampling Artifacts in the Los Angeles Basin. *Atmos. Environ.* **28**:3061-3071.

U.S. Census. 1994. Census Data for the United States, U.S. Census Official Statistics. Internet at Http://venus.census.gov/cdrom/lookup/866241683, Staste Level-place.

U.S. EPA. 1995. Appendix 3, Compilation of Air Pollutant Emission Factors, AP-42. EPA-454/C-95-001, U.S. Environmental Protection Agency. Research Triangle Park, 1995.

Watson, J.G. and J.C. Chow. 1993b. "Ambient Air Sampling." In Aerosol Measurements. Principles, Techniques and Applications, K. Willeke and P. Baron, eds. Van Nostrand Reinhold, New York, NY, pp. 622–639.

Watson, J.G., J.C. Chow, C.F. Rogers, D. DuBois, and C. Cahill. 1997. Analysis of Historical PM_{10} and $PM_{2.5}$ Measurements in Central California. Prepared for California Air Resources Board, Sacramento, CA.

Watson., J.G., P.A. Solomon, and K.L. Magliano. 1996. Data Analysis Activities for the California Regional PM_{10} Air Quality Study (CRPAQS). Prepared for the San Joaquin Valleywide Air Pollution Study Agency.

Watson, J.G., J.C. Chow, F. Lurmann, and S. Musarra. 1994. Ammonium Nitrate, Nitric Acid, and Ammonia Equilibrium in Wintertime Phoenix, AZ. Air & Waste, 44,261–268.

Watson, J.G. and J.C. Chow. 1997. X-Ray Fluorescence Analysis of Ambient Air Samples. In *Elemental Analysis of Airborne Particles*, S. Landsberger and M. Creatchman, eds. Gordon and Breach Publishers, USA.

Wright, D.B. and P.T. Roberts. 1996. Collection of Continuous Gas-Phase Data at Two Sites during IMS95. Final report prepared for San Joaquin Valleywide Air Pollution Study Agency, California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Santa Rosa, CA, STI-95173-1625-FR, December.

Appendix A

CRPAQS DATA ANALYSIS PLAN—
MAJOR QUESTIONS AND RATIONALE

CRPAQS DATA ANALYSIS PLAN—MAJOR QUESTIONS AND RATIONALE

The overall CRPAQS data analysis plan by Watson et al. (1996) includes a series of activities for answering specific questions about the development of conceptual models for the causes of high PM in the SJV as well as examining the potential effect of emissions reductions on ambient PM concentrations and other pollutants (e.g., visibility and O_3). The specific questions are subsets of 10 major questions, the last of which is an integration step. The overall plan includes codes for applying each activity to existing data, IMS95 data, and new data. The 10 major questions in the overall plan and the reasons why they are important are presented below in their entirety. Those indicated as being partially answered by IMS95 data are included in the IMS95 data analysis plan.

1 **Measurement Methods:** How well do PM and aerosol precursor species measurement systems and related laboratory chemical analysis methods quantify mass and chemical component concentrations, including precursor species? How well do meteorological measurement systems quantify meteorological variables at the surface and aloft? Should other variables be measured, and do suitable collection and analysis methods exist for those measurements?

- **Objective:** These data analyses will determine the validity of current databases for future analyses and identify measurements needed in future routine and research monitoring networks.

- **Motivation:** Suspended particles are complex moieties, containing numerous chemical components and spanning size ranges of 0.01 to 100 μ AD. Precursor species include those emitted directly into the atmosphere (NO_x, NH_3, SO_x, and gas phase organic species) and those formed in the atmosphere (HNO_3, H_2SO_4, and secondary gas phase organic species). With regard to collecting PM mass, the major components have been identified, often accounting for over 90% of the collected mass; however, other components may provide unique insight into chemical processes or source-receptor relationships. Evaluating current methods, Chow (1995) and Watson et al. (1995a, 1995b) identify major limitations of existing monitoring technology with respect to accurately and precisely quantifying suspended particles. Chemical analysis methods also must be evaluated in conjunction with the sample collection methods, because other biases can result during the chemical analysis process as well. The validity and accuracy of measurement methods for wind speed, wind direction, temperature, RH, and solar radiation at the surface and aloft must be better understood with clearly quantified uncertainty limits; upper air measurements are particularly weak in this area. QA and QC methods must be addressed for all measured variables as well, because these methods improve confidence in the measurements, setting uncertainty bounds to each measured data point. Deviations from SOPs might also result in discrepancies. Nonroutine methods for quantifying species that are typically not measured, or for quantifying routinely measured species at higher time or wider spatial resolution, will also be examined to identify knowledge gaps that might be filled by these measurements if performed routinely or during special studies.

2 **Optimizing Network Design:** What are the optimum temporal and spatial requirements for research and routine monitoring networks?

- **Objective:** These data analyses will determine the adequacy of monitoring networks for understanding the spatial and temporal nature of aerosols in the SJV.

- **Motivation:** Current understanding of average and maximum PM concentrations is limited because of every-sixth-day sampling over 24-hour averaging times at a few sites (relative to the size of Central California). The measurement locations and sampling periods are not optimized to support air quality assessment models, quantify source contributions, determine human exposures, or call air pollution alerts. Since resources are limited, the number of sites and frequency of sampling must remain relatively small for long-term compliance monitoring, and they will still be limited during research monitoring. It is therefore important to understand the area or scale (neighborhood to regional) that a single site represents within different environment types, such as urban (motor vehicle, industrial, and residential), agricultural (field crops and livestock), rural, and background. Temporal variations in meteorology and source activities and strengths are also important for defining the frequency of sampling, especially for compliance networks

3 **Descriptive Analysis:** What are the temporal, spatial, chemical, and size characteristics of suspended particles and precursor gases in Central California?

- **Objective:** These data analyses, focusing on peak and seasonal variation, determine the spatial and temporal nature of PM, PM components, and related species.

- **Motivation:** The timing, location, chemical composition, and AD of suspended particles and the temporal and spatial characteristics of precursor gases provide a better understanding of their sources, transport properties, formation, and health effects. These descriptive analyses over many years of measurements at many locations, as well as during intensive measurement campaigns, focus subsequent analyses on time periods and sites that are most likely to provide a link to atmospheric processes and emissions sources. In this way, these analyses yield an improved understanding of the causes of elevated PM concentration in the atmosphere. These analyses also make it possible to relate the frequency of occurrence of conditions found in special studies to similar occurrences over a multiyear period.

4 **Meteorology:** What meteorological characteristics are associated with elevated PM_{10} and $PM_{2.5}$ concentrations?

- **Objective:** These descriptive analyses determine which meteorological variables are likely to affect different components of PM and indicate where meteorological measurements are needed to better understand the influence of meteorology on PM concentrations in Central California.

- **Motivation:** Meteorological variables affect the suspension, accumulation, transport, deposition, formation, and transformation of suspended particles. Current understanding suggests that the usually measured meteorological variables (temperature, wind speed, wind direction, RH, and solar radiation) are the ones needed to obtain an understanding of PM processes in the atmosphere. However, other meteorological variables not currently measured may be important (e.g., details of

cloud coverage, distribution, depth and water content of fog, solar radiation as a function of altitude and wavelength).

5 **Emissions:** What are the spatial, temporal, size, and chemical characteristics of emissions from specific sources that allow their contributions to ambient PM concentrations to be distinguished from one another? What are the specific source contributions to the 24-hour, monthly/seasonal, and annual average PM_{10} and $PM_{2.5}$ concentrations?

- **Objective:** These analyses determine where and when emissions exist, their zones of influence under different meteorological conditions, and the characteristics that allow the contributions from one emitter to be differentiated from other emitters.

- **Motivation:** Emissions are the only variable that can be affected by pollution control planning to attain standards. However, emissions characteristics are poorly known for many sources of primary particles and primary precursor gases—in particular, ammonia and organic aerosol precursor species. Often, emissions inventories or estimates do not agree with what is found in the ambient air under conditions where they should agree, thus questioning both the emissions estimates and/or the measurement methods. Little is known about the precursor emissions of secondary aerosols or how the precursor emissions relate to ambient concentrations or about the zone of influence of sources for most components of PM.

6 **Atmospheric Chemistry:** What are the chemical processes involved in PM formation? How does the presence of fog affect aerosol formation?

- **Objective:** These data analyses examine chemical processes occurring in all phases (gas, liquid, and solid) and determine relationships among aerosol precursors, aerosol species, and oxidation and acid-base chemistry that often drive gas or liquid phase species to the solid phase.

- **Motivation:** Secondary aerosols play a significant role in the valley, particularly in the fall and winter. Data analysis activities will investigate the interactions of aerosol precursors to form secondary ammonium nitrate, ammonium sulfate, and organic species and address the vertical and horizontal distributions of precursor species. In addition, the role of fog in aerosol size distributions and chemistry will be explored.

7 **Visibility:** What are the temporal and spatial characteristics of visibility-related parameters (B_{scat}, B_{abs}, total extinction), and how do the chemical and size characteristics of suspended particles affect visibility reduction in the SJV, in nearby Class I areas, and the Mojave Desert?

- **Objective:** These data analysis activities will determine where, how often, and how much visibility is reduced in the SJV, the major PM components that contribute to light extinction, and how visibility-reducing particles are transported to pristine areas.

- **Motivation:** The relationships between suspended particles and light extinction are well established (Malm, 1979; Watson and Chow, 1994), and reductions in PM_{10}, and especially the $PM_{2.5}$ fraction, are likely to cause improvements in the frequency, intensity, and duration of visibility peaks. However, the frequency and magnitude of reduced visibility in the valley is not

well understood as well as the impact of the transport of visibility-reducing pollutants to downwind pristine areas.

8 **Annual Average:** How do 24-hour average PM concentrations that exceed 24-hour PM standards impact the related current or proposed annual average standards, and what is the impact of PM values between an annual standard and its related 24-hour standard on annual average PM concentrations? Which chemical components, as a function of space and time, play the most important role in defining annual average concentrations?

- **Objective:** These data analyses will determine what factors are most important for attaining the annual average standard.
- **Motivation:** Annual average PM_{10} concentrations exceed the current federal and state PM_{10} standards in many locations in the SJV. It is likely that annual average $PM_{2.5}$ concentrations will also exceed proposed future federal $PM_{2.5}$ standards. PM_{10} or $PM_{2.5}$ annual average values are influenced by peak PM concentrations that occur during any season of the year (i.e., during any of the conceptual model scenarios described below). A determination is needed as to which periods most strongly influence the annual average and whether controlling the peak concentrations during those periods will allow compliance of current and proposed annual average standards. Also impacting the annual average PM concentrations are nonepisodic PM concentrations with values greater than the annual average standard but less than the 24-hour standard. An evaluation of the chemical components for lower PM levels is needed to improve the understanding of source and receptor relationships that impact the annual average. This determination is needed in both space and time, because sources and meteorology during different seasons will impact the annual standard differently, as will different land use patterns (such as urban versus agricultural).

9 **Other Pollutants:** What is the relationship of the PM peak and the PM precursors' peak to other pollutant issues, such as O_3?

- **Objective:** These data analyses help to determine, develop, and refine a conceptual model for the interrelationships among the various pollution issues.
- **Motivation:** Because of the recognized relationships among pollutant issues, there is now a desire at the federal level to begin an integrated approach to pollution control for O_3, PM, visibility, and regional haze. Other programs (e.g., NARSTO Continental and the SCAQS 97) also recognize these relationships and are attempting to develop integrated programs and obtaining information on O_3, PM (particularly $PM_{2.5}$), and their related precursor species. Thus, integrated studies to develop a more comprehensive conceptual model and to develop and test comprehensive air quality models must be initiated and must include air quality, meteorological, emissions, and deposition measurements.

10 **Integration and synthesis:** What has been learned, and what are the recommendations for future studies?

The intent of this task is to integrate and summarize the information from the previous nine questions, indicate what portion of each question has been answered for each phase, clearly define where knowledge gaps still exist, and recommend what studies are needed to obtain the information to fill those gaps. Analysis of existing data has already identified four types of peaks or conceptual models that are differentiated on the basis of meteorological conditions and/or major chemical components/source types. A clear and accurate conceptual model describing the causes for violations of annual average standards must still be developed. Therefore, one aspect of the synthesis effort will be to modify and refine the initial conceptual models, determine how often each occurs when PM_{10} and/or $PM_{2.5}$ concentrations are high, and develop a conceptual model for the annual average. Specific subquestions about the conceptual models to be addressed under the integration task include the following:

- How accurate and prevalent is the low wind speed (< 10 m/s) fugitive dust conceptual model?

  The highest PM_{10} concentrations are dominated by fugitive dust contributions resulting from a nearby activity, such as tilling, construction, traffic on a dirty paved road, or excessive traffic on an unpaved road. This can occur at any time during the year, but it is most prevalent during the summer and fall, when the land is dry and when agricultural and construction activities are more numerous. The impact of fugitive dust on fine particle (<2.5 μm AD) emissions occurring during this scenario will also be evaluated, because this may impact attainment of proposed PM standards using $PM_{2.5}$ as the indicator.

- How accurate and prevalent is the high wind speed (>10 m/s) fugitive dust conceptual model?

  The highest PM_{10} concentrations in this scenario are dominated by fugitive dust contributions, resulting from suspension, elevation to high altitudes, and transport by high-speed winds. These high winds often precede a frontal passage. The impact of fugitive dust on fine-particle (<2.5 μm AD) emissions occurring during this scenario will also be evaluated. Activities will also examine when wind speeds are high and no excessive 24-hour average PM_{10} concentrations are observed (i.e., values at or above the annual average standard), to determine how dust contributions might be reduced under these conditions as PM at these concentrations may impact annual average concentrations.

- How accurate and prevalent is the clear sky stagnation model?

  The clear sky stagnation model usually occurs between mid-September and mid-November, when PM consists of a combination of fugitive dust, agricultural burning, motor vehicle exhaust, and secondary ammonium nitrate contributions. Since temperatures are moderate and RHs are low, nitrate may be more influenced by nearby ammonia sources than by low-temperature equilibria.

- How accurate and prevalent is the stagnation with fog model?

  The stagnation with fog model describes elevated PM situations dominated by the $PM_{2.5}$ size fraction, especially ammonium nitrate, that occur across most of Central California during winter months (typically mid-November through mid-February). The maximum concentrations often

occur between (not during) intense fogs, though fog is present somewhere at some time nearly every day. A combination of primary and secondary contributors is needed to exceed standards.

- What drives exceedances of the annual average standard?

  Current annual average federal and state PM_{10} standards are exceeded at numerous locations in the SJV. The current model indicates that these exceedances are not dominated by peak values, but instead are the result of a sufficient number of days with concentrations above the annual average standard value but below the value of the 24-hour average standard. A combination of primary and secondary pollutants contributes to exceedances of the annual average, with crustal material dominating during dry periods and secondary species dominating during the winter when fog, rain, and stagnant conditions keep the soil-related material on the ground.

  A number of other questions will be addressed in Section 7, including imprecisions in source contribution estimates and the effect of population growth and changes in emissions caused by currently implemented or proposed emissions reduction efforts.

Appendix B

ABBREVIATIONS AND ACRONYMS

ABBREVIATIONS AND ACRONYMS

AAAR	American Associaton for Aerosol Research
APT	acoustic pulse transponder
ARB	California Air Resources Board
ASCII	American Standard Code for Information Interchange
AtmAA	Atmospheric Assessment Associates
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments
AVASP	AeroVironment Audit Software Package
AVR	AeroVironment responder
AWMA	Air and Waste Management Association
BAK	Bakersfield, ARB/District Monitoring Site
BAM	beta attenuation monitor
BAV	Bakersfield/Van Horn School
BFK	Bakersfield
CADMP	California Acid Deposition Monitoring Program
CALTRANS	California Department of Transportation
CAR	Caruthers
CASCC2	Caltech active strand cloudwater collector version 2
CE-CERT	College of Engineering Center for Environmental Research and Technology, University of California at Rierside
CEIDARS	California Emissions Inventory Data Reporting System
CHO	Cholame
CIMIS	California Irrigation Management Information System
CMB	chemical mass balance
COA	Coalinga

ABBREVIATIONS AND ACRONYMS (continued)

COH	Coefficient of Haze
COP	Corcoran core site for Fall Study
COR	Corcoran
CRPAQS	California Regional PM_{10} Air Quality Study
CRT	Caruthers
CSASP	classical scattering aerosol spectrometer probe
CSI	Campbell Scientific, Inc.
CSMCS	Carbonaceous Species Methods Comparison Study
CSU	Colorado State University
DAS	Doppler acoustic sounder
DBF	database file extension
DOAS	differential optical absorption spectroscopy
DOC	dissolved organic carbon
DOS	disk operating system
DQO	data quality objective
DRI	Desert Research Institute
DVI	dichotomous vertical impactor
DWR	Department of Water Resources
EC	elemental carbon
ELN	El Nido
EMS 95	1995 Emissions Modeling System study
EOF	empirical orthogonal function
EPA	U.S. Environmental Protection Agency
EQAP	external quality assurance program
FEI	Fresno

ABBREVIATIONS AND ACRONYMS (continued)

FEL	Fellows
FEP	Fresno/Einstein Park
FID	flame ionization detector
FRE	Fresno, ARB/District Monitoring Site
FRI	Friant
FTIR	Fourier transform infrared spectroscopy
FTP	file transfer protocol
GC	gas chromatography
GPS	global positioning system
GPT	gas phase titration
HER	Herndon
HiVol	high-volume sampler
HPLC	high-performance liquid chromatograph
HRGC	high-resolution gas chromatography
HVDVI	high-volume dichotomous vertical impactor
IC	ion chromatography
ID	inside diameter
IESL	Institute for Environmental Studies large
IMS95	1995 Integrated Monitoring Study
KRN	Kernridge
KWR	Kern Wildlife Refuge
LAP	lower atmospheric profiler
LAS	Las Vegas
LBS	Los Banos
LCV	Lindcove

ABBREVIATIONS AND ACRONYMS (continued)

LHA	Lost Hills Airport
LMOS	Lake Michigan Ozone Study
LOO	Lookout Point
MID	Midland
MKR	Mouth of the Kings River
MLD	Monitoring and Laboratory Division of the California Air Resources Board
MLR	multiple linear regression
MOUDI	micro-orifice uniform deposit impactor
MS	mass spectrometry
MTL	Mettler
NARSTO	North American Research Strategy for Tropospheric Ozone
NCAR	National Center for Atmospheric Research
NDIR	nondispersive infrared radiation
NIST	National Institute of Standards and Technology
NMD	North of Madera
NMOC	Non-methane organic carbon
NOAA	National Oceanic and Atmospheric Administration
NSMCS	Nitrogen Species Methods Comparison Study
NWS	National Weather Service
OAT	outside air temperature
OC	organic carbon
OGI	Oregon Graduate Institute
PAH	polycyclic aromatic hydrocarbon
PAN	Panoche
PCA	principal components analysis

ABBREVIATIONS AND ACRONYMS (continued)

PM	particulate matter
PM_{10}	particulate matter below 10 µm
$PM_{2.5}$	particulate matter below 2.5 µm
PM_{coarse}	particulate matter from 10 µm to 2.5 µm
PMS	Particle Measurement Systems
PSD	prevention of significant deterioration
PVA	Porterville Airport
PWR	Pixley Wildlife Refuge
QA	quality assurance
QAPP	quality assurance program plan
QC	quality control
R&P	Rupertech and Potashnic
RASS	radio acoustic sounding system
REY	Reyes Station
RFP	request for proposal
RH	relative humidity
RNO	Reno
RWP	radar wind profiler
SAQM-AERO	San Joaquin Valley Air Quality Model - Aerosol
SARMAP	SJVAQS/AUSPEX Regional Model Adaptation Project
SCAQS 97	1997 Southern California Air Quality Study
SFCASCC	size-fractionating Caltech active strand cloudwater collector
SFO	San Francisco
SFS	sequential filter sampler
SGS	sequential gas sampler

ABBREVIATIONS AND ACRONYMS (continued)

SHC	Shafter
SIM	selective ion monitoring
SIP	state implementation plan
SJV	San Joaquin Valley
SJVAQS	San Joaquin Valley Air Quality Study
SJVUAPCD	San Joaquin Valley Unified Air Pollution Control District
sonic	sonic anemometer
SOP	standard operating procedure
SPR	Springville
SR	solar radiation
SSI	size-selective inlet
STI	Sonoma Technology, Inc.
SWC	southwest of Chowchilla
TC	Total Carbon
TC/EC	Ratio of Total Carbon to Elemental Carbon
TC/OC	Ratio of Total Carbon to Organic Carbon
TD	time difference
TEH	Tehachapi
TEI	Thermo Environmental Instruments, Inc.
TEOM	tapered element oscillating microbalance
TES	Technical and Ecological Services
TNMHC	total nonmethane hydrocarbons
TNMOC	total nonmethane organic carbon
TOA	time of arrival
TOC	total organic carbon

ABBREVIATIONS AND ACRONYMS (continued)

TOG	total organic gas
TSP	total suspended particulate
TSS	technical support study
UAM	urban airshed model
UAM-AERO	aerosol version of urban airshed model IV
USGS	U.S. Geological Survey
UV	ultraviolet
VAPS	versatile air pollution sampler
VAQS	Valley Air Quality Study
VIZ	VIZ Manufacturing, Inc.
VLA	Visalia
VOC	volatile organic compound
WLC	Westland
WSO	Westside Operators
XRF	x-ray fluorescence

Appendix C

CHEMICAL SYMBOLS

CHEMICAL SYMBOLS

CH_4	methane
Cl^-	chloride
CO	carbon monoxide
CO_2	carbon dioxide
DDL	diacetyldihydrolutidine
DNPH	dinitrophenylhydrazine
Hg	mercury
HMS	hydroxymethanesulfonate
HMSA	hydroxymethanesulfonic acid
HNO_3	nitric acid
MEK	methyl ethyl ketone
N_2	Nitrogen Molecule
NaCl	sodium chloride
NH_3	ammonia
NH_4NO_3	ammonium nitrate
NH_{4+}	ammonium
Ni	nickel
NO	nitric oxide
NO_2	nitrogen dioxide
NO_{3-}	nitrate
NO_X	oxides of nitrogen or nitrogen oxides

CHEMICAL SYMBOLS (continued)

NO_y	total reactive odd-nitrogen compounds
O_3	ozone
POPA	parahydroxyphenylacetic acid
SF_6	sulfur hexafluorine
S(IV)	Sulfur in the +4 Oxidation State
S(VI)	Sulfur in the +6 Oxidation State
SO_2	sulfur dioxide
$SO_4^{=}$	sulfate
SO_x	sulfur oxides

Appendix D

UNITS OF MEASUREMENT

UNITS OF MEASUREMENT

~	approximately
<	less than
>	greater than
A	ampere
AD	aerodynamic diameter
agl	above ground level
B_{abs}	Atmospheric Absorption Coefficient
b_{scat}	atmospheric scattering coefficient
C	Celsius
cc	cubic centimeter
cm	centimeter
DC	direct current
K	Potasium
km	kilometer
km^2	square kilometer
l	liter
l/min	liters per minute
Ly/min	Langleys per minute
M	mole
mb	megabytes
mbar	milibar
megohm	mega ohm
MHz	megahertz

UNITS OF MEASUREMENT (continued)

ml	milliliter
mm	millimeter
m/s	meters per second
msl	mean sea level
μ	micron
μg/m	micrograms per meter
μl	microliter
μM	micromolar
μm	micrometer
μN	micronormal
N	Normality
nm	nanometer
pH	-log [H^+]
ppb	parts per billion
ppbv	parts per billion volume
ppm	parts per million
pptv	parts per trillion volume
PST	Pacific Standard Time
s	second
T	temperature
T_V	virtual temperature
V	volt
W	Watts