

**Appendix F**

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**SJV PM2.5 SIP Modeling Protocol**

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# San Joaquin Valley Air Pollution Control District State Implementation Plan PM2.5 Modeling Protocol

**A revision of the PM10 Modeling Protocol  
to focus on the fine fraction PM2.5 particles  
and address requirements of new guidance.**

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**Attachments:**

- A1 SJV PM Conceptual Model 1998 (64 pages) – Conceptual description of PM10 and PM2.5 episode dynamics. Performed for the CRPAQS study as part of an integrated monitoring study (IMS-95) designed to evaluate conceptual issues. Based on 1995 data collected in the San Joaquin Valley.
- A2 Modeling Domain –Domain map annotated with model basic operating parameters
- A3 Modeling Boundary Conditions – Average annual surface boundary conditions
- A4 PMF procedure (5 pages) – Methodology for the Positive Matrix Factorization approach to identify key contributing sources
- A5 Receptor Modeling Analysis Layout (4 pages) – Documentation of receptor rollback revisions and conversion from analysis of PM10 to PM2.5
- A6 Regional Air Quality Modeling Methodology – Model selection, emissions and meteorology for PM2.5 annual modeling

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## Introduction

The PM<sub>2.5</sub> State Implementation Plan (SIP) Modeling Protocol is a document that describes air quality modeling analyses performed to demonstrate that proposed control strategies are sufficient to achieve compliance with the PM<sub>2.5</sub> National Ambient Air Quality Standards (NAAQS) for protection of public health. The PM<sub>2.5</sub> SIP Modeling Protocol is a descriptive framework for the analysis to be conducted to determine the amount of reductions needed to achieve compliance with the standards. The Protocol is utilized as the plan of approach, but is considered to be a working document, subject to revision during the SIP development process in response to unexpected findings or technical issues. The modeling protocol and SIP submittal must include a description of how the analysis was conducted by providing information on the ambient monitoring data and meteorological data used, identification of the models used, the justification for model selection, assumptions involved in model application, and model input and output data. The U. S. Environmental Protection Agency (EPA) has final approval authority for the protocol, especially for any variations from standard guidance that are necessary for special circumstances that affect our selection of models and analysis approach. EPA guidance was established to provide a best general fit for the entire country but there are technical issues for San Joaquin Valley PM<sub>2.5</sub> identified by EPA, ARB and the District that vary from the national average and require special analysis or evaluation. Adjustments to the recommendations of EPA guidance are contained in the Protocol.

### **SJVAPCD PM<sub>2.5</sub> SIP Protocol Review Process**

The Protocol is released as a working document open to revision during the preparation of the PM<sub>2.5</sub> Plan. The California Air Resources Board (ARB) is performing some of the tasks within the protocol but will also act as a review agency. EPA has authority for approval of modifications from general guidance as well as review for technical aspects and completeness. The protocol is released for review by the Study Agency Policy Committee and CRPAQS (particulate studies) Technical Committee due to their specific expertise. Stakeholder and public comment should be directed to the District for attention at:

San Joaquin Valley Air Pollution Control District  
1990 E. Gettysburg Avenue  
Fresno, CA 93726

Attn: James Sweet, PM<sub>2.5</sub> Protocol

Or by electronic message to : [james.sweet@valleyair.org](mailto:james.sweet@valleyair.org)

The protocol will be released for public review no later than the release of the Draft Plan, currently scheduled for November 20, 2007. Comments on major issues that

would modify the approach extensively are requested within thirty days of release of the Protocol to accommodate modifications that may be recommended. However, the protocol will remain an open working document until the PM<sub>2.5</sub> Plan is submitted for receive and file. Improvements to methodology, minor modifications to procedures or assumptions and corrections to text may be considered until modeling is finalized to prepare the receive and file version of the plan.

## **SJVAPCD PM<sub>2.5</sub> SIP Protocol Contents**

The SJVAPCD PM<sub>2.5</sub> SIP Modeling Protocol describes the selection of general approach, methods of analysis and identification of data pertinent to support analysis. The protocol proposes comprehensive analysis combining the results of evaluations, correlated and reconciled to establish by preponderance of results (weight of evidence) that all non-attainment areas will be adequately addressed. EPA guidance recommends that models be used in a relative sense due to their uncertainties and the differences that exist between model input data and design values applicable to determine attainment. EPA directs that model results and other analysis be combined to establish a confirmed finding of attainment in a “weight of evidence” determination; particularly if the predicted future values are close to the standard. New approaches recommended by EPA guidance also require special processing of speciated data and a Speciated Modeled Attainment Test (SMAT).

The PM<sub>2.5</sub> modeling Protocol updates the PM<sub>10</sub> modeling Protocol with revisions for PM<sub>2.5</sub> air quality observations, revised and updated rollback and regional modeling and additional analysis and discussion to meet requirements of revised modeling guidance. Extensive evaluation of fine (PM<sub>2.5</sub>) particles completed as part of the PM<sub>10</sub> SIP for coarse and fine particles provides the basis for PM<sub>2.5</sub> Protocol. PM<sub>2.5</sub> evaluation will be supplemented by analysis of more recent air quality data and new regional modeling.

The PM<sub>2.5</sub> protocol includes the following component evaluations that will be combined to provide the attainment demonstration:

- **Meteorological Evaluation** The District has performed meteorological analysis of time periods related to episode conditions and the entire monitoring period of the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS). ARB and the District evaluated the meteorological factors and influences related to PM<sub>10</sub> and PM<sub>2.5</sub> episodes. This analysis is essential to identify contributing sources and factors. Supplemental analysis for additional episodes for PM<sub>2.5</sub> may be required to evaluate compliance with the revised daily standard of 35 micrograms, but the requirements for this plan are to meet the previous 65 micrograms per cubic meter standard. All sites in the District currently comply with the 65 micrograms standard.
- **Receptor Modeling** Receptor modeling is performed by the District to establish a link between observed particulates and contributing emission sources using the combined outputs and techniques of several models. Receptor analysis of observed

events and annual average particulate levels was performed by ARB in consultation with the District using the chemical mass balance (CMB) model. The output of this model is used in a receptor modeling speciated rollback model developed by the District to calculate the effect predicted emission trends and adopted and proposed control measure reductions. The District developed receptor speciated rollback as one of its earliest improvements to standard rollback modeling, with documented assumptions for the isolation of natural emissions and transport of emissions that would not be affected by the control program. The effort to remove sampling artifact and non-reactive species has been incorporated into EPA SMAT methods to correct similar issues for the regional modeling. The District added a spatial area-of-influence element to reflect the effect of controls on contributing sources more accurately. Receptor modeling methods used for the PM<sub>10</sub> SIP have been revised to evaluate PM<sub>2.5</sub> by modifying assumptions to address fine particle mechanisms and with methodology revisions to reduce uncertainties for the PM<sub>2.5</sub> annual standard. Further revision may occur to incorporate new findings of current regional modeling of secondary particle formation.

This receptor modeling method works well for analysis of directly emitted particles, but is less certain in predicting the effect of reductions of secondary precursors (gases that form particles in the air that may not produce particles in amounts directly proportional to the amount of emissions). The formation of secondary particulates has been examined with regional modeling to determine appropriate adjustments to predictions of secondary particulates. The receptor modeling approach uses direct (linear) assumptions for the connection of emissions changes to projected future contributions. This is adjusted to reflect the nonlinear chemistry associated with nitrate formation as determined by the regional model. Sulfate formation approaches linear relationship and is not adjusted for nonlinear chemistry in the receptor modeling. The expected result of linear projection is an over-prediction of future concentration. The method anticipates uncertainty in the inputs and uses the over-prediction as a safety margin for attainment modeling. The PM<sub>10</sub> receptor modeling resulted in a sizable margin of safety, projecting attainment several years after actual compliance was achieved. Comparing the results of PM<sub>2.5</sub> receptor modeling with regional modeling results and other pertinent information is important to develop a weight of evidence approach to determining when attainment will be achieved.

- **Regional Modeling** EPA guidance expects regional modeling to play a larger role in the PM<sub>2.5</sub> modeled attainment test. The primary purpose of the regional modeling for the PM<sub>2.5</sub> SIP is to provide an independent analysis of the reductions needed to achieve attainment. Regional photochemical modeling has limitations for depicting the dispersion and removal processes that occur in scales finer than the grid resolution but provide equilibrium modeling for the most significant contributions to observed mass. Regional modeling uses the known emissions inventory in a bottom-up analysis that calculates the amount of mass that should be present due to the emissions. Using the model to predict mass from a future emissions inventory provides the best assessment of nitrate and sulfate levels that can be provided. The

use of the model results in relationship to the design value provides a reasonable estimate of future PM<sub>2.5</sub> nitrate and sulfate mass components.

Regional modeling of secondary particulates has been conducted by ARB using several different data sets and models. Results of regional modeling improve understanding of particle formation rates and ratios of precursors to particle formation, particularly for nitrate particulates. These results have been used in conjunction with receptor modeling to enhance the accuracy and reliability of predicted effects of emission trends and adopted and proposed control measure reductions of secondary precursors. The first regional assessment used the Urban Airshed Model, modified to address aerosol chemistry (UAM Aero). This used the IMS-95 dataset (an early component of CRPAQS) to evaluate a monitored event of nitrate particulate formation. Regional modeling was also conducted for the later 2000-2001 CRPAQS data, providing an update to the PM<sub>10</sub> receptor modeling projections in 2006. A third round of regional modeling with the CMAQ model is currently in progress by ARB. If this provides a different regional photochemistry analysis for nitrate formation, the receptor modeling estimates for nitrates will be reviewed.

- **Statistical Analysis** PM<sub>2.5</sub> monitoring is a relatively new program; therefore the historical record of data does not provide a sufficient history to evaluate long-term trends and patterns. The District and ARB will continue evaluation of observed data using a variety of statistical methods to identify potential key factors. Results of these evaluations will be used to improve our conceptual understanding of events and may be considered to provide substantive data in the process of establishing a weight of evidence finding for attainment.
- **Technical Issues** The PM<sub>2.5</sub> receptor modeling examines the 15 microgram per cubic meter annual federal standard. When evaluating the 50-microgram annual standard for PM<sub>10</sub>, an uncertainty of one-microgram represented only a two percent variation; however, a one-microgram uncertainty in the PM<sub>2.5</sub> analysis represents a variation that is almost seven percent of the total allowed. This sets a very difficult benchmark for accuracy. Furthermore, PM<sub>2.5</sub> is not a single material but a host of different materials with both separate behaviors and dependent interactions. Although there is a solid foundation of conceptual understanding, there are many technical issues that remain open questions for continued study. The PM<sub>2.5</sub> SIP will utilize all completed analyses available at this time; however, we expect emerging technical information to enhance our understanding of observed events and subsequently improve our ability to predict future PM<sub>2.5</sub> concentrations.

Annual meteorology has seasonal components, reflected in EPA guidance recommending at least quarterly evaluation and analysis. Regional modeling is being performed for an entire year on a daily basis that can be processed to monthly or quarterly analysis as needed. Receptor modeling, with a speciated rollback approach used for the PM<sub>10</sub> SIP with monthly meteorological analyses and source identification combined into an annual composite, is being updated for the PM<sub>2.5</sub>



analysis. Prior analysis determined that fall and winter seasons are most important for PM<sub>10</sub> in the San Joaquin Valley and the winter remains the most important for PM<sub>2.5</sub> due to increased carbon and nitrate particulates.

EPA guidance acknowledges the difficulty in obtaining a data set for modeling that exactly matches the current design values and has developed a methodology to break down the modeling into the component constituents and use the model response in a relative sense to predict the reductions needed to achieve attainment. The Speciated Modeled Attainment Test (SMAT) methodology is generally applicable throughout the country but conflicts with certain important considerations critical to San Joaquin Valley Air Basin (SJVAB) assessment. Specific adjustments will be made to address technical issues specific to the SJVAB and to provide the most accurate means to reflect the effects of emission reductions.

- The SMAT methodology separates out trapped water and ammonium, sulfate and nitrate ions. This is necessary in portions of the country that are dominated by sulfate emissions. Decreases in sulfate emissions can actually cause increase in nitrate formation in areas dominated by sulfates and the associated water content of sulfates is much different than for nitrates. The SJVAB is dominated by ammonium nitrate particulates with low sulfate particulate concentrations; therefore this process is of minimal effect. ARB will determine appropriate methodology for retained water for the regional modeling. The receptor modeling will use the alternate linear estimations for trapped water. The linear approximation method for receptor modeling allows the water to remain incorporated with the ammonium sulfate and ammonium nitrate mass in the rollback method because the trapped water is assumed to be proportional to the ammonium nitrate and ammonium sulfate mass. The linear assumption avoids the need to handle trapped water as a separate calculation.
- The SMAT methodology calculates remaining mass other than the nitrates and water as organic carbon. This approach is too coarse for use for our District. The basis for this method is that most areas of the country do not have extensive control programs for geologic material (fugitive dust) or extensive emissions from carbon sources subject to direct control (residential wood combustion and agricultural burning). SMAT methodology for regional modeling will be adjusted to isolate the geologic material portion so that the effect of our control program can be reflected for its benefit in this analysis. The SMAT method may be further assessed for its adequacy for carbon. Carbon particle size growth and trapped carbon particles within nitrate and sulfate particulates that are not measured in the analysis methods are further losses not addressed by SMAT. CRPAQS modeling for particle size growth is under development but not available at this time. Metals are also not isolated by SMAT methods. For any elements not well supported by the regional model results, receptor modeling or other substantive data will be reviewed to establish a weight of evidence finding for attainment.

### **Determination of Attainment**

The Protocol provides a program of analysis to demonstrate attainment by assessing exceedance of the PM<sub>2.5</sub> standards detected by the monitoring network. The entire District is classified as nonattainment if any monitoring site is classified as nonattainment. Receptor modeling will examine all four counties that are not in compliance with the annual standard. Regional modeling will assess the entire SJVAB and will allow review of areas without monitors. Reliable conclusions are established by knowledgeable evaluation to resolve any contradictory indications that arise from the uncertainties and limitations inherent in the various methods of evaluation. Analysis procedures were selected to establish objective and reliable conclusions with the highest confidence that can be established from the best available data. The SIP control plan establishes demonstration of attainment by determining emission reductions requirements, if any, needed to achieve attainment for all counties in the District nonattainment area.

### **Attachments to the Protocol**

Attachments are provided with the Protocol to identify results of research efforts that provide analysis of key technical issues or provide supporting documentation for the protocol or the SIP.

## San Joaquin Valley Air Pollution Control District State Implementation Plan PM<sub>2.5</sub> Modeling Protocol

The San Joaquin Valley Air Pollution Control District State Implementation Plan PM<sub>2.5</sub> Modeling/Analysis Protocol (Protocol) outlines the plans of the California Air Resources Board (ARB) and the San Joaquin Valley Unified Air Pollution Control District (SJVAPCD) to develop analysis and modeling evaluation of San Joaquin Valley PM<sub>2.5</sub> to support development of control plans to achieve compliance of the federal annual and 24-hour PM<sub>2.5</sub> standards in accordance with EPA guidance for the State Implementation Plan (SIP). The Protocol is utilized as the plan of approach, but is considered to be a working document subject to revision during the SIP development process in response to unexpected findings or technical issues. The Protocol outlines the procedures and technical considerations involved in the modeling analysis for the SIP for submission to EPA Region IX for review and comment. The ARB, District and Valley transportation planning agencies jointly prepare data analyses, emissions inventories and modeling analyses to address modeling requirements for the SIP. Modeling is conducted with jointly developed input files and mutually accepted modeling assumptions.

### Goal of the Protocol

The goal of the Protocol is to determine an effective program of emission control, establishing the amount and types of emission reduction that must be implemented to achieve compliance with the federal annual and 24-hour PM<sub>2.5</sub> National Ambient Air Quality Standards (NAAQS). It should be understood that a protocol is a working document that is subject to amendment based on comments received or technical modifications developed during the analysis process. As specified in guidance: "Major steps to implement the protocol should be discussed with the appropriate U.S. EPA Regional Office(s) as they are being decided. States/Tribes may choose to update the protocol as major decisions are made concerning forthcoming analyses."

### Regulatory Requirements for Protocol Contents

"Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM<sub>2.5</sub> and Regional Haze," EPA -454/B-07-002, April 2007, provides information on the expected contents of the Model/Analysis Protocol.

"The protocol should detail and formalize the procedures for conducting all phases of the modeling study, such as describing the background and objectives for the study, creating a schedule and organizational structure for the study, developing the input data, conducting model performance evaluations, interpreting modeling results, describing procedures for using the model to demonstrate whether proposed strategies are sufficient to attain the NAAQS

and/or reasonable progress goals, and producing documentation to be submitted for EPA Regional Office review and approval.”

Guidance recommends that the protocol should:

- Identify who will help the local air quality agency undertake and evaluate the analyses needed to support a defensible demonstration (i.e., the stakeholders).

The District is in consultation with ARB and EPA and will involve the Study Agency Policy Committee and particulate study CRPAQS Technical Committee due to their expertise. The Study Agency Policy Committee has been involved in guiding particulate research for central California for more than a decade and includes representatives of several federal agencies, ARB, adjacent air Districts, stakeholders and environmental representatives. Public release will seek input from stakeholders and the general public. The District may also distribute the Protocol to additional experts identified during the review process to solicit their review or assistance.

- Identify how communication will occur to develop consensus on various issues.

Meetings with ARB on PM<sub>2.5</sub> Plan development and modeling began in March 2007. Interagency discussions involving EPA staff began in June 2007. The District intends to continue these discussions by conference calls and meetings with the agencies having approval authority for the protocol. The District will conduct conference calls or meetings as needed to facilitate comment on the Protocol and/or the Plan to advance consensus on the modeling approach. District communication pathways include mail, electronic mail, meetings and videoconference meetings, teleconferences, workshops and Governing Board meetings.

- Describe the review process applied to key steps in the demonstration

The District will request ARB, EPA, the Study Agency Policy Committee and the particulate study CRPAQS Technical Committee to provide technical review and recommendations to the District during the SIP development process. The public process will include posting of the Protocol on the District website. Comments received in writing or at workshops will be reviewed to determine if modification of the Protocol is warranted. The District will consult with ARB and EPA regarding any suggestions that propose procedures that are alternatives to recommendations of guidance prior to accepting a suggested modification. The District will review comments received and requests for meetings to determine the scope, method and frequency of discussions necessary to advance consensus on critical issues.

- Describe how changes in methods and procedures or in the protocol itself will be agreed upon and communicated with stakeholders and the appropriate U.S. EPA Regional Office.

The District will evaluate recommended revisions to the methodology of the PM2.5 modeling protocol in consultation with ARB and EPA staff. The Air Resources Board and EPA Region IX have final approval of modifications. Workshops on the PM2.5 Plan will notify the public if substantive changes to the Protocol are accepted. If there are major revisions to the Protocol, a revised version will be posted to the District web site.

The guidance document stresses that the name of the protocol has been revised in their terminology to “Modeling/Analysis Protocol” to emphasize that the protocol needs to address modeling as well as other supplemental analyses. The difficulties and uncertainty in modeling PM2.5 call for careful interpretation of results in a “weight of evidence” approach to establish reliable findings.

The San Joaquin Valley Air Pollution Control District State Implementation Plan PM2.5 Modeling Protocol (Protocol) contains the required elements, presenting data discussions first because the analysis of the data guides model selection and application. Because the Valley is a large geographic area with emissions that vary extensively by location and season, the Protocol proposes a comprehensive analysis by combining, correlating and reconciling results of a series of evaluations to establish by preponderance of results (referred to as weight of evidence) that the SIP adequately addresses all nonattainment areas. The Protocol proposes a series of evaluation elements that include: meteorological evaluation of the influence of factors affecting PM2.5 concentrations, statistical analysis of representativeness and comprehensiveness of episodes evaluated, receptor modeling to establish the contributions of major source types and predicted control effects, and regional modeling to enhance predictions of secondary particulates in the receptor modeling and to provide a separate assessment of reductions needed to achieve attainment in accordance with EPA guidance for a Speciated Modeled Attainment Test (SMAT). The Protocol also discusses how the results of the modeling will be processed to develop reliable findings and how the results will be utilized to determine the effectiveness of proposed additional controls to achieve attainment of the federal PM2.5 standards.

The following portions of this Protocol and its attachments provide the basis and justification for the approach selected for PM2.5 modeling analysis. Descriptions for each element of the analysis are provided. The conceptual model for PM2.5 source contributions is provided by a referenced attachment. The conceptual model was developed from extensive research efforts conducted for the specific purpose of understanding the dynamics of PM10 and PM2.5 in the Valley.

## **Revision of PM10 Receptor Methods to address PM2.5**

The PM2.5 receptor modeling analysis requires a minimal set of revisions from the methods used for the PM10 SIP. New guidance issued by EPA requires additional analysis and documentation. The District and ARB will ensure that all analysis and documentation requirements are met prior to final submittal. EPA Guidance also

reflects that prior modeling methodology guidance remains effective with additional clarification provided by the new Guidance. "Much of the information in U.S. EPA (1991a) regarding modeling protocols remains applicable. States/Tribes should review the 1991 guidance on protocols." The Protocol for the PM10 SIP will serve as the foundation for PM2.5 receptor modeling analysis with the following updates:

- The annual rollback analysis for PM10 events will be updated with PM2.5 speciation, using linear and aerosol modeling conducted with IMS95 and CRPAQS data for the PM10 SIP and 2006 PM10 update. The analysis will investigate the emissions reductions predicted for future years to quantify improvement. Additional reductions for new control measures will be evaluated.
- Additional regional aerosol modeling, to adjust rollback assumptions and provide supporting weight of evidence evaluation, is being conducted by ARB and is expected to provide results for evaluation after the first workshop. This modeling is being conducted with the CMAQ model.
- Newer years of data have been evaluated with CMB to examine changes in observed species after the year 2000 to evaluate progress and to provide information that might indicate revision to species mass allocation in the rollback. This effort was conducted by ARB with speciation profiles identified in consultation with the District.
- CART analysis performed for the PM10 SIP will be replaced by PMF evaluation for weight of evidence comparison. This analysis is being conducted by ARB.

### **CMB speciation for PM2.5 for Annual Rollback Modeling**

The speciation data and CMB modeling results for PM10 contain a combination of coarse and fine particles. The relationship between PM10 and PM2.5 is not proportional; therefore special evaluation is required to develop an appropriate speciation set for PM2.5 rollback analysis from the CMB modeling performed for PM10. To convert the PM10 annual CMB modeling and rollback analysis to PM2.5, the mass distribution must be replaced by PM2.5 speciation data or be calculated by other methods from the mass determined by PM10 CMB modeling.

The methodology includes the following components and considerations:

- Fresno, Kern, Kings and Tulare counties have 2005 PM2.5 design values that exceed the 15 microgram annual standard. Analysis is required for each of these counties to determine emission reductions required to achieve compliance. PM2.5 speciation measurements are collected at Bakersfield, Fresno, Modesto and Visalia. Fresno speciation data for PM2.5 covers the period used for the rollback foundation annual PM10 CMB analysis (2000-2001). Complete data for Bakersfield and Visalia is available for 2002 and thereafter, but is not available for 2000-2001. No PM2.5

speciation data is collected for Kings County; however, prior PM10 speciation analysis and CMB modeling determined that Tulare and Kings County conditions are quite similar, allowing use of Tulare County speciation data with minor adjustments. The speciation data provides total mass for annual evaluation, nitrates, sulfates, geologic material and metals

- Natural and regional background for PM2.5 cannot be directly measured and is easily identifiable or separable from other measured local contributions. Background concentrations have been established in the same manner as was used to establish background values for the PM10 rollback analysis. The significance of background levels is that such material will not be affected by the District's control efforts. Since rollback provides a linear projection of affect for reducing emissions, failure to exclude background will over-predict the effect of control efforts. All assumptions for background are now expressed as percentages of material. The background values for geologic material, nitrate and sulfate particulates have been set at 10% of the observed concentration instead of a fixed concentration. Dynamic background contributions of 10% were too high for use with PM10 due to high deposition rate and short average distance of travel; however, PM2.5 has greater travel distance and persistence in the atmosphere.
- Mobile exhaust and tire and brake wear were determined by CMB annual analysis for PM10. From the emissions inventory we are able to establish that slightly over 90% of the mobile exhaust emissions are PM2.5 and approximately half of the tire and brake wear material is PM2.5. The mass determined for PM10 rollback has been adjusted accordingly to establish a reasonable mass attribution for these sources.
- Fresno annual rollback uses a design value derived from the annual speciation data set for the years 2000 and 2001. Fresno annual rollback uses limited elements of the annual PM10 CMB analysis, performed for the year 2000 with additional data from the first quarter of 2001, to provide mass estimates for motor vehicles and tire and brake wear. The modeled contribution for motor vehicles and tire and brake wear has been adjusted by factors determined from the emissions inventory to be representative of PM2.5 material. The average of 2000 and 2001 PM2.5 speciation data is used to provide PM2.5 species for nitrates, sulfates, geologic material and unassigned (elements). Organic carbon and vegetative burning is composed organic and elemental carbon similar to the motor vehicle emissions but contains both large and small particles. The mass for organic carbon and vegetative burning has been calculated as the remainder of the annual PM2.5 speciated mass not assigned to the other categories.
- Bakersfield uses the same elements from the annual PM10 analysis but is required to use 2002 PM2.5 speciation data as the earliest complete speciation available for this purpose. Modeling may be revised or adjusted in other ways if improvements to the methodology are identified by technical evaluation.

- Visalia uses the same elements from the annual PM10 analysis but is required to use 2002 PM2.5 speciation data as the earliest complete speciation available for this purpose. Modeling may be revised or adjusted in other ways if improvements to the methodology are identified by technical evaluation.
- Kings County uses Visalia speciation data for the year 2002 to establish PM2.5 mass with adjustment to motor vehicle and tire and brake wear. The PM10 speciation data was very similar for Kings and Tulare counties in previous years, with the exception of fugitive PM10 emissions that are large particles. Motor vehicle contributions were similar to Visalia in Hanford but much less in Corcoran. Corcoran is the site that sets the design value for Kings County. Prior CMB modeling of the same event at both Visalia and Corcoran establishes an approximate ratio of the motor vehicle and tire and brake wear contributions at the two sites. Based on this evaluation, motor vehicle emissions and tire and brake wear are adjusted to 55% of the Visalia concentration to reflect the smaller urban contribution found in Corcoran.
- CMB results for Fresno and Kern provided by ARB were adjusted by 0.6 micrograms reassigned from OC to unassigned mass as found with earlier CMB modeling. Inert material is common in SJV samples and the method of assigning all unaccounted mass to OC overestimates that profile.

#### **Other Revisions to the PM10 methodology for PM2.5 for Annual Receptor Rollback Modeling**

- Cooking emissions, previously grouped with vegetative burning, are included in organic carbon associated with industrial and commercial emissions.
- The speciated rollback analysis developed by the District provides spatial projection of the area of influence of contributions. The PM10 methodology utilized different assumptions for contributions dominated by large particles and contributions dominated by fine particles PM2.5 and smaller. The PM10 travel distance assumptions for geologic and construction, tire and brake wear and unassigned mass utilized large particle assumptions which are modified for the PM2.5 analysis to be consistent with travel distance assumptions for other contributions dominated by fine particles. Methodology for the defined apportionment of mass to local and regional intrabasin transport has been adjusted from a fixed ratio to a mass weighted calculation to improve accuracy and correlation to the conceptual model.
- For categories that are comprised of directly emitted particulates and secondary aerosol (SOA) formation of organic carbon compounds a default split was used for earlier receptor modeling assuming an even split for the two pathways. CRPAQS results indicate a maximum of secondary aerosol formation of fifteen percent of the observed carbon. The rollback analysis has been revised for this updated information. The emissions linkage to SOA is ROG instead of TOG.



- Nitrate mass will be reevaluated to determine if any adjustments to linear projection are required. The 2003 analysis included nonlinearity adjustments obtained from analysis of UAM-AERO regional modeling of CRPAQS IMS-95 data. The variation of nitrate chemistry is represented by the monthly variations of CMB modeling for the annual, which inherently incorporates the variation in nitrate chemistry throughout the year. Regional modeling nitrate nonlinearity adjustments are appropriate for episode evaluation but potentially introduce a redundant penalty in the annual speciated rollback modeling. The linear projection of annualized rollback already includes assessment of the variation of nitrate formation; therefore further adjustment with modeling response may constitute a redundant adjustment. The comparison of linear model estimation to the projections with regional modeling penalties for nonlinear nitrate response will be preserved until technical discussions on this matter are complete.
- Receptor modeling will use the alternate linear estimation assumptions for trapped water. Water bonded to ammonium nitrate is approximated as equivalent to twelve percent of the mass and water bonded to ammonium sulfate is approximated as 26 percent of that mass. This method allows the water to remain incorporated in the proportional rollback because the trapped water is assumed to be proportional to the ammonium nitrate and ammonium sulfate mass. The linear assumption avoids the need to handle trapped water as a separate calculation.

## Data: Meteorological

Collecting meteorological data is as important as obtaining reliable pollutant data to predict PM<sub>2.5</sub> formation, concentration and response to change. Meteorological data is used with pollutant data to improve day-to-day meteorological and air quality forecasting, characterize the nature and extent of pollutant problems, and prepare air quality trend analyses. Evaluation of air quality model performance relies on meteorological as well as pollutant data to support modeling processes to make long-term control strategy assessments and decisions as part of the continuing air quality management process of SIP planning

Meteorology and climate play important roles in determining the levels of air pollution in the Valley. Some meteorological patterns cause higher levels of air pollution by preventing the dispersion of pollutants. Pertinent meteorological parameters include wind speed and direction, ambient atmospheric temperature and inversion layers (i.e., layers where the air temperature increases with height), and precipitation. Substantial temporal and spatial variations in PM<sub>2.5</sub> speciation profiles occur in the District in part because the types and quantities of source emissions are different in each major city and county, but meteorological factors also affect PM<sub>2.5</sub> levels, affecting emissions, secondary particle formation and dispersion. Meteorology should not be considered as

merely an input in the modeling, but rather as a key parameter to understanding and predicting PM<sub>2.5</sub> formation and concentrations.

The Protocol includes evaluation elements distinct from data selection for modeling. The evaluation and interpretation of meteorological influences is essential to reliable control strategy and trend evaluations.

- **Meteorological Evaluation** The District performed meteorological analysis of time periods related to episode conditions and the entire CRPAQS monitoring period. This information was reviewed by ARB and the District to evaluate the meteorological factors and influences related to PM<sub>10</sub> and PM<sub>2.5</sub> episodes. The analysis also establishes the representativeness of transport and formation of PM observed in historical episodes. It is essential to evaluate episodes with this perspective to identify contributing sources and factors.

Meteorological evaluation also assesses whether monitoring captured the peak values. In accordance with EPA guidelines for PM<sub>2.5</sub> monitoring, monitoring is not conducted on a daily basis at all sites. Where monitoring does not provide a daily record it may not detect the maximum value. Evaluation of meteorological factors on days that were not monitored has been compared to historical monitored days to evaluate the representativeness and comprehensiveness of monitored exceedances by examining the relative severity of the associated factors. The control program must consider conditions identified by meteorological analysis that were not captured by monitoring. The design of the control plan is sufficient to provide attainment if monitoring captures a representative sampling of the most severe days.

- **Statistical Analysis** Evaluation using a variety of accepted statistical methods will be conducted with available air monitoring data and other data identified as related to high concentrations of particulates. The process will evaluate the factors related to known and observed episodes and identify other combinations, patterns and factors not captured by monitoring that are potentially capable of causing PM<sub>2.5</sub> episodes. Results of this process provide evaluation of: sufficiency of available data to establish reliable conclusions and reasonableness of results of other methods. Results also provide verification of the completeness of the meteorological assessment to establish sufficiency of the control program to provide attainment of the annual and 24-hour standard for all predictable conditions.

Analysis of long-term trends is difficult for PM<sub>2.5</sub> due to the recent deployment of the sampling network. The mass sampling values and speciated data have been examined for implied trends and factors but the number of years of sampling reduces the ability to apply normal procedures, such as three year averaging to reduce the influence of meteorological variation. The District implemented several major programs that reduced emissions during this time period and there was a noted national and international trend of declining PM<sub>2.5</sub> and PM<sub>10</sub> values. The limited record of monitoring data makes it difficult to isolate changes resulting from controls from regional or national trends without supplemental evaluation through

receptor or photochemical modeling. The ARB is also evaluating the positive matrix factorization (PMF) model to determine if it can provide useful analysis of contributing sources. The data available is believed sufficient for the PMF approach.

### **Justification for Meteorological Evaluations**

Justification for including the meteorological evaluation elements as well as using appropriate meteorological data for modeling derives from prior analysis of meteorological influences on PM10 concentrations conducted for development of daily forecasting of air quality and prior SIP development efforts. The chemical mechanisms involved in secondary particle formation and inversion patterns affecting retention and build up of PM2.5 concentrations must be effectively interpreted to support trend evaluation, atmospheric modeling, receptor modeling and consequent control strategy evaluations and decisions.

Meteorological data are used to assess the potential for air pollution to accumulate in certain locations. Weather factors that may restrict horizontal and vertical air movement of air masses are important factors in air quality. Vertical movement of air disperses pollutants vertically while horizontal movement spreads the pollutants over a wider geographic area.

Extensive seasonal variation has been established for sources contributing to PM2.5 concentrations and atmospheric processes contributing to particle formation and retention. Analysis of filters reveals that different meteorological conditions and sources contribute to increased PM2.5 formation in the fall and winter. During the October to January period the PM2.5 concentrations undergo a shift from dominance by primary particles to dominance by secondary particles. Secondary particles are a major fraction in colder, wetter periods, but are generally less important before mid-November. Colder, frequently stagnant conditions occurring in December and January favor formation of ammonium nitrate.

### **Inversion Layers**

Inversion layers exist when the air temperature increases with elevation above the ground. The strength, altitude of, and duration of inversions determine the amount of vertical atmospheric mixing which occurs, which subsequently contributes to PM2.5 concentrations in the District. Temperature inversions occur in a stable atmosphere of warm air over cooler air hindering the upward dispersion of pollutants. Mixing ceases at the base of the inversion, which is also known as the mixing height. The Valley experiences two common types of inversions; radiation inversions and subsidence inversions.

Nocturnal cooling of an air layer near the Valley surface causes radiation inversions. It extends upward several hundred feet and occurs during the evening and early morning hours. During a radiation inversion, little vertical mixing occurs near the surface. The inversion dissipates when solar radiation warms the ground, which in turn heats the

lower layers of the atmosphere. This heating causes the surface-based inversion to weaken, and finally dissipate, which allows vertical mixing through a greater depth in the atmosphere. Inversions are more persistent (stable) during the winter months, when inversions occur from 50 to 1,000 feet above the Valley floor. Studies in the southern part of the Valley indicate more frequent and persistent early morning radiation inversions than in the northern part of the Valley due to the lack of marine air intrusion.

Subsidence inversions are caused by downward vertical motion in the atmosphere. This is common when the semi-permanent Pacific High pressure system is located off the west coast. As air descends, it warms due to compression, and as a result becomes warmer than the air beneath it. Daytime temperature inversions during the summer are usually encountered 2,000 to 2,500 feet above the Valley floor. During the summer months, the Pacific High also protects the Valley Air Basin from weather fronts, which could otherwise bring cleansing rains and help reduce PM<sub>2.5</sub> concentrations.

### **Horizontal Mixing and Dispersion**

In addition to vertical mixing, horizontal mixing, or transport, is also important in the dispersal of air pollutants. The greater the velocity of wind in the mixing layer, the greater the amount of mixing (dispersion) and transport of pollutants. Analysis of wind flow shows that during the winter months, the mean flow is through the Valley from the southeast. By mid-spring, coastal breezes enter the Valley from the northwest, which reverses the airflow pattern. By summer, the northwest to southeast airflow is at its strongest point. During the spring and summer, average wind speeds reach 6-10 mph. The frequency of very light winds (0-3 mph) does not exceed 23 percent of all spring and summer wind speeds. In the fall and winter, average wind speeds range between 5-9 mph; however, very light winds occur from 20 to 40 percent of the time.

PM<sub>2.5</sub> originating from or going to other air basins, referred to as pollutant transport, has not been definitively quantified. PM<sub>2.5</sub> readings in the SJVAB are most severe during the fall and winter periods when wind speed and direction are not conducive to interregional transport. Monitoring and speciation techniques currently available are not able to identify the origin of PM<sub>2.5</sub> sources with sufficient detail to indicate if the SJVAB is experiencing transport from outside the air basin or contributing transport of PM<sub>2.5</sub> to other air basins. Transport of some PM<sub>2.5</sub> precursors has been studied as part of ozone transport evaluation, identifying transport of ozone and ozone precursors from and to other air basins surrounding the SJVAB. The transport of ozone was documented during the summer when the highest ozone readings are more likely to occur. This transport includes precursors of ozone and PM<sub>2.5</sub>; however, the amount of PM<sub>2.5</sub> that could be generated in the SJVAB or other air basins from such transport has not been quantified. Pollution from areas outside of the Valley may or may not contribute to high PM<sub>2.5</sub> levels within the Valley.

## **Air Basin Topography**

Air pollution within the SJVAB is intensified by topographical and meteorological conditions, which hinder the movement of air, thereby reducing the dispersion and dilution of emissions. The surrounding mountain ranges block dispersion, minimizing wind flows into and out of the basin. Meteorological conditions contributing to poor air quality also includes transport of pollutants into the SJVAB from upwind sources.

The San Joaquin Valley is a major geographic, population, and agricultural subregion of California. The District, and the corresponding air basin, includes the counties of San Joaquin, Stanislaus, Merced, Madera, Fresno, Kings, Tulare, and the Valley portion of Kern County. Comprising nearly 25,000 square miles, it represents approximately 16% of the geographic area of California. The Valley has a population of over 3 million people, with major urban centers in Bakersfield, Fresno, Modesto and Stockton.

The SJVAB consists of a continuous inter-mountain valley approximately 250 miles long and averaging 80 miles wide. On the western edge is the Coast Mountain range, with peaks reaching 5,020 feet, and on the east side of the Valley is the Sierra Nevada range with some peaks exceeding 14,000 feet. The Tehachapi Mountains form the southern boundary of the Valley. This mountain range includes peaks over 6,000 feet, and contains mountain passes to the Los Angeles basin and the Mojave Desert.

## **Wind Speed and Direction**

Wind speed and direction play an important role in dispersion and transport of air pollutants. Wind at the surface and aloft can disperse pollution by vertical mixing and by transporting it to other locations. Wind speed and direction data indicate that during the summer the light and variable winds usually result from an influx of air from the Pacific Ocean through the Bay Area delta region, entering the north end of the Valley. The wind generally flows in a south-southeasterly direction through the Valley, through the Tehachapi Pass, and into the Southeast Desert Air Basin portion of Kern County. During the winter, wind speed and direction data indicate that wind occasionally varies from the south-southeasterly direction, and originates from the south end of the Valley, flowing in a north-northwesterly direction. Also during the winter months, the Valley experiences light, variable winds of less than 10 mph. Low wind speeds, combined with low lying inversion layers in the winter, create a climate conducive to the formation of high PM<sub>2.5</sub> concentrations.

## **Temperature**

The San Joaquin Valley floor is characterized by warm to hot, dry summers and cooler winters. The average mean temperature over a 30-year period is 65°F. High daily temperature readings in summer average 95°F in the Valley. The Valley also experiences mild winters; the winter average daily low temperature is 45°F. Over the last 30 years, the Valley averaged 106 days per year 90°F or hotter, and 40 days a year

100°F or hotter. The daily summer temperature variation can exceed 30°F. The Valley has an "inland Mediterranean" climate averaging over 260 sunny days per year.

### Precipitation

Precipitation in the Air Basin is confined primarily to the winter months with some occurring in late fall and early spring. Nearly 90% of the annual precipitation in the Valley falls between the months of November through April. Average annual rainfall for the entire Valley is about 10 inches on the Valley floor. There are north-south and east-west regional differences, with higher rainfall occurring in the northern and eastern parts of the Valley. Historical evaluations have correlated increased annual rainfall to decreased PM10 concentrations, reducing the fugitive emission of geological material. The impact of rainfall on PM2.5 concentrations has not been well established and will continue to be studied.

**Table 1**

### SJVAPCD Meteorological Monitoring Meteorological Parameters

Station Name	Wind Speed	Wind Direction	Outdoor Temperature	Relative Humidity	Barometric Pressure	Solar Radiation
Arvin	X	X	X	X	X	X
Bakersfield-California	X	X	X	X	X	X
Bakersfield-Golden St	X	X	X	X	X	X
Clovis-Villa	X	X	X	X	X	X
Corcoran-Patterson	X	X	X		X	
Edison-Johnson	X	X	X			
Fresno-Drummond	X	X	X		X	
Fresno-First Street	X	X	X	X	X	
Fresno-Sky Park	X	X	X			
Hanford-Irwin					X	
Madera-Pump Yard	X	X	X	X	X	X
Maricopa-Stanislaus	X	X	X		X	
Merced-Coffee	X	X	X			
Modesto-14th Street	X	X	X		X	
Oildale-Manor	X	X	X			
Parlier	X	X	X	X	X	X
Sequoia National Park-Ash Mountain	X	X	X	X		X
Sequoia National Park-Lower Kaweah	X	X	X	X		X
Shafter-Walker Street	X	X	X	X	X	X
Stockton-Hazelton	X	X	X	X		
Tracy-Airport	X	X	X		X	
Turlock-Minaret	X	X				
Visalia-Church	X	X	X		X	
Visalia-Airport	X	X	X	X	X	X

## General Weather Types and Seasons

Additional description of the general patterns and influences affecting the SJVAB is provided from excerpts from "Climate of the San Joaquin Valley Air Basin," C. D. Unger, State of California Air Resources Board, December 1974.

The climate of the San Joaquin Valley is characterized by hot, dry summers and cool, rainy winters. The most significant single control of the weather pattern is the semi-permanent subtropical high-pressure belt, often referred to as the "Pacific High". It is located off the west coast of North America and is a cell in which air descends almost continuously. The descending air is compressed, thereby raising its temperature and lowering the relative humidity. Major storms and region-wide precipitation are not typical when this pressure cell is dominant. This belt of high pressure migrates north and south seasonally. The SJVAB is under its influence almost continuously during summer months. In winter, the influence of the Pacific High is intermittent, giving rise to alternate periods of stormy, unsettled weather and periods of stable, rainless conditions. Annual rainfall totals vary from north to south, with northern counties experiencing as much as eleven inches of rainfall and southern counties experiencing as little as four inches per year. Air pollutants are generally transported from the north to the south and in a reverse flow in the winter due to these influences. Strong temperature inversions occur throughout the Valley in the summer, fall and winter.

### Summer

During summer months the Pacific High pressure cell is positioned over the ocean to the west, off the northern California coast. The clockwise flow of air around the high results in persistent northwest winds over most offshore areas and enhances northwesterly flow through the interior valleys of California. The orientation of this trough and the pressure gradient between coastal and inland stations determines the variability in the summer weather pattern. Strong onshore pressure gradients occur with deep penetration of marine air through the Carquinez Strait into the Central Valley. Cooler temperatures and stronger northwest-to-southeast winds result from this pressure distribution.

Summertime relative humidity is quite low on the Valley floor, thereby causing large diurnal temperature variations. Daytime temperatures often exceed 100°F, and nighttime temperatures can often drop into the upper 50's. Daytime temperatures are generally warmer in the southern than in the northern end of the Valley because of the persistent influx of marine air under the influence of the thermal trough. Air over Bakersfield in the southern portion of the basin comes in through the Carquinez Strait where it was originally about 65°F, but is warmed in its journey down the Valley, reaching Bakersfield with an average maximum air temperature of 98°F at the surface.

When the pressure differential between the coast and the interior is weak, stagnant conditions result and dispersion is relatively poor. This may occur when a high-pressure cell aloft is located to the east of the Valley during the summer, thereby

offsetting the westerly wind component. The thermal trough is weaker on days when Valley surface heating is minimal which also brings about poor ventilation conditions.

On a few days each summer, tropical air will be advected into the area at mid and high levels and may result in thunderstorms. The thunderstorms are most prevalent over the mountains east of the Valley floor; occasionally a vigorous thunderstorm occurs over the floor of the Valley, preceded by gusty winds and blowing dust.

## **Fall**

During the transition season of autumn, the storm belt and zone of strong Westerlies shifts southward through California, and passing frontal systems may produce showers and rain. With the approach of winter, the subtropical high shrinks and frontal passages become more vigorous. The advent of a high-pressure ridge over the area causes the formation of morning fog. As the intensity of solar radiation steadily diminishes through the fall months, daytime surface temperatures in the Valley decrease. This brings about a weakening in the thermal trough in the Valley, and the influx of marine air becomes negligible. Significant air stagnation occurs under these conditions.

## **Winter**

As the Pacific High shifts southward, it diminishes in strength, allowing storms, which develop in the Gulf of Alaska to penetrate further south. This can bring clouds and rain into the San Joaquin Valley. Occasionally, these storms will stall and deepen off the coast, and rainy weather will continue for several days. In between these periods, warm ridges may influence the Valley and there is a buildup of pressure through the interior of California. Mild, bright, sunny weather usually accompanies these synoptic types.

Another high-pressure cell that affects the San Joaquin Valley is the Great Basin High, which develops during the winter months in the area east of the Sierra Nevada. When this high is very strong, the descending winds will scour out the Valley, and dry, bright winter days result. When the high is weaker, a layer of cool, damp air is trapped in the basin and may last for a week or longer. Climatic records for Bakersfield show that heavy fog occurs on the average of 20 days each winter, with December and January having the most frequent fog. The top of the low stratus and fog is usually below 3,000 feet; therefore, higher elevations are usually clear under these conditions. Ventilation conditions below the inversion base are usually poor.

Many of the frontal systems, which pass through the San Joaquin Valley, are considerably weakened by the time they have reached this latitude. During the period when a weak, slow-moving frontal system is approaching the Valley, surface winds and vertical mixing may be light. This often results in stagnant conditions, which may persist, from 12 to 48 hours in advance of the front.

The Southern San Joaquin Valley is generally in the rain shadow of the Tehachapi and the Coast Ranges to the south and west. For this reason, the southern Valley depends



on cold, unstable, northwesterly flow for its precipitation, which produces showers following frontal passages. The northwesterly flow up the Valley is almost unobstructed by terrain barriers. The prefrontal southerly winds result in relatively little precipitation in the extreme southern end of the Valley. Winter temperatures in the San Joaquin Valley are generally mild. Temperatures will drop below freezing occasionally, but throughout the Valley, winter daytime highs are around 55°F, with lows around 35°F. Despite the latitudinal extent of the Valley, the variation of temperature in winter is small. The average January temperature is about 44°F, with little difference between the northern and southern portions of the Valley. Surface temperatures are dependent on elevation, with colder temperatures on the mountain ridges both east and west of the Valley floor.

## Spring

This is a transitional period in the San Joaquin Valley Air Basin. Cold pools of Gulf of Alaska air frequently move across the region, bringing instability and associated showery weather. In addition, the increased surface heating induces further instability. Frontal passages become steadily weaker and less frequent as summer approaches. Occasionally, in late spring, when Valley surface temperatures near the 90°F mark, vigorous updrafts along the Sierra range trigger the development of intense thunderstorms in the mountains in the afternoon and evening. Surface winds assume more of an up-valley component as the temperatures become warmer.

On infrequent occasions, a high-pressure system will stagnate over the Pacific Northwest, resulting in strong northerly winds, which may persist for several days. These are dry, desiccating winds that may cause severe crop damage, but bring generally favorable ventilation.

## Data: Atmospheric Chemistry and Sources

Secondary PM<sub>2.5</sub> species, such as ammonium nitrate, ammonium sulfate, and organic particles are formed through chemical interactions from directly emitted SO<sub>x</sub>, NO<sub>x</sub>, VOC and ammonia. Particulate sulfate and nitrate can form via both gas and aqueous phase pathways. In the aqueous phase, which is the main pathway during winter fog and cloud conditions, secondary ammonium nitrate and ammonium sulfate form when nitric acid and SO<sub>2</sub> dissolve in water droplets and then react with dissolved ammonia. Since the sulfate and nitrate ions compete with each other for the available ammonia, SO<sub>x</sub>, NO<sub>x</sub>, and ammonia must be treated as a coupled system in order to adequately understand the interactions and subsequent formation of nitrate and sulfate particles.

Source apportionment receptor modeling has identified the major contributing sources to PM<sub>2.5</sub> during the summer as motor vehicle emissions, secondary sulfate, and primary geological material from the fine particle fraction of airborne soil entrained by a variety of sources and mechanisms. Winter and spring are heavily dominated by secondary ammonium nitrate with moderate contributions of secondary sulfate, motor vehicle emissions, primary geological material and direct emission or secondary organic

aerosol identified as biomass burning from one or more source types including residential wood combustion, wild fires or agricultural burning. The secondary organic aerosol will also contain small contributions from biogenic VOC emissions.

## Data: Ambient Monitoring

The federal Clean Air Act set the health-based National Ambient Air Quality Standards (NAAQS) specifying maximum acceptable levels of pollutants and authorized the EPA to revise and enforce the standards. Primary NAAQS protect public health with an adequate margin of safety, and secondary NAAQS are established to protect public welfare (i.e. soil, crops, vegetation, animals, visibility, building materials, etc.) from known or anticipated harmful effects. The levels for the primary NAAQS for PM<sub>2.5</sub> were established as 15 µg/m<sup>3</sup> (micrograms per cubic meter) for an annual arithmetic mean averaged at each site over a three year period and 65 µg/m<sup>3</sup> for the 24-hour PM<sub>2.5</sub> standard maximum 24-hour concentration not to be exceeded more than three times in three years as determined by calculating the expected number of exceedances when monitoring at less than daily frequency. The District exceeds the federal annual PM<sub>2.5</sub> standard but meets the applicable 65 µg/m<sup>3</sup> 24-hour PM<sub>2.5</sub> standard. The 24-hour standard has been revised to 35 µg/m<sup>3</sup> but that revised standard is not applicable to this required SIP. A separate calendar has been established for preparing a plan to attain the new 24-hour standard.

To quantify our understanding of the PM<sub>2.5</sub> problem in the Valley we have evaluated PM<sub>2.5</sub> data collected by the NAMS/SLAMS network. This includes federal reference method (FRM) samplers and speciation samplers. The monitoring frequency and years of available data vary from site to site. Only four sites have speciation sampler data, provided by sampler technology that does not provide an identical match with FRM monitoring data due to differences between the sampler technologies. The differences in data availability, sampling frequency, and availability of speciation data make it difficult to establish site or District patterns and trends. The use of supplemental data collected for special studies is valuable to enrich this data for a better understanding of sources and trends.

Data collected at locations other than District and ARB operated NAMS/SLAMS continuously operated sites (referred to as off site data) is used to support analysis. Supplementary data is also used from extra monitoring equipment at continuously operated sites or off site temporary monitoring. The supplemental monitoring includes additional instruments that comply with federal reference methods (FRM), devices that provide additional readings but may not be FRM equivalent and additional equipment that measures other atmospheric parameters to support evaluation and modeling. Data from equipment or sites which do not meet SLAMS criteria will not be used to demonstrate attainment or compute the design value; however, data from additional monitoring devices and sites is used to analyze the sources and components of ambient PM samples and assess regional and local variations. This data is used to analyze

episodes of high ambient PM and determine effective controls to achieve and maintain attainment of the PM<sub>2.5</sub> NAAQS.

### **Monitoring Network Representativeness**

The EPA requires that the state and the District measure the ambient levels of air pollution to determine compliance with the NAAQS. The District and state operate the ambient monitoring network in order to comply with this mandate. Monitoring for PM<sub>2.5</sub> occurs at fourteen sites within the San Joaquin Valley Air Basin. Eleven of the fourteen sites use filter-based units and three contain a real-time particulate monitor. Of the eleven sites seven of them also contain real time particulate monitors in addition to the filter-based units. Twelve of the sites are neighborhood scale and the remaining two are urban scale. All of the PM<sub>2.5</sub> sites measure representative concentration.

Air quality monitoring for PM<sub>2.5</sub> is performed at State and Local Air Monitoring Stations (SLAMS) within the District, including National Air Monitoring Stations (NAMS) and Photochemical Assessment Monitoring Stations (PAMS). The EPA uses data from NAMS sites to develop national air quality trends.

Federal regulations require SLAMS networks to meet four basic monitoring objectives, which include:

- 1) Monitoring the highest concentration of a pollutant,
- 2) Monitoring representative concentrations in areas of high population density,
- 3) Monitoring the impact of major pollutant sources, and
- 4) Monitoring pollutant background concentrations.

The physical siting of an air monitoring station must achieve a spatial scale of representativeness that is consistent with the monitoring objective. Spatial scales of representativeness are categories of sampling exposure. The spatial scale for each site results from the physical location of the site with respect to the pollutant sources and the population or area, which is to be represented, by the monitoring site. The categories are classified by the size of the area surrounding the monitoring site which experiences uniform pollutant concentrations. The categories of spatial scale are:

- 1) Microscale - An area of uniform pollutant concentrations with a radius ranging from several meters up to 100 meters.
- 2) Middle Scale - Uniform pollutant concentrations in an area with a radius of approximately 100 meters to 0.5 kilometers.
- 3) Neighborhood Scale - Uniform pollutant concentrations in an area with a radius of approximately 0.5 to 4.0 kilometers.
- 4) Urban Scale - Citywide pollutant concentrations in an area with a radius ranging from 4 to 50 kilometers.
- 5) Regional Scale - Uniform pollutant concentrations that would be characteristic of a very large (for example, rural) area that has a radius from tens to hundreds of kilometers.

The relevant spatial scale for each site is determined from the physical location of the site with respect to the pollutant sources and the population or area represented by the monitoring site. The middle, neighborhood, and urban scales typically are used for meeting the objective of monitoring in high-density populated areas.

**Table 2****PM<sub>2.5</sub> Monitoring Stations in the San Joaquin Valley APCD**

Site Name	Sampling Interval/Frequency	Scale	Monitoring Objective	Type	Agency
Bakersfield-California *	24 Hour/Daily 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	SLAMS	CARB
Bakersfield-Golden St *	24 Hour/X 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	SLAMS	SJVAPCD
Bakersfield-Planz	24 Hour / 3 <sup>rd</sup> day	Neighborhood	Representative Concentration	SLAMS	CARB
Clovis-Villa *	24 Hour/X 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	SLAMS	SJVAPCD
Corcoran-Patterson *	24 Hour/X 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	SLAMS	SJVAPCD
Fresno-First Street *	24 Hour/Daily 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	NAMS	CARB
Fresno-Hamilton/Winery	24 Hour/X	Neighborhood	Representative Concentration	SLAMS	SJVAPCD
Huron	1 Hour/Continuous EBAM	Neighborhood	Representative Concentration	Special Purpose	SJVAPCD
Merced-2334 M Street	24 Hour/X	Neighborhood	Representative Concentration	SLAMS	SJVAPCD
Modesto-14 <sup>th</sup> Street *	24 Hour/ 3 <sup>rd</sup> day 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	SLAMS	CARB
Stockton-Hazelton *	24 Hour/ 3 <sup>rd</sup> day 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	SLAMS	CARB
Tracy Airport *	1 Hour/Continuous BAM	Urban	Representative Concentration	SLAMS	SJVAPCD
Turlock-Minaret *	1 Hour/Continuous BAM	Urban	Representative Concentration	SLAMS	SJVAPCD
Visalia-Church *	24 Hour/ 3 <sup>rd</sup> day 1 Hour/Continuous BAM	Neighborhood	Representative Concentration	SLAMS	CARB

\* In addition to any filter-based sampling that may be present, the site also contains a real time continuous particulate matter monitor.

X Sampling frequency for Apr-Sep is every six days, sampling every three days for the months of Oct-Mar.

## PM2.5 Monitoring Frequency and Network

PM2.5 scheduling is varied according to season. Sampling frequency for April-September is every six days and increases to every third day for the months of October-March. There are eleven PM2.5 Federal Reference Method (FRM) monitors located throughout the San Joaquin Valley. Federal equivalent method (FEM) sites are operated to provide hourly real time measurement of PM2.5. To supplement the PM FRM network the District monitors real-time hourly PM2.5 monitors at Bakersfield-Golden, Corcoran-Patterson, Clovis, Tracy-Airport, Huron, and Turlock. The CARB has real-time PM2.5 monitors at Bakersfield-California, Fresno-First, Modesto-14th Street, Stockton-Hazelton and Visalia-Church. The data gathered by these units is being used to document diurnal variations in particulate matter concentrations, and to document PM2.5 concentrations for Air Quality Index (AQI) reporting and forecasting.

**Table 3**

### PM 2.5 Monitoring Summary

MSA/County	Pop. (2006)	FRM Monitors	FEM Real-time Monitors
San Joaquin	668,265	1	2
Stanislaus	514,370	1	2
Merced	210,554	1	0
Madera	144,396	0	0
Fresno	799,407	3	2
Kings	129,461	1	1
Tulare	420,619	1	1
Kern	661,653	3	2

## Variations in Ambient Data

Ambient air quality samples suggest different causes of elevated PM2.5 levels at different times during the year. Ambient monitoring samples are analyzed to determine the chemical make-up of the PM2.5 collected on the filter. Air monitoring data indicates that during cooler parts of the year when meteorological conditions produce little or no air movement, secondary particulate levels (largely ammonium nitrate) are elevated in the entire Valley. Meteorological conditions have a direct influence. Extended periods of stagnant air interspersed with cold, damp, foggy conditions are conducive to the formation of particulate nitrate in amounts that are frequently the dominant component of PM2.5. Nitrates start increasing beginning in mid November to mid December and extending through February. The samples during this period are dominated by

secondary particulates. Secondary particulates are particles that are the end products of many chemical reactions that occur in the atmosphere. Precursors, the chemicals that are involved in the chemical reactions, are NO<sub>x</sub>, VOC, SO<sub>x</sub> and ammonia.

### **Diurnal Variations**

Hourly monitors allow the examination of variation throughout the day. Prior monitoring with 24-hour samples required additional evaluation to detect diurnal patterns. During a special study as part of the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study, Integrated Monitoring Study-1995 (IMS95), special monitors were run on a daily basis for approximately one month with the filters being changed every three hours. This sampling process provided data analyzed to provide information about the variability of PM<sub>10</sub> and PM<sub>2.5</sub> throughout the day. IMS95 data showed that in urban areas, the greatest concentrations of PM<sub>10</sub> during December and January are measured in the evening hours after most people arrive home from work. This data suggest that PM<sub>10</sub> could be emitted and forming at increased rates during the evening hours (6:00 PM through midnight). Other findings from CRPAQS have already been incorporated in our discussions of our understanding of seasons, episode development and patterns.

New monitoring technologies are in place to allow data to be collected in real time for the mass of PM<sub>2.5</sub> on an hourly basis at a limited number of locations. Data from federal reference monitors (FRM) does not provide a breakdown of the source material. Speciation samplers provide source identification information but the measurements are not entirely consistent with the FRM samplers due to differences between technologies.

### **Transport**

PM<sub>2.5</sub> or precursors originating from or going to other air basins, referred to as pollutant transport, has not been definitively quantified. Readings in the SJVAB are most severe during the fall and winter periods when wind speed and direction are not conducive to interregional transport. Monitoring and speciation techniques currently available are not able to identify the origin of PM<sub>2.5</sub> sources with sufficient detail to indicate if the SJVAB is experiencing transport from outside the air basin or contributing transport of PM<sub>2.5</sub> to other air basins. Transport of some PM precursors has been studied as part of ozone transport evaluation, identifying transport of ozone and ozone precursors from and to other air basins surrounding the SJVAB. The transport of ozone was documented during the summer when the highest ozone readings are more likely to occur. This transport includes precursors of ozone and PM; however, the amount of PM that could be generated in the SJVAB or other air basins from such transport has not been quantified. Pollution from areas outside of the Valley may or may not contribute to high PM<sub>2.5</sub> levels within the Valley. Regional modeling may be utilized to examine this issue in the future.

## Trend Analysis

The San Joaquin Valley Air Basin has followed the national trend of declining particulate levels since the 1980s. The national long-term trend of declining particulate values affects District PM2.5 trends. Complex meteorological phenomena make it challenging to isolate the effect of national trends to be able to clearly document the effect of improvements made in ambient air quality due to regulatory actions and voluntary emission reduction projects.

## Statistical Analysis

Evaluation using a variety of accepted statistical methods will be conducted with air monitoring data and other data identified as related to high concentrations of particulates. The evaluation will examine the factors related to known and observed episodes and assess the representativeness and comprehensiveness of monitored exceedances. Evaluation of components of the mass on PM10 and PM2.5 filters has been conducted to establish an analysis of episode sources to compare and contrast to receptor modeling with the Chemical Mass Balance (CMB) model. Results of this analysis provide evaluation of: sufficiency of available data to establish reliable conclusions to determine control program sufficiency and reasonableness of results of other methods.

## Data: Speciation Adjustments “SANDWICH”

Attainment status is dependent upon FRM measurements and concentrations. No revision to the standard is intended or implied in the following discussion of adjustments to utilize data from different instruments and models. Adjustments are made to allow the information to be handled in a compatible manner that adjusts for inherent limitations and artifacts and allows a more accurate assessment of the effect of reductions for specific chemical species. For compliance with the air quality standards, the culmination of this process must return to a comparison with the PM2.5 mass as measured by the FRM sampler.

The various physical and chemical components that contribute to the PM2.5 mass must be evaluated as separate species to determine efficient reduction methods to attain the air quality standards. However, federal reference sampler (FRM) measurements of PM2.5 are subjected to a number of known positive and negative artifacts due to the sampler construction and operational characteristics. FRM measurements do not necessarily capture the PM2.5 concentrations precisely as they exist in the atmosphere. Nitrate and semi-volatile organics can be lost from the filter during the equilibration process, and particle bound water associated with hygroscopic species like sulfate provides a positive artifact. FRM measurements may differ substantially from what is measured by speciation monitors, which have artifacts and operational characteristics of their own. Differences between samplers require careful consideration when speciated

measurements are used to apportion the bulk FRM mass to individual species and are subsequently used to assess the affect of reductions.

The FRM is the basis for attainment status; therefore, reconstructed PM<sub>2.5</sub> mass used for modeling or analysis should be based on, or be made consistent with, the composition of the mass measured by the FRM. This is accomplished by evaluation and adjustment for the differences in methods and artifacts. The method developed to speciate FRM PM<sub>2.5</sub> mass with known FRM limitations in mind is referred to as “SANDWICH” the measured sulfate, aadjusted nitrate, derived water, inferred carbonaceous mass and estimated aerosol acidity (H<sup>+</sup>). The approach serves to provide the basis for a connection between observations, modeled PM<sub>2.5</sub> concentrations, and the air quality standard. The “Sandwich” mathematical procedures are documented in the **Model: Analysis of Results** section of the Protocol

### “SANDWICH” Analysis

Confidence is high in determining the concentrations of the specific ions (sulfates, ammonium, sodium and chloride) and the measurements of directly emitted elemental and crustal components. Components represented on the FRM filter include elemental carbon, crustal material, sea salt, and passively collected mass. Nitrate filter mass loss is expected. Primary and secondary organic compounds express greater monitoring and analytical variability and the “SANDWICH” method proposes to minimize this uncertainty. Previously, analysis of speciated particulate data used measurements of ammonium, sulfate, nitrate, organic carbon and elemental carbon. The difference between the total filter mass and the sum of the five components was categorized as the “other” or unassigned mass. Other mass included the crustal [metals] components, sea salts and was used to account for any particle-bonded water, filter blank contamination and uncertainties in the data monitoring or laboratory analysis.

The “SANDWICH” method for data analysis (Frank, 2006) calculates the PM<sub>2.5</sub> organic carbon mass from the difference between the total mass of the particulate sample and the other component species. The “SANDWICH” method for PM<sub>2.5</sub> accounts for the calculation of bonded water adds a filter blank contamination term estimation of 0.5 µg/m<sup>3</sup> and substitutes organic carbon as the “others” component to be estimated from the mass difference. The “SANDWICH” method estimates ammonium (if not directly measured) and uses either a linear or polynomial empirical equation to approximate the mass of bonded water in the sample. The linear equation approximates bonded water assuming that the water content bonded to ammonium nitrate is equivalent to 12 percent of the mass and that the water bonded to ammonium sulfate is approximately equal to 26 percent of that mass. The “SANDWICH” methodology does not exclude the use of directly measured ammonium or organic carbon. Estimates of ammonium calculated using a empirical relationships (0.29 X nitrate and 0.375 X sulfate) closely matched the measured ammonium.



Speciated measurements of carbonaceous PM are considered highly uncertain. This is due to the large number of carbon compounds in the atmosphere and the measurement uncertainties associated with samplers of different configurations. In the “SANDWICH” approach, organic carbonaceous mass is calculated by difference. The sum of all non-organic carbon components may be subtracted from the FRM PM<sub>2.5</sub> mass as an estimate of organic carbon. This method has a higher uncertainty where there are known to be substantial “other” mass contributions. This is the case for the San Joaquin Valley with documented substantial levels of mass not quantified by the analysis methods. The contributions from soil, metals, plant material and other inorganic mass that are not assessed by ion measurement require that we give careful review to use of methodology that may falsely assign remaining mass to organic carbon as the contributing source. Adjusted speciated data, particularly for the quantification of organic carbon, will be carefully reviewed for its correlation to supporting information prior to accepting findings for control significance.

## Data: Design Value Determinations

**Table 4**  
**PM<sub>2.5</sub> Design Values and Attainment Test**  
 (Based on 2004-2006 monitoring data)

Monitoring Site	Attainment Tests (Sites must pass both tests)				Attainment?
	24-hour PM <sub>2.5</sub> NAAQS (Test 1)		Annual PM <sub>2.5</sub> NAAQS (Test 2)		
	Design Value ( $\mu\text{g} / \text{m}^3$ )	Within the NAAQS?	Design Value ( $\mu\text{g} / \text{m}^3$ )	Within the NAAQS?	
Stockton	41	Yes	12.9	Yes	Yes
Modesto	51	Yes	14.1	Yes	Yes
Merced	45	Yes	14.7	Yes	Yes
Fresno-1st	58	Yes	<b>16.7</b>	<b>No</b>	<b>No</b>
Fresno-Winery	59	Yes	<b>17.2</b>	<b>No</b>	<b>No</b>
Clovis	57	Yes	<b>16.2</b>	<b>No</b>	<b>No</b>
Corcoran	58	Yes	<b>17.2</b>	<b>No</b>	<b>No</b>
Visalia	56	Yes	<b>18.2</b>	<b>No</b>	<b>No</b>
Bakersfield-Golden	64	Yes	<b>18.5</b>	<b>No</b>	<b>No</b>
Bakersfield-California	62	Yes	<b>18.5</b>	<b>No</b>	<b>No</b>
Bakersfield-Planz	65	Yes	<b>18.9</b>	<b>No</b>	<b>No</b>
<b>San Joaquin Valley Air Basin</b>					<b>No</b>

Applicable EPA guidance defines the design concentration as the ambient PM<sub>2.5</sub> level for a particular site that must be reduced to the level of the NAAQS. The PM<sub>2.5</sub> annual and 24-hour NAAQS require two separate design concentrations, one for each standard per site. The District consulted with ARB and EPA staff to identify methodology for

calculating PM<sub>2.5</sub> design values. The need for consultation stems from decisions on including or excluding data that has been marked with quality assurance concerns and procedures for data substitution for missing data or data rejected due to quality assurance screening criteria established by EPA.

### **Data: Justification for Use of Off-Site Data**

Data additional to the NAMS and SLAMS monitoring data have been utilized to enhance understanding of PM sources and characteristic patterns. This information was used to assist in the development of effective control strategies for the SIP but does not qualify for use to establish design values or demonstrate attainment. Data from equipment or sites that do not meet SLAMS criteria is considered as supplementary data to be used to analyze the sources and components of ambient PM samples and to analyze episodes of high ambient PM to increase the understanding of significant factors and determine effectiveness of control strategies to achieve and maintain attainment.

Evaluation using a variety of accepted statistical methods will be conducted with air monitoring data and other data identified as related to high concentrations of particulates. Supplemental field program sample collection at District sites and other temporary monitoring locations will be included. The evaluation will examine the factors related to known and observed episodes and assess the representativeness and comprehensiveness of monitored exceedances. Evaluation of components of the mass on PM<sub>10</sub> and PM<sub>2.5</sub> filters was conducted to establish an analysis of episode sources to compare and contrast to receptor modeling with the Chemical Mass Balance (CMB) model. Results of this analysis provide evaluation of: sufficiency of available data to establish reliable conclusions, determine control program sufficiency and reasonableness of results of other evaluations.

### **California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study**

The California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study is a comprehensive public/private sector collaborative program whose goals are to provide an improved understanding of particulate matter and visibility in central California and to provide decision-makers with the tools needed to identify equitable and efficient control methods. The study is intended to evaluate both the national and State air quality standards for particulate matter smaller than 10 microns in diameter (PM<sub>10</sub>) and the new national standards for particulate matter smaller than 2.5 microns (PM<sub>2.5</sub>), which are consistently exceeded in central California. This adverse air quality compromises the health of the more than 10 million people living in the region, reduces visibility, affects crop yields, causes materials damage, and adversely impacts quality of life.

The information developed by the study allows apportionment of high PM<sub>10</sub> and PM<sub>2.5</sub> concentrations to contributing sources, thereby avoiding burdens on the regulated community from excess or ineffective control requirements. Implementation of the

control plans improved by analysis of study data will result in significant improvements in visibility, and the health and well being of the citizens of central California.

The study has involved extensive planning and preparatory research. Early projects included literature review of previous studies, development of conceptual models for episode behavior, a multi-year assessment of agricultural practice contributions to particulate emissions, a preliminary field monitoring program known as the 1995 Integrated Monitoring Study (IMS95) that evaluated our conceptual understanding of particulate episodes and evaluated monitoring equipment and data collection needs, analysis and modeling of historical and IMS95 data to improve our understanding through analysis of collected data, and emission inventory improvements.

As part of the California Regional PM10/PM2.5 Air Quality Study, an integrated field monitoring study (IMS) was conducted during the winter of 1995. The objectives of the IMS were to: 1) support the objectives of several planning studies comprising the core of the IMS, 2) develop a refined conceptual model of winter-like exceedances, and 3) provide a database for preliminary modeling and data analysis. Daily PM10 and PM2.5 monitoring with three-hour resolution were conducted at four core air quality sites located in the region between Fresno and Bakersfield. Samples were analyzed for mass, ions, elemental and organic carbon, and elemental constituents. These data were supplemented with collection of fog measurements, surface and aloft meteorological data, measurement of gaseous precursors, and saturation sampling.

Based upon extensive analysis of data from the 1995 Integrated Monitoring Study and the improved understanding gained from this and other early elements, a major field program was designed and undertaken to address fall and winter particulate matter episodic conditions as well as annual average particulate matter assessment. Input to the design of the field program was solicited from regulatory agencies, data analysts and modelers, and the research/contracting community. The objective of the field program, as with the earlier efforts, was to obtain a documented data set, with appropriate data qualification statements, suitable for characterizing the nature and causes of particulate concentrations and visibility impairment in central California by supporting modeling and data analysis activities.

The field program commenced in December of 1999 and continued through February of 2001. The monitoring consisted of 14 months of data collection throughout the San Joaquin Valley (SVJ) and surrounding regions, as well as intensive, shorter-term monitoring during fall and winter-like episodic conditions when PM10 and PM2.5 concentrations are highest. The program established an array of monitoring throughout the period, enhanced during summer months along with a companion ozone study (Central California Ozone Study) and considerably expanded during the fall and winter with intensive data gathering and monitoring operations.

Air quality sampling locations for the annual monitoring program built upon and took advantage of, the extensive existing PM10 network, as well as the new PM2.5 monitoring networks established by the Air Resources Board and local air pollution

control districts. More than 70 PM<sub>10</sub> sites and 50 PM<sub>2.5</sub> sites comprised this backbone network. Study enhancements to these networks included full scale “anchor” monitoring sites measuring gaseous and aerosol species, through both filter-based and continuous species specific methods. In addition, “satellite” monitoring sites measured aerosol species using portable PM monitors and nephelometers. Surface and aloft meteorological measurements were collected utilizing a network of surface meteorological sites, radar profilers, and sodars. A special 100-meter tower collected data at several elevations on meteorological and air quality parameters.

The fall episodic program took place in October and November of 2000 in the central portion of the San Joaquin Valley. This monitoring window corresponds to periods of historically high PM<sub>10</sub> concentrations that are dominated by geological material. Specific issues addressed in the fall monitoring program included identification of the sources of geological material, determination of the zone of influence of these sources, and development of improved data on dust suspension and deposition. The fall measurement program included neighborhood scale saturation monitoring and measurement of organic species and particle morphology.

The winter episodic field study took place during December 2000 through February 2001. PM<sub>2.5</sub> concentrations have been historically highest during the winter months, with secondary ammonium nitrate and carbonaceous material the dominant constituents. Specific issues addressed in the winter monitoring program included identification of the sources of carbonaceous material, determination of the limiting precursors for secondary PM species, surface and aloft transport and mixing mechanisms under low wind speed conditions, and the zone of influence of both primary and secondary sources of PM. The winter measurement program included an expanded set of anchor sites, and an enhanced upper-air monitoring network. On days forecasted to have the highest PM concentrations, additional special measurements were collected including organic species tracers, fog chemistry, time-of-flight mass spectrometry, and measurement of wet deposition. Special emphasis was placed on collection of continuous and species-specific particulate measurements to support both receptor and grid-based modeling approaches. Methods for collecting information on air quality aloft included use of the 100-meter tower, an elevated site in the Sierra Nevada mountains, and a remotely piloted blimp, which has been specially designed to fly under low visibility, stagnant conditions.

Episode specific and enhanced emission inventory estimation data was also collected. Several projects were targeted at collecting improved information for transportation sources, including development of updated chemical speciation profiles, and vehicle traffic counts. Other emissions projects include development of a GIS-based ammonia inventory, and collection of day-specific emissions. A comprehensive emissions inventory for the region is being developed to complement the field measurements.

The CRPAQS main field program collected extensive data during the period of December 1999 to February 2001. The data has been processed into a centralized database. Quality assurance evaluation of the data is complete. Data analysis

contracts have been completed and are in final report approval. Advanced modeling of the data collected during the field program is being conducted with experimental modeling methods. Extensive analysis of the results can be found in the report "California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Initial Data Analysis of Field Program Measurements," Chow, et al July 29, 2005. For additional reports and documents go to: <http://www.arb.ca.gov/airways/crpaqs/publications.htm>

## Model: Selection Justification

It is important to select a modeling and analysis methodology appropriate for the San Joaquin Valley (SJV) that considers and compensates for the strengths and weaknesses of available approaches. Data requirements and availability for emissions, meteorology, and air quality as well as the validity of the representation for 24-hour and annual average PM2.5 concentrations must be considered in selecting the appropriate approaches. Based upon availability of emission estimates, meteorology, and air quality data in the Valley, there are two fundamental methods available and appropriate to evaluate current and future emissions for the SIP:

- Receptor analysis with speciated-rollback using receptor chemical mass balance analysis of observed particulate levels
- Regional grid-based modeling with episode specific chemistry, photochemistry, aerosol chemistry and meteorology.

Supplemental evaluation with other modeling tools, analysis of trends and other supporting evidence are permitted to establish a weight of evidence synthesis.

If a single source is contributing to PM NAAQS violations with a significant coarse fraction and identification and emission strength of that source is known, then dispersion model, such as AEROMOD, can be used to evaluate control strategies for that source. The method can be extended to include a few major well-defined sources, but Chemical Mass Balance (CMB) modeling and wind trajectory analysis to define the probable area of contributing sources to determine the available emission source types is more informative as the number of sources increases and source strengths decrease and is therefore more appropriate for the San Joaquin Valley. Multiple sources with low to medium source strengths are the predominant cause of PM2.5 NAAQS violations in the Valley. The grid-based photochemical methods provide a stronger analysis of atmospheric chemistry for nitrate and sulfate particulates, but have difficulty with representation of organic carbon and geologic materials that are important contributing elements in the San Joaquin Valley. The receptor method developed for the SJV is able to divide the organic carbon into separate segments to assess motor vehicle, stationary source and vegetative carbon separately. This is more effective for analysis of these control programs. Receptor modeling with CMB uses linear assumptions for all portions of particulate matter. Although the CMB model can determine the total amount of a secondary aerosol species, it cannot estimate specific source contributions to secondary aerosols. Photochemical modeling incorporating aerosol chemistry to determine appropriate formation ratios and relationships will be used to assess

modeling of the secondary fraction. The regional modeling is expected to provide a more accurate assessment of sulfate and nitrate particulate controls. The combination of the two modeling packages provides the best path for the SJVAPCD.

Receptor chemical mass balance (CMB) modeling is an emission source reconciliation approach that relates ambient air quality measurements with emission sources that contribute to the air quality of a region. CMB modeling requires chemically speciated ambient data and emission source profiles. This data is available through CRPAQS field programs. Some of the chemical speciation data is collected using methods, samplers and chemical analysis supplemental to NAAQS monitoring. Although CMB modeling cannot identify the sources contributing to secondary particulate matter formation, the method can provide insight into the major contributors to primary PM<sub>2.5</sub> as well as a bounding estimate of total secondary contributions. It is important that the CMB model use current information on source profiles because changes in fuels and control technology may make older data inappropriate. Evaluation of source profile selection including temporal and spatial evaluation of available emission sources improves expected accuracy of the method. Response to control projections and trends can be estimated using projections of future emissions to provide an equivalent projection of future concentration with a technique referred to as rollback analysis. This technique assumes linear chemistry and assumes predominance by local emissions; an assumption that may not be appropriate for secondary particulate formation which is not believed to be linear in chemistry and is known to typically have larger source zones of influence. It is therefore desirable to supplement this approach with improved physical assessment parameters and assessment of aerosol chemistry involved in formation of secondary particulates.

To improve the physical representation, the receptor modeling developed by the District incorporates elements of a speciated-rollback approach. To apply this method baseline and future years must be established and emission estimates generated for various precursor gases (reactive organic gases (ROG), SO<sub>x</sub>, and NO<sub>x</sub>) and directly emitted particulate matter (soil related components, mineral dust, primary organic carbon, elemental carbon) for each episode and area to be evaluated. The inventory is developed for the region over which emissions will affect the local air quality. This requires an evaluation of the area of influence of local sources for each episode and determination of regional contributions to the observed concentrations. The District established zones of influence for local sources by meteorological analysis to enhance profile selection in receptor modeling, to identify contributing emissions that would affect the observed concentrations, to calculate intra-basin transport contributions, and to quantify the effect of controls.

Regional grid-based dispersion modeling with chemistry, photochemistry and aerosol chemistry is the most sophisticated and comprehensive approach. Regional grid-based models are theoretically the best type of model for SIP applications. These models have a fundamental advantage over speciated-rollback and CMB modeling because of their ability to simulate the integrated effects of emissions, meteorology, and air quality in time and three-dimensional space over large spatial areas. Grid models furthermore

undergo a model performance evaluation by comparing model estimates of historical concentrations with observational data. This allows an assessment of the model's reliability to estimate ambient air concentrations. However, grid-based models require extensive input data for emissions, meteorology, and air quality for each episode to be evaluated. For each episode this requires generation of an hourly-gridded-emission inventory as well as three-dimensional meteorological data, such as winds and temperatures, and hourly boundary conditions. Guidance adopted by EPA guides the use and interpretation of regional modeling results for PM<sub>2.5</sub> to address the strengths and weaknesses of the approach and the difficulties in comparing FRM monitoring data to species predicted by the model.

### **EPA Guidance on Selection of Modeling Technique**

New guidance from EPA encourages reliance on regional models, used in a relative sense in part due to uncertainties but primarily because the modeled concentrations and events are not usually the same as the design values. ARB is performing regional modeling with the specifications consistent with EPA guidance. Further adjustment and application of model results is to be performed using a procedure that breaks the results into component constituents. This processing is called the Speciated Modeled Attainment Test (SMAT). The results of this analysis are to be compared to other analyses to establish a weight of evidence determination for attainment.

Provisions of EPA guidance allow reliance on receptor modeling when it is determined to be the most suitable approach. "The chemical mass balance (CMB) model is considered to be the most advanced of the available receptor models and its use is the most acceptable for attainment demonstration purposes." "Under certain conditions, there may be no recommended dispersion model, or the recommended model may not be applicable. For example, if area sources are the dominant contributors to ambient PM<sub>10</sub> concentration, an attainment demonstration might be based on rollback of the apportionment derived from two reconciled receptor models. In such instances, the modeling approach must be approved by the appropriate Regional Office on a case-by-case basis." (EPA Guideline Document, pp 6-8, 1993). Previous efforts with receptor modeling identified 55 to 64 percent contribution in urban areas from "area" sources. Contributions from receptor modeling, attributed majority contribution from "soil," construction, and vegetative burning. This circumstance for the SJV supports selection of CMB modeling as the appropriate modeling technique in accordance with the recommendations of EPA guidance.

### **Proposed SIP Modeling Approach**

The Protocol proposes using regional modeling supported by receptor CMB modeling, PMF analysis and statistical data evaluations combined to establish weight of evidence findings.

The regional modeling will be conducted by ARB and be used to support a SMAT process. Regional aerosol modeling to evaluate secondary formation ratios has been and will be used to enhance receptor modeling, with profile selection for CMB modeling enhanced by assessment of local temporal and spatial emissions. The complementary suite of modeling methods we propose to employ for this is based on relying on CMB to analyze the episode specific primary fraction of PM<sub>2.5</sub> and regional modeling with aerosol chemistry to provide general formation ratios for secondary particulates for nitrates. CMB modeling will identify emission source contributors by chemical species, which will be used with rollback modeling to estimate reductions of emissions and emission controls needed to attain ambient standards. Rollback projection to forecast future concentrations will rely on CMB episode evaluation for primary particles and episode application of formation rate dynamics for the secondary fraction.

As previously referenced, EPA guidance allows for the attainment demonstration to be derived from two reconciled receptor models. The CMB receptor model, with modifications described in the preceding paragraph, provides the primary receptor model analysis. Reconciliation with alternative receptor evaluation will be accomplished by modeling separate species configurations for 2000 and 2005 and by PMF analysis and comparison with the regional modeling. The process of comparison will have to compare the relative abilities of the models to capture fine features and explain atmospheric dynamics. The receptor modeling represents a “top down” analysis evaluating observations to determine components. The regional modeling represents a “bottom up” method of using emission inventory information with a photochemical model to simulate the observed events. Both methods have uncertainties. The comparison is a valuable method to establish a weight of evidence finding.

### **Technical Justification for Regional Modeling Approach**

Secondary particulate matter is formed in the atmosphere from gaseous precursors. It is well established through the vast experience of ozone modeling that atmospheric chemistry of secondary particulates may be non-linear and the concentrations of nitric acid (HNO<sub>3</sub>) and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), may not be linearly proportional to the concentrations of either NO<sub>x</sub> or VOC. Therefore, an essential component of developing emissions control strategies involves gas and particle phase photochemical modeling.

### **References:**

**Primary Reference:** Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM<sub>2.5</sub> and Regional Haze,” EPA –454/B-07-002, April 2007.



**Specifically cited guidance:**

<sup>1</sup> 51.112 of 40 CFR Demonstration of adequacy. As also cited by PM10 SIP Development Guideline, EPA-450/2-86-001, June 1987, section 4.1 "Section 51.12 of 40 CFR requires that the adequacy of a control strategy for attainment and maintenance of NAAQS be demonstrated by means of a dispersion model or other appropriate procedure which is shown to be adequate and appropriate for this purpose."

<sup>2</sup> Based upon review of several guidance documents. Applicable citations include:  
Appendix W 40 CFR Part 51, sections 3.2, 7.2.2, 7.2.2d, 8.2.10, 11.1.b, 11.2.2.b approval for use of alternative models, guidance on PM modeling, limits of dispersion models, stagnation concerns, cases dispersion modeling is not acceptable, areas dominated by nontraditional sources;

PM-10 SIP Development Guideline, Supplement, June 1988, page 9 and 10 discusses treating area sources as background in dispersion modeling;

PM10 SIP Development Guideline, EPA-450/2-86-001, June 1987, page 4-10 dispersion modeling less reliable for 24 hour standard;

Example Modeling to Illustrate SIP Development for the PM10 NAAQS, EPA-450/4-87-012, May 1987, page 10 through 19 especially section 2.3.1 and section 6.4.1 small sources are added to area sources and assumed to not dominate local air quality, dispersion modeling assumes point sources to be the primary cause of Nonattainment;

Protocol for Reconciling Differences Among Receptor and Dispersion Models, EPA-450/4-87-008, March 1987, page 2 and 7, CMB is better for categories, DM for known individual sources, grouped to mimic and compare to CMB; and

EPA PM-10 Guideline Document and Appendix A & B, EPA-452/R-93-008, April 1993, especially sections 6.3, 6.5.3, and 6.7.5 predominant area sources call for rollback on receptor modeling, area sources for dispersion modeling to be based on average annual emissions – not a method intended to identify area source hot spots, reference to inappropriateness of dispersion modeling for nontraditional source in GAQM.

<sup>3</sup> PM10 SIP Development Guideline, EPA-450/2-86-001, June 1987, section 4.3.2 page 4-10. "Dispersion models are more reliable for estimating longer time-averaged concentrations (e.g., annual average) than for estimating short-term concentrations (e.g., 24-hour) at specific locations."<sup>11</sup> Reference 11 cited by this passage is Rhoads, R. G., "Accuracy of Air Quality Models," Memorandum to Air and Hazardous Division Directors, U. S. Environmental Protection Agency, Research Triangle Park, NC, July 22, 1981.

**List of applicable guidance reviewed:**

- 40 CFR Appendix V 2.2 e. (7-1-92 edition, currently in force)
- 40 CFR Appendix W (7-1-99 edition, currently in force although newer editions are under review)
- EPA PM-10 Guideline Document and Appendix A & B, EPA-452/R-93-008, April 1993
- PM-10 Serious Area SIP guidance: Final Staff Work Product, September 24, 1993

- EPA Receptor Model Technical Series, Volume III (1989 Revision), CMB7 User's Manual, EPA-450/4-90-004, January 1990
- PM-10 SIP Development Guideline, Supplement, June 1988 (OAQPS - no number)
- Response to Questions Regarding PM10 State Implementation Plan (SIP) Development, June 1988
- Chemical Mass Balance Receptor Model diagnostics, EPA-450/4-88-005, April 1988
- PM10 SIP Development Guideline, EPA-450/2-86-001, June 1987
- Example Modeling to Illustrate SIP Development for the PM10 NAAQS, EPA-450/4-87-012, May 1987
- Protocol for Applying and Validating the CMB Model, EPA-450/4-87-010, May 1987
- Protocol for Reconciling Differences Among Receptor and Dispersion Models, EPA-450/4-87-008, March 1987

## **Model: Modes Used**

### **Receptor Modeling**

The EPA Chemical Mass Balance Model version 8.0 will be used for receptor modeling. Validation procedures for use of the model outlined in the EPA "Protocol for Applying and Validating the CMB Model" will be followed. The validation process includes the following steps:

- Determine the general applicability of the CMB model to the application at hand.
- Setup the model by identifying and assembling the source types, source profiles, and receptor concentrations needed for model input. Make a preliminary application of the model to these data.
- Examine the model's statistics and diagnostics to identify potential deviations from the model assumptions.
- Evaluate problems that might result from problems with model input data.
- Make model input changes which can be justified to resolve the identified problems and re-run the model.
- Assess the stability of the model results and their consistency with the preliminary analyses.

### **Regional Modeling**

New modeling is underway conducted by ARB in accordance with Guidance published by EPA. For the SIP modeling, the plan is to use boundary conditions extracted from the MOZART (Model for Ozone and Related Chemical Tracers) global chemical transport model. ARB is conducting modeling of the entire CRPAQS 2000-2001 dataset to evaluate annual PM2.5 secondary formation. Modeling and performance analysis will be released when complete.

Previously for PM<sub>10</sub> Plans ARB modeling has included CMAQ and UAM-Aero to evaluate secondary formation of nitrate and sulfate particulates. This information was used to improve the receptor modeling representation of secondary particulates. CMAQ evaluated the CRPAQS 2000-2001 winter episode. UAM-Aero was applied to the IMS-95 winter database.

The modeling domain covers the entire SJV in current modeling. Prior CMAQ modeling covered the entire domain, but the available dataset for IMS-95 covers approximately 215 km east to west and 290 km north to south and extends from the Coastal Range to the crest of the Sierra Nevada and from the Tehachapi Mountains to Merced. The grid resolution used will be twelve kilometer or four-kilometer squares depending on performance evaluation.

Selecting a chemical mechanism that represents both NO<sub>x</sub> and VOC chemistry in detail is important because HNO<sub>3</sub> is a secondary product whose precursors are NO<sub>x</sub> and VOC and HNO<sub>3</sub> is one of the gaseous precursors to NH<sub>4</sub>NO<sub>3</sub>. Almost all chemical mechanisms available have robust NO<sub>x</sub> chemistry but the sophistication of VOC chemistry varies widely. Of the mechanisms available to ARB, those generated at the State-wide Air Pollution Research Center (SAPRC) of University of Riverside have the best representation of VOC chemistry.

## **Model: Analysis and Use Description**

The Protocol establishes an approach that combines the best information that can be developed at this time by technical and statistical analysis of meteorology and other parametric data, receptor modeling and regional modeling. PM<sub>2.5</sub> concentrations in the San Joaquin Valley vary between sites and seasons with regard to sample speciation and contributions from specific source types. Achieving attainment requires an understanding of the seasonal variations as well as average contributions. Analysis of PM<sub>2.5</sub> concentrations, chemical composition and meteorology has provided information of the temporal and spatial behavior of PM<sub>2.5</sub> in the Valley.

Based on the attainment status, model evaluation is required for the annual PM<sub>2.5</sub> standard for the southern four counties of the District, Fresno, Kern, Kings and Tulare. The regional model will evaluate the entire District for a full year of data. Receptor analysis will evaluate the required four counties for the annual standard. The annual standard is considered to be the controlling standard at this time for the PM<sub>2.5</sub> standards in effect for this Plan requirement, because the 65 microgram per cubic meter 24-hour standard has been achieved at all sites but the annual standard has not been met. Receptor modeling will not be conducted for the 24-hour standard at this time due to two key considerations:

- No speciation profile for a 24-hour episode can be identified that would be useful for receptor analysis because the starting point for the analysis will already be below the standard and emissions are decreasing. Speciated rollback receptor analysis would

not provide useful information to determine emission reductions needed to achieve this standard because the standard has already been met.

- The 65 microgram per cubic meter standard has been superceded by a new standard that has a different schedule for analysis and compliance.

### **Regional Modeling**

Regional modeling of secondary particulates is being conducted by ARB. Results of regional modeling improve understanding of particle formation rates and ratios of precursors to particle formation, particularly for nitrate particulates. Previously these results have been used in conjunction with receptor modeling to enhance the accuracy and reliability of predicted effects of emission trends and adopted and proposed control measure reductions of secondary precursors. While use of regional modeling results will continue to be used to support receptor modeling evaluation for this Plan, EPA guidance expects regional modeling to play a larger role in the PM<sub>2.5</sub> speciated modeled attainment test. The additional purpose of the regional modeling for the PM<sub>2.5</sub> SIP is to provide an independent analysis of the reductions needed to achieve attainment. However, EPA recognizes the uncertainties associated with all modeling methods and recommends comparing the results of the regional model to other evaluations to establish a weight of evidence finding that attainment will be achieved, particularly if the projected future value is close to the required standard.

### **Receptor Modeling**

Receptor modeling using the chemical mass balance model (version CMB 8) will be conducted for sites that currently do not comply with the federal annual PM<sub>2.5</sub> air quality standard. Analysis of collected air monitoring samples and information about the chemical composition of contributing sources are used to evaluate the link between observed conditions and emission sources. The District uses the results of the CMB analysis with a modified rollback approach to calculate the effect of predicted aggregate adopted and proposed control measure reductions and other predicted emission trends to establish attainment at sites noncompliant with the standard. This method works well for analysis of directly emitted particles but is less certain in predicting the effect of reductions of secondary precursors (gases that form particles in the air that may not produce particles in amounts directly proportional to the amount of emissions). Findings developed by regional modeling of secondary particulate formation rates typical to the Valley are used to account for the nonlinear secondary particle formation.

### **Receptor Simulation of Observed Particulate Concentrations**

CMB receptor modeling is an analysis method used to link observed levels of particulates to the sources of emissions grouped into source categories. The CMB model links the speciated chemical composition of the filter sample at the site to emissions inventories that represent the emissions at the time of the 24-hour observation, or represent seasonal or annual average values as appropriate. A

representative CMB analysis for the annual design value establishes the base case situation at sites that need emissions reductions to achieve attainment. Evaluation of annual concentrations by receptor modeling to determine probable source contributions must include appropriate consideration of, and adjustments for, seasonal differences in sources and seasonal differences in atmospheric conditions that affect particle origin, formation and atmospheric residence time. The relative merits of running the overall average, quarterly averages, monthly averages, or every day have been reviewed and the protocol reflects the determination that the monthly average approach is the best approach with available data for the receptor analysis.

### **Receptor Simulation of Future Particulate Concentrations**

From the CMB receptor modeling identification of emissions source contributions by chemical species, future source contributions are estimated using baseline and projected inventories with speciated rollback techniques to evaluate the effects of trends and proposed emissions reductions in future years. The speciated annual average concentrations are modeled at each site where concentrations were measured that exceeded the federal PM<sub>2.5</sub> standards and where adequate data is available to support a valid analysis.

Rollback techniques assume a proportional relationship between source categories (separable by CMB analysis) and types of emissions. Rollback projection can be applied based on either a regional (county or multi-county) emission inventory or a local emission inventory of sources located around a monitoring site to the extent that the meteorological analysis of the episode can determine an appropriate zone of influence for the local emissions and determine appropriate "background concentrations" for each chemical component.

The appropriate areal extent of sources to include in the inventory for rollback calculation is determined from evaluation of back trajectories, atmospheric residence time, pollutant deposition rates, and emission distributions and activity data. Back trajectories were calculated from two-dimensional wind fields constructed from available surface wind data. Potential sources within the area indicated by back trajectories were examined in detail and included in the rollback calculation.

Baseline and projected future year seasonal and annual emissions inventories are compared with a rollback analysis that assumes linear relationships between emissions and concentrations. To improve rollback projection of future secondary particulate levels in correspondence to future emission levels, regional modeling of formation ratios is used to establish secondary particulate nonlinear relationships.

The receptor model uses annual speciation data available for the analysis of the required counties based upon their attainment status. Two different sets of data from different years are being used which will provide a dual check of the receptor evaluation. Data from the intensive CRPAQS database for the year 2000 is used for all

four counties (Fresno, Kern, Kings, Tulare). Speciation data for 2005 will also be used for annual evaluation of Fresno and Kern. The 2000 data is modeled forward to the year 2005 to provide an equivalent starting point for all of the receptor evaluations. The 2005 species are modeled to the required future year and the relative change from 2005 to the future year is used with the applicable design value for the location in a relative reduction calculation to determine attainment or the need for additional reductions.

### **Utilization of Regional Modeling Reaction Rates for Proportional Rollback Receptor Modeling Analysis**

Results of the regional modeling performed by ARB are used to adjust the receptor modeling analysis nitrate rollback relationship. The grid-based photochemical model will provide the conversion factors of precursors into secondary particles that can be used to correct the proportional rollback analysis of secondary particulates. The conversion factors will be used in the receptor analysis of control strategies projections.

Evaluating the complexity of the relationships involved in particle formation provides information to determine whether an assumption of linear response is acceptable or whether specific ratios and factors must be used to predict the secondary particle formation. The atmospheric chemistry of secondary particle formation is complex. Particle formation from gaseous precursors (such as NO<sub>x</sub>, VOC, and NH<sub>3</sub>) is being evaluated with the best information available about atmospheric chemistry and formation rates. Particle formation rates may vary due to influences of meteorology and precursor ratios. Temperature, relative humidity, photochemical energy flux, wind speed and atmospheric mixing affect the formation rates of secondary particulates. The balance of precursors and concentrations of ozone and carbon dioxide also influence particle formation.

### **Demonstration of Attainment**

Attainment is demonstrated for each site that is projected to have future concentrations at or below the federal standards. The predicted PM<sub>2.5</sub> concentration may also be achieved with different equivalent reductions in individual sources or source categories.

EPA guidance acknowledges the difficulty in obtaining a data set for modeling that exactly matches the current design values and has developed a methodology to use the modeled response for each contributing type of PM<sub>2.5</sub>. This is necessary because the different types of materials come from different types of sources and the emissions inventories of these sources vary at different rates and have different relationships for the contribution of PM<sub>2.5</sub> mass. Therefore, the constituent materials that contribute to PM<sub>2.5</sub> are not directly additive and must be calculated separately and be added together as a final step to determine the total PM<sub>2.5</sub> mass.

The model response is used in a relative sense to predict the reductions needed to achieve attainment. Speciated Modeled Attainment Test (SMAT) calculations determine the amount of reductions needed from the major source categories to achieve compliance with federal PM<sub>2.5</sub> standards at all monitoring sites. The results of this process predict future PM<sub>2.5</sub> concentrations that would result from trends and current and proposed control programs. EPA guidance identifies how these calculations should be performed for a regional model. The District has determined applicability to the receptor analysis.

The Speciated Modeled Attainment Test (SMAT) methodology is generally applicable throughout the country but conflicts with certain important considerations critical to San Joaquin Valley Air Basin (SJVAB) assessment. Specific adjustments will be made to address technical issues specific to the SJVAB and to provide the most accurate means to reflect the effects of emission reductions.

- The receptor analysis exceeds SMAT requirements by providing extensive separation of contributing direct and secondary carbon sources. Secondary formation rate information developed by the CRPAQS program is used to quantify the secondary aerosol partition. By means of CMB model evaluation, carbon mass, along with associated trace metals and other contributions to the source signature, is divided between:
  - Motor vehicle emissions,
  - Tire and brake wear,
  - Stationary and area sources carbon mass, and
  - Vegetative burning.
- The receptor analysis exceeds SMAT requirements that recommend quarterly evaluation by performing monthly evaluation and determining that CMB performance meets standards on a monthly basis. The annual CMB modeling adjusts speciation selections for wood burning to reflect seasonal changes but otherwise uses a consistent set of speciation signatures. Performance verification demonstrates that the selected profiles are acceptable for identifying and representing the contributing sources throughout the year.
- The receptor analysis exceeds SMAT requirements by separating the contributions of geologic material from other sampling artifacts and unknowns. This is of particular importance to the SJV due to the District regulations for control of fugitive dust. The benefit of the District programs must be modeled separately from artifacts to quantify reductions appropriately.
- Receptor modeling addresses the SMAT requirement regarding trapped water in ammonium nitrates and sulfates using approved alternate linear assumptions. The linear assumption avoids the need to consider trapped water as a separate calculation. According to the linear assumption, water bonded to ammonium nitrate is approximated as equivalent to twelve percent of the ammonium nitrate mass and is proportional to the amount of ammonium nitrate particulate mass present. Water bonded to ammonium sulfate is approximated as 26 percent of that mass and is proportional to the amount of ammonium sulfate particulate mass present. Because the amount of trapped water is established by the linear assumption method as

proportional to the amount of the ammonium related mass contributions, the speciated rollback analysis processes the trapped water as an incorporated linear component of the ammonium nitrate and ammonium sulfate particulate masses and does not establish a separate calculation column.

Technical note: The SMAT methodology separates out trapped water and ammonium, sulfate and nitrate ions. This is necessary in portions of the country that are dominated by sulfate emissions. Decreases in sulfate emissions can actually cause increase in nitrate formation in areas dominated by sulfates. The associated water content of sulfates is much different than for nitrates and can require mass recalculation for areas with high sulfates. The SJVAB is dominated by ammonium nitrate particulates with low sulfate particulate concentrations; therefore this process is of minimal effect on the Valley PM2.5 mass calculation.

- The SMAT methodology calculates remaining mass other than the nitrates and water as organic carbon. This approach is too coarse for use for our District. The basis for this method is that most areas of the country do not have extensive control programs for geologic material (fugitive dust) or extensive emissions from carbon sources subject to direct control (residential wood combustion and agricultural burning). SMAT methodology for regional modeling will be adjusted to isolate the geologic material portion so that the effect of our control program can be reflected for its benefit in this analysis. The SMAT method may be further assessed for its adequacy for carbon. Carbon particle size growth and trapped carbon particles within nitrate and sulfate particulates that are not measured in the analysis methods are further losses not addressed by SMAT. CRPAQS modeling for particle size growth is under development but not available at this time. Metals are also not isolated by SMAT methods. For any elements not well supported by the regional model results, receptor modeling or other substantive data will be reviewed to establish a weight of evidence finding for attainment.

## **Model: Application Assumptions**

### **Regional and Receptor Modeling General Assumptions**

Establishing modeling assumptions and background values requires discussion of particle size, formation, composition and chemistry in accordance with current scientific understanding of particulate matter in the air. This information provides a basis for addressing issues such as natural background and regional and local contribution. Assumptions involved in model application are based on data analysis and an understanding of the physical and chemical properties, sources and behavior of particulate matter. Developing an understanding of the principle factors and influences of PM2.5 concentrations provides a greater degree of certainty that proposed control strategy reductions will have the desired and expected results and that a projection of attainment has the highest degree of reliability achievable with current information.



## Receptor Modeling Assumptions

Receptor-oriented air quality models for particulate matter in the air infer source contributions by searching for patterns formed by the chemical elements present in the ambient samples. The CMB model consists of a set of linear equations that express the ambient concentrations of chemical species as the sum of products of source compositions and source contributions. The basic model equations represent the source receptor relationship. The effective variance weighting and the error propagation are all based on physical principals. The fundamental CMB model equations have been subjected to verification and evaluation using both real and simulated data as part of the Quail Roost II Conference (Stevens and Pace, 1984). Additional verification and evaluation efforts have been undertaken by several investigators, including, but not limited to: Watson et al. (1984), DeCesar and Cooper (1982), Dzubay et al. (1984), Gerlach et al. (1982), Currie et al. (1984), Watson and Robinson (1984), Javitz and Watson (1986), Watson and Chow (1986), Henry and Kim (1986). Detailed citations for these studies are available through the ARB or from "Protocol for Applying and Validating the CMB Model," EPA-450/4-87-010, 1987.

The fundamental assumptions of the CMB model are: 1) Compositions of source emissions are constant over the period of ambient and source sampling; 2) Chemical species do not react with each other; (i.e. they add linearly) 3) All sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized; 4) The number of sources or source categories is less than the number of species; 5) The source compositions are linearly independent of each other; 6) Measurement uncertainties are random, uncorrelated, and normally distributed. Minor deviation from the assumptions does not invalidate the results. "Model evaluation studies based on synthetic data sets (Stevens and Pace, 1984; Javitz et al., 1988) show that modest departures from the above assumptions can be accepted within the context of actual applications." (Appendix A to Sonoma Technology, Inc. "PM-10 Air Quality Models for Application in the San Joaquin Valley PM-10 SIP," page 11, Cass, 1996).

CMB was designed to determine sources of primary particulate emissions from analysis of observed samples. The CMB model cannot estimate specific source contributions to secondary aerosols, but it can be used to determine the total amount of a secondary aerosol species such as ammonium nitrate or ammonium sulfate. The following conditions must be met for the CMB modeling to be applicable:

- A sufficient number of receptor samples of particulate matter have been taken with accepted sampling methods to evaluate compliance with the federal annual and 24-hour PM<sub>2.5</sub> standard.
- These samples are amenable to and have been analyzed for a variety of chemical species. Minimal analyses include concentrations of aluminum, bromine, calcium, chlorides, copper, lead, manganese, nickel, potassium, silicon, titanium, vanadium,

and zinc. Preferable additional analyses would include other elements such as arsenic, chromium, selenium, trace elements, cations, anions, elemental carbon and organic carbon.

- From the identified species, the potential source contributions can be identified and grouped into source categories of distinct chemical compositions
- From the identified species and source categories, compositions for the source categories are obtainable which represent the source profile as it is perceived at the receptor.
- The number of source types in a single application of the CMB must be fewer than the number of chemical species at the receptor measured at concentrations greater than the lower quantifiable limits. In other words, to model the source types, a sufficient number of chemical species must be collected in the sample that are measured in amounts greater than the minimum reliable detection limits for the analysis techniques used.

CMB modeling is well established as a good technique for the San Joaquin Valley and meets these requirements. "Chemical mass balance methods are known to be applicable to modeling long-term average air quality relationships for particulate matter in the San Joaquin Valley because a study of that kind has been conducted by Chow et al. (1992). Existing emissions inventories for the Valley provide a basis for identifying the most important sources that should be considered for inclusion in the model. Extensive libraries of source composition profiles exist based on source measurements made in the Valley (Houck et al., 1989) and elsewhere." (Appendix A to Sonoma Technology, Inc. "PM-10 Air Quality Models for Application in the San Joaquin Valley PM-10 SIP," Cass, 1996).

### **CMB Analysis with Linear Rollback**

CMB analysis with linear rollback can be applied to short and long term data. However, the lack of treatment of meteorology in the model affects seasonal and annual average modeling less than modeling of a 24-hour episode. If the meteorology and source activity of a specific exceedance day used for modeling is not representative of other exceedance days, the resulting analysis may not be generally representative. "If a receptor model study were undertaken for a short time period, it must be shown that the period covered was generally representative of the type of source activity and meteorology associated with exceedances observed in other receptor model studies." (EPA Guideline Document, page 6-3, 1993).

In the rollback projection, ambient pollutant concentrations are linked to CMB receptor analysis of source contributions. "The CMB model is believed to be the most reliable model for determining the source contributions of primary particles, especially for fugitive dust sources, because it does not rely on emissions rate estimates or characterization of atmospheric transport... The principle limitations of the CMB model

are that 1) it can only separate the source contributions of a small number of sources... and 2) it cannot estimate source contributions to secondary aerosol species.” (Sonoma Technology, Inc. “PM-10 Air Quality Models for Application in the San Joaquin Valley PM-10 SIP”, page 7-1, 1996). The output of the CMB receptor model will be used with speciated linear rollback; utilizing the most accurate source identification available with a reliable technique for assessing control programs.

The future year source contributions, excess of regional background concentrations, are assumed to respond in a linear relationship to controls. This means the change in concentration is expected to be in direct proportion to changes in area-wide emissions. For an inert pollutant or source contribution, such as geologic material, the rollback projection is a valid predictor of future pollutant concentrations provided that the relative spatial and temporal emissions distribution is the same before and after emissions controls have been implemented. When the rollback projection is used to predict the effects of reductions in gaseous precursor emissions on secondary aerosol constituents, chemical transformation processes are assumed to be linear. Significant departures from linearity in the atmosphere could undermine the accuracy of results; however, “Despite the clearly nonlinear nature of the fundamental chemical transformation mechanisms, there is considerable evidence from nonlinear models and observations that the conversions are approximately linear for many of the practical emissions control situations studied to date.” (Sonoma Technology, Inc. “PM-10 Air Quality Models for Application in the San Joaquin Valley PM-10 SIP”, page 4-7, 1996).

### **Factors Essential for Modeling Analysis**

Particulate matter represents a broad class of chemically and physically diverse substances. In addition to characterizations by size, particles can be described by their formation mechanism or origin, chemical composition, physical properties, and in terms of what is measured by a particular sampling technique. To be able to prepare to conduct modeling the principal factors for input data must be established. To be able to interpret the model output, a clear understanding of the influences of the principal factors must also be established. The EPA document “Air Quality Criteria for Particulate Matter” contains an extensive analysis of PM10 scientific information. Particulate matter concentrations are composed of materials from a variety of sources including:

- Secondary particle formation of ammonium nitrate,
- Elemental and organic carbon from a variety of sources including motor vehicles, wood smoke from wildfires, residential fireplaces and agricultural burning and direct and secondary carbon from fuel combustion (from vehicles, power generation, and industrial facilities),
- Secondary formation of ammonium sulfate,
- Fugitive dust including wind blown dust and road dust
- Other primary inorganic particulate matter including metals
- Particle bound water included with the sulfates and nitrates and other sampling artifacts

The properties, sources and behavior of PM<sub>2.5</sub> must be clearly understood to perform modeling. Modeling requires an understanding of the spatial influence of emissions sources and sufficient information to estimate background PM<sub>2.5</sub> levels. Apportionment of secondary PM<sub>2.5</sub> is difficult because it requires consideration of atmospheric reaction processes and rates. Current scientific knowledge is used to select and evaluate modeling methods and results.

Factors essential for modeling analysis include:

- Origin of particles, sources and properties – emissions inventories and model formulations must be comprehensive
- Chemistry and physics of atmospheric particles – modeling methods must include key technical factors to produce valid results
- Atmospheric behavior, transport and fate of airborne particles – modeling methods must include key technical factors to produce valid results
- Background concentrations to support modeling – background contributions are not responsive to District control efforts and must be modeled as an unaffected contribution to the observed mass
- **Key Findings from Scientific Studies and SJV Evaluations** – All relevant technical information should be considered including findings of scientific studies and measurements evaluated in the SJV

### **Origin of Particles, Sources and Properties**

The chemical complexity of airborne particles requires that the composition and sources of a large number of primary and secondary components be considered. Airborne particulate matter is not a single pollutant, but a mixture of many subclasses of pollutants with each subclass containing many different chemical species.

Fine particulate matter is produced mainly by the condensation of gases in the high temperature environment of combustion chambers; the condensation of atmospheric precursor gases, some of which may undergo further reactions in particles; and the condensation of low vapor pressure photochemical reaction products. Major sources of these fine mode substances are fossil fuel combustion by electric utilities, industry and motor vehicles; vegetation burning; and the smelting or other processing of metals. Major components of fine particles are: sulfate, strong acid, ammonium, nitrate, organic compounds, trace elements (including metals), elemental carbon, and water.

Primary (directly emitted) fine particles are formed from condensation of high temperature vapors during combustion. Particles formed as a result of chemical reaction of gases in the atmosphere are termed secondary particles because the direct emissions from a source are a gas that is subsequently converted to form a particle. Fine particles, both directly emitted primary particles and secondary particles formed later in the atmosphere are usually formed from gases in three ways: (1) nucleation (gas molecules coming together to form a new particle), (2) condensation of gases onto existing particles, and (3) by liquid phase reactions. Gases may dissolve in a liquid,

react with another dissolved gas, and when fog and cloud droplets evaporate, particulate matter remains, usually in the fine particle mode. Particles formed from nucleation also coagulate to form relatively larger particles. Although directly emitted particles are found in the fine fraction, particles formed secondarily from gases dominate the fine fraction.

**Table 5**

**Ambient Fine Particles**

<b>Property</b>	<b>Material</b>
Formed from:	Gases
Formed by:	Chemical reaction Nucleation Condensation Coagulation Evaporation of fog and cloud droplets in which gases have dissolved and reacted
Composed of:	Sulfate, $\text{SO}_4^-$ Nitrate, $\text{NO}_3^-$ Ammonium, $\text{NH}_4^+$ Hydrogen ion, $\text{H}^+$ Elemental carbon, Organic compounds (e.g., PAHs, PNAs) Metals, (e.g., Pb, Cd, V, Ni, Cu, Zn, Mn, Fe)
Solubility:	Particle-bound water Largely soluble, hygroscopic and deliquescent
Sources:	Combustion of coal, oil, gasoline, diesel, wood Atmospheric transformation products of $\text{NO}_x$ , $\text{SO}_2$ , and organic compounds including biogenic organic species, e.g., terpenes High temperature processes, smelters, steel mills, etc.
Atmospheric half-life:	Days to weeks
Travel distance:	100s to 1000s of km

Excerpt from source: USEPA 1996 Criteria Document, page 3-145, adapted from Wilson and Suh (1996)

**Chemistry and Physics of Atmospheric Particles**

The major chemical constituents of  $\text{PM}_{2.5}$  are sulfates, nitrates, carbonaceous compounds (both elemental and organic carbon compounds), acids, ammonium ions, metal compounds, water, and crustal materials. The amounts of these components vary from place to place and over time. Fine particulate matter is composed of sulfates,

acids, nitrates, elemental carbon, volatile organic carbon compounds, water and trace elements such as metals.

In the ambient atmosphere, fine particulate matter is mainly composed of varying proportions of six major components: sulfates, acids, nitrates, elemental carbon, organic carbon, and trace elements such as metals. A variety of transition metals and non-metals are volatilized during the combustion of fossil fuels, smelting of ores, and incineration of wastes and are emitted as fine particles or vapors that rapidly form fine particles. Varying amounts of water may also be present. Sulfates, nitrates, and some organic compounds are hygroscopic, that is, they absorb water and form solution droplets. A variety of atmospheric pollutant gases can dissolve in the water component of the particle. Some types of higher molecular weight organic compounds react with hydroxyl (OH) radicals, and olefinic compounds also react with ozone, to form oxygenated organic compounds that can condense onto existing particles. Chain agglomerates of very small elemental carbon (EC) particles are formed during combustion, such as in open-hearth fireplaces, wood stoves and diesel engines.

Several categories of organic carbon (OC) compounds are also often found in ambient air: primary anthropogenic - incomplete combustion forms hundreds of organic compounds with low enough vapor pressure to be present in the atmosphere as particles including polyaromatic hydrocarbons (PAHs); secondary anthropogenic - some organic compounds, including aromatics larger than benzene, cyclic olefins and diolefins, and other C7 (compounds with seven carbon atoms in the chain) or higher hydrocarbons react with O<sub>3</sub> or OH to form polar, oxygenated compounds with vapor pressures low enough to form particles; primary biogenic - viruses, some bacteria, and plant and/or animal cell fragments may be found in the fine mode; secondary biogenic - terpenes, C10 cyclic olefins released by plants, also react in the atmosphere to yield organic particulate matter.

Particles are designated as secondary if they form following a chemical reaction in the atmosphere which converts a gaseous precursor to a product which either has a low enough saturation vapor pressure to form a particle or reacts further to form a low saturation vapor pressure product. Fine particulate matter is derived from combustion material that has volatilized and then condensed to form primary particulate matter or from precursor gases reacting in the atmosphere to form secondary particulate matter. New fine particles are formed by the nucleation of gas phase species, and grow by coagulation (existing particles combining) or condensation (gases condensing on existing particles). Fine particles are composed of freshly generated particles, in an ultrafine or nuclei mode, and an accumulation mode, so called because particles grow into and remain in that mode.

SO<sub>2</sub>, NO<sub>x</sub>, and certain volatile organic compounds are major precursors of fine secondary particulate matter. SO<sub>2</sub> and nitrogen dioxide (NO<sub>2</sub>) react with hydroxy radical (OH) during the daytime to form sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>). Both VOC and NO<sub>x</sub> are important in the formation of free radicals that contribute to the formation of nitric acid (HNO<sub>3</sub>).

NO<sub>x</sub> is formed during combustion or any high temperature process involving air. The NO is converted to NO<sub>2</sub> by ozone (O<sub>3</sub>) or other atmospheric oxidants. During the daytime, NO<sub>2</sub> reacts with the hydroxyl radical (OH) to form HNO<sub>3</sub>. During the nighttime NO<sub>2</sub> reacts with O<sub>3</sub> and forms HNO<sub>3</sub> through a sequence of reactions involving the nitrate radical (NO<sub>3</sub>). Ammonia (NH<sub>3</sub>) reacts preferentially with H<sub>2</sub>SO<sub>4</sub>, but if sufficient NH<sub>3</sub> is available, particulate ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) will form. An example of this process is the conversion of NO<sub>2</sub> to HNO<sub>3</sub> that may react further with NH<sub>3</sub> to form particulate ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>).

SO<sub>2</sub>, mainly from combustion of fossil fuel, is oxidized in the atmosphere to form H<sub>2</sub>SO<sub>4</sub> particles that nucleate or condense on existing particles. The H<sub>2</sub>SO<sub>4</sub> may be partially or completely neutralized by reaction with NH<sub>3</sub>. Since the particles usually contain water, the actual species present are H<sup>+</sup>, HSO<sup>-</sup>, SO<sup>-</sup>, and NH<sup>+</sup>, in varying proportions depending on the amount of NH<sub>3</sub> available to neutralize the H<sub>2</sub>SO<sub>4</sub>. Strong acidity of particles is due to free H<sup>+</sup> or H<sup>+</sup> available from HSO<sup>-</sup> or H<sub>2</sub>SO<sub>4</sub>. SO<sub>2</sub> also dissolves in cloud and fog droplets where it may react with dissolved O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, or, if catalyzed by certain metals, with O<sub>2</sub>, yielding sulfuric acid or sulfates, that lead to particulate matter when the droplet evaporates.

### **Atmospheric Behavior, Transport and Fate of Airborne Particles**

Fine particles are small enough that the random forces from collisions with gas molecules largely overcome gravitational forces. Fine particles tend to follow air streams and are typically not removed by impaction. As a result, they are not easily traced back to their individual sources. Fine particles formed from accumulation processes are significantly larger than gas molecules and their diffusion velocity is low. These particles have very long half-lives in the atmosphere, travel long distances, and tend to be more uniformly distributed over large geographic areas than coarse-mode particles. Removal by dry deposition is inefficient since they do not readily diffuse through the boundary layer of still air next to surfaces. The atmospheric half-life of fine accumulation particles with respect to dry deposition is on the order of weeks; however, removal occurs when the particles absorb water, grow into cloud droplets, grow further to raindrops, and fall out as rain. This process reduces the typical atmospheric half-life to a few days. Ultrafine or nuclei-mode particles, formed by nucleation of low saturation vapor pressure substances, tend to exist as disaggregated individual particles for very short periods of time (less than minutes) in the ambient atmosphere and tend to age rapidly into larger accumulation particles that may be dispersed more widely over long distances. Secondary fine particles are formed by atmospheric transformation of gases to particles. Atmospheric transformation can take place locally during stagnations or during transport over long distances. Fine particles have very low dry deposition velocities, which contribute to their uniformity throughout the air mass. Aerosol effects on visibility and climate, through light scattering and changes in cloud microphysics, primarily arise from fine particles.

## Background Concentrations to Support Modeling

Background concentrations are an input for the speciated rollback modeling. Background estimates for each identifiable chemical species were determined based upon available data. The appropriate definition of background for speciated-rollback is the air quality concentrations at the influxes boundaries for the sites to be modeled. Existing SJV monitoring sites are intended to represent concentrations in populated areas; therefore none of the SJV criteria pollutant sites are intended to provide an ideal background site for determining natural or interregional contributions to the local air quality. Evaluation of CRPAQS sites in remote areas assisted in determination of background, with support from technical literature, especially the compilation of technical information in the EPA Criteria Documents.

Natural sources contribute to both fine and coarse particles in the atmosphere. For modeling purposes, background particulate matter includes the distribution of particulate matter from natural sources as well as anthropogenic emissions of particulate matter and precursor emissions of VOCs, NO<sub>x</sub>, and SO<sub>x</sub> from areas outside of the SJVAB. To discriminate the portion of the measured PM<sub>10</sub> affected by control strategies, emissions from outside of the SJVAB must be treated as background. If these emissions are not treated as background during the modeling process and are attributed to local emissions, control effects would be overestimated in the modeling process. This definition of background is different than would be used for health assessment studies, where background is limited to natural sources and all anthropogenic emissions are evaluated for their cumulative health impact.

Background levels of particulate matter vary by geographic location and season. The natural component of the background arises from physical processes of the atmosphere that entrain fine particles of crustal material (i.e., soil) as well as emissions of organic particles resulting from natural combustion sources such as wildfires. In addition, certain vegetation can emit fine organic aerosols as well as their precursors. The exact magnitude of the natural portion of particulate matter for a given geographic location cannot be precisely determined because they are difficult to separate from the long range transport of anthropogenic particles or precursors. Only broad estimates for longer averaging times can be developed at this time. Regional annual average natural background levels are estimated as 1-4  $\mu\text{g}/\text{m}^3$  PM<sub>2.5</sub> for the western US.

CRPAQS scientific findings on natural background assist in further review of assumptions and quantification for receptor analysis. "Non-Anthropogenic Background Collins (1998) showed that non-anthropogenic background concentrations were not a significant contributor to SJV PM<sub>2.5</sub> concentrations. Ammonium nitrate, ammonium sulfate, OM, and EC originate from anthropogenic sources in the SJV. The crustal component of PM<sub>2.5</sub> was usually less than one  $\mu\text{g}/\text{m}^3$  during winter episodes. Moreover, geological material in the SJV during winter stagnation episodes was at least partially due to agricultural activity and/or road dust. Typical annual average PM<sub>2.5</sub> concentrations at remote sites in California were on the order of 1.5 to 3.5  $\mu\text{g}/\text{m}^3$



(Motallebi et al., 2003; IMPROVE, 2003). Wintertime PM<sub>2.5</sub> concentrations at the cleanest remote sites (i.e., Lassen National Park, Redwood North Coast National Park, and Yosemite National Park) in California were 1.0 to 2.0 µg/m<sup>3</sup>. Assuming these concentrations are solely due to nonanthropogenic sources, 1.0 to 2.0 µg/m<sup>3</sup> is likely the best estimate for typical nonanthropogenic background concentrations in the SJV.” Source: BACKGROUND AND BOUNDARY CONDITIONS FOR PARTICULATE MATTER AND PRECURSORS IN THE SAN JOAQUIN VALLEY IN WINTER TECHNICAL MEMORANDUM STI-902325-2779-TM. By: Michael C. McCarthy, Hilary R. Hafner, Steven G. Brown, Fredrick W. Lurmann, Paul T. Roberts, Sonoma Technology, Inc., 1360 Redwood Way, Suite C, Petaluma, CA 94954-1169, July 29, 2005

**Natural Background Emissions: Bioaerosols** As part of establishing background concentrations, the mass contributed by living organic matter and biogenic emissions must also be considered. Ambient bioaerosols include fungal spores, pollen, bacteria, viruses, endotoxin, and animal and plant debris. Bacteria, viruses and endotoxin are mainly found attached to aerosol particles, while entities in the other categories are found as separate particles. Data for characterizing ambient concentrations and size distributions of bioaerosols are sparse.

Most fungal spores are 2 to 4 µm in size, but range in size from 1.5 µm to over 100 µm. Spores form the largest and most consistently present component of biological aerosols in ambient air. Levels vary seasonally, usually being lowest when and where snow is on the ground. Fungal spores often reach levels of 1,000 to 10,000 spores/m<sup>3</sup> during the summer months (Lacey and Dutkiewicz, 1994; Madelin, 1994) and may be as high as 100,000/m<sup>3</sup> near some anthropogenic sources (agriculture activities, compost, etc.).

Bacterial aerosol counts may range as high as 30,000 bacteria/m<sup>3</sup> downwind of sewage treatment facilities, composting areas, waterfalls from polluted rivers, or certain agricultural activities. Typical levels in urban areas range from several hundred to several thousand bacteria/m<sup>3</sup> (Lighthart and Mohr, 1994). Levels of bioaerosols (fungi and bacteria) are generally higher in urban than in rural areas (Lighthart and Stetzenbach, 1994).

Gaseous hydrocarbon emissions from plants also form secondary particulates. These particles are not identified as bioaerosols and cannot be distinguished from secondary particles from anthropogenic activities with information available at this time.

### **Key Findings from Scientific Studies and SJV Evaluations**

The CRPAQS research program has provided a wealth of scientific analysis specifically targeted to answer key questions that inform decision-making for effective reduction of particulate concentrations in the San Joaquin Valley. The findings cover a wide range of technical topics. The information may have value to other areas of the country, but in some cases the information discloses how California circumstances are different. For example: EPA methods consider a strong relationship between sulfate decrease

causing a potential and nitrate formation increase. That issue was studied for the SJV and found not to be a concern.

### **Ammonium Nitrate Sensitivity to Sulfate Levels**

Ammonium nitrate levels are sensitive to changes in sulfate under ammonia limited conditions. Sulfate and nitrate compete for ammonia when its supply is limited, and the thermodynamics indicates that ammonium preferentially associates with sulfate (forming ammonium sulfate or ammonium bisulfate) rather than nitrate under ambient conditions. Under ammonia limited conditions, reductions in sulfate may not be an effective means to reduce PM mass because ammonium sulfate removed from the aerosol is replaced with ammonium nitrate, thereby inhibiting significant reduction in PM mass.

The effects of changes in sulfate levels on ammonium nitrate in the SJV were investigated using the eight cases for which isopleth diagrams were constructed. These were cases with relative high sulfate levels for the SJV (3 to 4 mg/m<sup>3</sup>). The effects of 50 and 100 percent reduction in sulfates on ammonium nitrate concentrations are listed in Table 3-10. The results indicate ammonium nitrate concentrations are not sensitive to large changes in sulfate levels. The lack of ammonium nitrate sensitivity to sulfate in the SJV is due to the ammonia-rich conditions and the low amounts of sulfate compared to nitrate.

ANALYSIS OF ATMOSPHERIC CHEMISTRY DURING 1995 INTEGRATED MONITORING STUDY, STI-997214-1791-FR, Authors: Naresh Kumar, Frederick W. Lurmann, Sonoma Technology, Inc., Petaluma, CA; Spyros Pandis, Asif Ansari, Carnegie Mellon University, Pittsburgh, PA, July 1998

The issue of limiting precursors and secondary formation products has been extensively evaluated for the CRPAQS research program.

- Particulate NH<sub>4</sub>NO<sub>3</sub> concentrations are limited by the rate of HNO<sub>3</sub> formation, rather than by the availability of NH<sub>3</sub>
- HNO<sub>3</sub> is formed via both daytime photochemistry and aloft nighttime chemistry
- Secondary organic aerosol formation from VOC emissions may account for 15% to 25% of the total OC
- Relatively low NMOC/NO<sub>x</sub> ratios indicate the daytime photochemistry is VOC-, sunlight-, and background –ozone-limited in winter. This is a nonlinear regime for the gas-phase chemistry.

Presented to: CRPAQS Data Analysis Workshop, Sacramento, CA, March 9-10, 2004, Tasks 6.1 and 6.2: Phase Distributions Tasks 6.1 and 6.2: Phase Distributions and Secondary Formation During Winter and Secondary Formation During Winter in the San Joaquin Valley in the San Joaquin Valley, Presented by: Fred Lurmann, Siana Alcorn, Manidipa Ghosh, Sonoma Technology, Inc., Petaluma, CA

“...Comparisons of ammonia and nitric acid concentrations indicate that ammonium nitrate formation is limited by the availability of nitric acid, rather than ammonia. Time-resolved aerosol nitrate data at the surface and on a 90-m tower suggest both the daytime and nighttime nitric acid formation pathways are active, and that entrainment of

aerosol nitrate formed aloft at night may explain the spatial homogeneity of nitrate in the San Joaquin Valley.....This study's analyses suggest that reductions in NO<sub>x</sub> emissions will be more effective in reducing secondary ammonium nitrate aerosol concentrations than reductions in ammonia emissions. Reductions in VOC emissions will reduce secondary organic aerosol concentrations and may reduce ammonium nitrate. ...Comparisons of ammonia and nitric acid concentrations show that ammonia is far more abundant than nitric acid, which indicates that ammonium nitrate formation is limited by the availability of nitric acid, rather than ammonia....The results indicate ammonium nitrate formation is ultimately controlled by NO<sub>x</sub> emission rates and the other species, including VOCs and background ozone, which control the rate of NO<sub>x</sub> oxidation in winter, rather than by ammonia emissions.” *Processes Influencing Secondary Aerosol Formation in the San Joaquin Valley During Winter*, Frederick W. Lurmann, Steven G. Brown, Michael C. McCarthy, and Paul T. Roberts, Sonoma Technology, Inc., 1360 Redwood Way, Suite C., Petaluma, CA 94954

The contributing sources to PM<sub>2.5</sub> have properties that are different. This makes analysis of reductions more difficult consequently complicating the development of effective control programs. Nitrates and carbon are the two largest components and their atmospheric behavior is entirely different.

“High concentrations of PM organic carbon (OC) were spatially limited to core urban sites while high concentrations of PM ammonium nitrate were regionally distributed throughout the SJV. Concentrations of PM and its precursors were typically lower at the elevated sites surrounding the SJV than at monitoring sites located on the SJV floor....At distances more than 50 km from the urban areas, OM concentrations typically declined by a factor of three or more. Emissions of OM at the urban core are either not rapidly transported to the rural sites or are diluted too much to substantially impact rural sites. Concentrations of OM at elevated sites were comparable to concentrations at rural sites on the Valley floor....Overall, these spatial patterns of OM suggest that the impact of emissions was largely confined to the local area and OM concentrations were unevenly distributed over the duration of the episode.

The contrast in spatial variability between the ammonium nitrate and OM components of PM<sub>2.5</sub> in the SJV winter episodes provides information on the spatial extent of the production of ammonium nitrate. PM<sub>2.5</sub> OM and ammonium nitrate are both subject to the same meteorological transport conditions, yet ammonium nitrate concentrations are relatively homogeneous and OM concentrations are much higher in the urban source areas. In addition, OM and ammonium nitrate components are expected to have the majority of their mass in a similar size fraction (PM<sub>0.1</sub> to PM<sub>1</sub>) (Lighty et al., 2000; Hughes et al., 1999; Bench et al., 2002) and, therefore, the rates of removal should be approximately the same. In summary, the likely explanation for the difference in spatial variability is the spatial distribution of the emissions or precursors. Primary OM emissions occur predominantly from mobile sources and wood smoke located in urban areas. The formation of ammonium nitrate from NO<sub>x</sub> precursors (Lurmann

et al., 2004) must occur throughout the SJV to account for its spatial homogeneity.

High concentrations of PM organic carbon were spatially limited to core urban sites while high concentrations of PM ammonium nitrate were regionally distributed throughout the SJV. The regional homogeneity of ammonium nitrate concentrations coupled with the stagnant wind conditions provides evidence that production of ammonium nitrate occurs at similar rates throughout the valley. In contrast, the OC component of PM indicates that production rates were much higher in the urban areas than at rural sites.”

BACKGROUND AND BOUNDARY CONDITIONS FOR PARTICULATE MATTER AND PRECURSORS IN THE SAN JOAQUIN VALLEY IN WINTER, TECHNICAL MEMORANDUM STI-902325-2779-TM, Michael C. McCarthy, Hilary R. Hafner, Steven G. Brown, Fredrick W. Lurmann, Paul T. Roberts, Sonoma Technology, Inc., 1360 Redwood Way, Suite C, Petaluma, CA 94954-1169, July 29, 2005

Annual PM<sub>2.5</sub> is dominated by winter concentrations and urban sites have more carbon

“For most of the sites within the SJV, 50 – 75% of the annual average PM<sub>2.5</sub> concentration could be attributed to a high PM<sub>2.5</sub> period occurring from November to January. At non-urban sites, the elevated PM<sub>2.5</sub> was driven by secondary NH<sub>4</sub>NO<sub>3</sub>. The temperature, RH, and stability of the valley boundary layer in winter are all favorable for the formation of NH<sub>4</sub>NO<sub>3</sub> from its NH<sub>3</sub> and NO<sub>x</sub>, and VOC precursors. Elevated OM (organic matter, organic carbon compounds) exacerbates air quality mostly at urban sites. This is consistent with the winter use of wood fuel for home heating, as well as with traffic. This distinct spatial distribution also reflects the difference between primary and secondary aerosols.”

“The urban sites experienced much higher BC (*black carbon*) concentration than non-urban sites. This suggested that BC particles were closely related to urban sources such as traffic, RWC, and cooking. Multiple spikes of hourly BC were frequently observed especially at urban sites, suggesting that those BC originated from nearby urban sources. At all urban sites, the morning BC peak was found around 0600 to 0800 PST and the large evening peak around 2000 PST prolonged through the midnight and early morning next day. Non-urban sites did not exhibit any distinct diurnal patterns.”

Initial Data Analysis of Field Program Measurements, DRI Document No. 2497, July 29, 2005 Judith C. Chow, L.-W. Antony Chen, Douglas H. Lowenthal, Prakash Doraiswamy, Kihong Park, Steven D. Kohl, Dana L. Trimble, John G. Watson, DESERT RESEARCH INSTITUTE, Division of Atmospheric Sciences, 2215 Raggio Parkway, Reno, NV 89512

## Utilization of Application Assumptions

Based upon review of the preceding information, default estimates of regional and background contributions have been established for use with the speciated receptor rollback modeling. Particle dynamics, physics, atmospheric behavior and fate establish background and regional contribution estimates. These estimates are assumptions considered in speciated rollback calculations to prevent overstating the probable effect of controls. If such assumptions were not utilized, the analysis would link all of the observed particulate to local quantified sources. This would overstate the predicted effectiveness of controls. The assumptions for background and regional components should not be set to the lowest possible level, which would overstate control effectiveness and potentially lead to a failure to attain or to the highest possible contribution, which would underestimate control effectiveness and require implementation of excessive control measures.

## Model: Input Data

### Emissions Estimates to Support Modeling

The District and ARB maintain annual emission inventories of permitted emissions and estimations of mobile source, area source and naturally occurring emissions. To achieve the greatest possible reliability and accuracy of evaluations and predictions, the emission inventories must be adjusted for modeling to examine specific episodes and seasons for current and future years. The modeling inventory is used as a tool to evaluate control measures, the impact of rulemaking, receptor modeling reconciliation, and projection to future years. The SIP emission limits should be based on the NAAQS (annual or 24-hour) that results in the most stringent control requirements. Specific control measures designed to achieve the required emission limitation must then be implemented in the SIP. The emissions inventories prepared to correlate with observed values for modeling are called baseline inventories. Projections of future year conditions with additional controls are referred to as future year inventories. Modeling is used to determine the amount of additional reductions, if any, required to achieve attainment for the projected future year.

## Regional Modeling

ARB is providing regional modeling for annual PM<sub>2.5</sub> by modeling every day of the year for the extensive data available from CRPAQS. The results of this process will establish model performance that will then be used for projection of base and future year projections to be used for a Speciated Modeled Attainment Test (SMAT). A regional air quality modeling methodology summary of model preparation will be included as an attachment to this Protocol.

## Receptor Modeling Source Profiles

Source profiles will be derived from the EPA source library, local geological and burning profiles collected during the 1988-89 Valley Air Quality Study, recent motor vehicle profiles, wood burning, and meat cooking source profiles. These are supplemented by soil profiles collected by U. C. Davis as part of their agricultural emission factor work for Technical Support Study 12 for CRPAQS. Profiles appropriate to regional and site-specific activities, as well as the season of the year were considered. Composite profiles were generated to reflect the contribution of sources that cannot be distinguished individually, such as paved versus unpaved roads.

## Receptor Modeling Chemical Species

The chemical species to be used in the CMB analysis are listed below. If the presence or absence of a specific species causes a large difference in source contribution estimates, the species will be retained if all performance measures are within target ranges. If the performance measures are not within target ranges, the species will be evaluated for possible errors and may be removed from the input file. Additional species and carbon fraction profiles will be added as they become available. This may include additional trace elements measured in newer source profiles, as well as elemental and organic carbon fractions.

<b>Abbreviation</b>	<b>Name</b>	<b>Abbreviation</b>	<b>Name</b>
TMAC	PM <sub>10</sub> Mass	MNXC	Manganese
N3IC	Nitrate	FEXC	Iron
S4IC	Sulfate	NIXC	Nickel
N4TC	Ammonium	CUXC	Copper
ALXC	Aluminum	ZNXC	Zinc
SIXC	Silicon	BRXC	Bromium
CLXC	Chlorine	PBXC	Lead
KPXC	Potassium	PHXC	Phosphorus
CAXC	Calcium	ECTC	Elemental Carbon
TIXC	Titanium	OCTC	Organic Carbon
VAXC	Vanadium	TCTC	Total Carbon
CRXC	Chromium		

## Receptor Modeling Ambient Data

The receptor modeling use two independent ambient data sets for evaluation.

CRPAQS data for the year 2000 is used for evaluation of source receptor relationships as previously conducted for the PM10 SIP. This data is available from the ARB website <http://www.arb.ca.gov/airways/>. This website provides access to the collected air quality data, surface and aloft meteorological measurements, and measurements from a variety of special and research instruments operated during the study. Also available from this website are documents reporting on and analyzing the collected data. The use of 2000 data remains valuable due to the extensive nature of the dataset and the technical reviews and analysis of the SJV during that time period. This robust dataset provides greater capability to examine the accuracy of model performance for simulating the observed conditions than is provided by the routine network measurements collected each year. The purpose of the data use is to provide a high quality, verified model construct that is then used to model future years. The regional modeling being conducted by ARB uses the same dataset, for the same reason. PM2.5 mass was determined by analysis of prior PM10 annual CMB modeling and rollback analysis with substitution of available PM2.5 speciation data and calculation of species mass proportions for segments provided in the pM10 evaluation but missing from the PM2.5 speciation data set. The 2000 data is modeled forward to the year 2005 to project species comparable to the observed 2005 speciation data.

Speciation data for 2005 for Fresno and Kern annual PM2.5 evaluation was provided by ARB via download from the EPA AIRS system. This data is used as an input for new CMB evaluations and subsequent use in the receptor speciated rollback analysis. Since this provides an independent set of data, it allows comparison to the model formulation initiated from 2000 data as well as providing a more current starting point of foundation data.

## **Model: Output Data**

EPA has recognized the difficulty faced by California for use of existing modeling techniques to adequately quantify the full effect of controls. "It is well-recognized that California faces a set of unique and exceptionally difficult challenges in meeting national air quality standards, including those for fine particulates.... Key uncertainties exist with regard to both emissions inventories and air quality modeling in the West, which may understate the effectiveness of certain controls....The magnitude of projected non-attainment is larger than any other state, making the task of simulating attainment much more challenging than elsewhere in the nation." The modeling systems also have inherent technical limitations to fully quantify reductions, particularly for evaluation of controls that would reduce secondary organic PM from VOC reductions.

"There is considerable uncertainty and lack of understanding of formation, fate, and properties of organic particles. It is estimated that only 10 to 20 percent of the PM organic compounds have been quantified using existing methodologies. Work is underway at EPA and elsewhere to improve our understanding of secondary organic aerosols and our ability to characterize these compounds and their precursors in air quality models. In view of these limitations and uncertainties, current air quality models, including CMAQ, may understate the

reduction in secondary organic PM from controls on particle-forming VOCs, including aromatic compounds and higher carbon alkanes and olefins.  
Source: Clean Air Interstate Rule (CAIR), *EPA Projection Methods for Air Quality Concentrations*.

## Regional Modeling

Regional modeling will output gridded projections of secondary particulate matter. Additionally, time series analysis of grid cells of interest will also be possible. Other parameters may also be plotted in grid or time series for evaluation. Valid results of interest will be included in final modeling documentation.

The model evaluates ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) formed from the gaseous precursors ammonia and nitric acid ( $\text{HNO}_3$ ). Ammonia is mainly emitted into the atmosphere from various sources.  $\text{HNO}_3$  is a secondary gaseous product of the reactions between oxides of nitrogen ( $\text{NO}_x$ ) and volatile organic compounds (VOC) in the presence of sunlight. The regional model will also simulate the formation of secondary organic aerosols (SOA) and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ). The representation of  $(\text{NH}_4)_2\text{SO}_4$  is robust but only minor amounts ( $\sim 5 \mu\text{g}/\text{m}^3$ ) of that pollutant is present in the San Joaquin Valley in observed episodes. The representation of SOA in the modeling tools currently available is not very robust; therefore, EPA developed a methodology for estimation of SOA by adjusting FRM and modeling outputs to incorporate calculations of the sampling artifacts and losses, assigning the remainder of mass as SOA after these adjustments. However, the methodology may not be fully suitable for the SJV as it does not have a strong method for determination of geologic material and metals. This may not be a problem for much of the nation but the San Joaquin Valley has extensive programs to address fugitive dust that may not be well represented by the EPA approach. Furthermore, the District has documented events where carbon emissions have increased observed levels of nitrates by mechanisms not incorporated into the regional model.

## Receptor Modeling

Outputs from the CMB 8 model follow standard formats. The primary output of interest is the source contribution estimate (SCE) for each episode and source category. Other outputs provide performance statistics discussed in the next section of the Protocol Model: Analysis of Results.

## Model: Analysis of Results

Excerpts from presentations provided by EPA staff help clarify what is intended in the analysis of model results.



### Modeled Attainment Tests

All O3/PM2.5/RH modeled attainment tests use model estimates in a “relative” sense

- Premise: models are better at predicting relative changes in concentrations than absolute concentrations
- Relative Response Factors (RRF) are calculated by taking the ratio of the model’s future to current predictions of PM2.5 or ozone
- RRFs are calculated for ozone and for each component of PM2.5 and regional haze

### Weight of Evidence/Supplemental Analyses

All attainment demonstrations should include “supplemental” analyses to corroborate the modeling results. Three main categories of supplemental analyses

- Modeling
- Trends
- Diagnostic analyses

*Weight of evidence* applies when future design values are “close to” NAAQS (either above or below). Recommended WOE range:

- Annual PM2.5 14.5-15.5 ug/m3
- 24-hour PM2.5 62-67 ug/m3

Source: “Guidance on the use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5, and Regional Haze”, Final version- April 2007, Brian Timin April 17, 2007

The following sections discuss performance analysis of model results, but we recognize and concur that analysis of PM2.5 modeling is a difficult process. “It is difficult to establish generally applicable numerical performance goals” Model performance is not particularly important for components with small observed concentrations relative to other components. In a relative attainment test, a small observed component cannot have a large influence. Source: PM2.5 Model Performance Evaluation- Purpose and Goals, Brian Timin EPA/OAQPS, PM Model Evaluation Workshop, February 10, 2004, Chapel Hill, NC.

### Regional Modeling

Once the base-case simulation is performed, the estimated emissions, meteorology, and air quality need to be compared with observations to assure that the modeling system (emissions, meteorology, and air quality) is a satisfactory representation of the episode modeled. Only with such an assurance one can use the modeling system to evaluate control strategies. The rigorous comparison of model estimates with observations is termed model performance evaluation. Emission model evaluation and meteorology model evaluation is limited to quality assurance testing. Rigorous evaluation of the air quality model performance is proposed. The statistical metrics used for the comparison of estimates are in accordance with guidance. For gaseous pollutants the comparison is straightforward. But, for particulate matter that has several

components, the comparison will be done for the total mass as well as for the mass of individual components.

### **Statistical Measures for Regional Modeling Performance Analysis**

#### **Peak Estimation Accuracy:**

Paired Peak Estimation Where,  $C_o(x,t)$  is the peak concentration observed at location  $x$  at time  $t$  and  $C_e(x,t)$  is the model estimated concentration at the same location at the same time. Then  $A_{ts}$ , is a measure of the extent to which the observed and estimated peaks are paired in space and time.

#### **Equation A1: Paired Peak Estimation**

$$A_{ts} = \frac{(c_e(x,t) - c_o(x,t))}{c_o(x,t)} \times 100\%$$

Temporally Paired Peak Estimation: In the above expression if we relax the requirement that the modeled estimate should be in the same grid cell as the observation, we measure the models ability to reproduce the observed peak at the correct hour in the vicinity of the observed peak (e.g. 25 km radius).

Spatially Paired Peak Estimation: In equation (A1), if we relax the requirement that the model estimate should be at the same time as the peak observation, we measure the model's ability to reproduce the observed peak at the correct location at a reasonably close hour (e.g. within 3 hours).

Unpaired Peak Estimation: In equation (A1), if we relax the requirement that model estimate should be at the same location and hour as the observation, we measure the model's ability to reproduce the peak in the vicinity (say, 25 km radius) of the monitor at a reasonably close hour (e.g. within 3 hours).

#### **Bias:**

**Equation A2: Mean Bias Error** where  $N$  is the number of valid hourly observation-estimation pairs drawn from all valid monitoring data on the simulation day of interest.

$$MBE = \frac{1}{N} \sum_{i=1}^N (c_e(x_i,t) - c_o(x_i,t))$$

**Equation A3: Mean Normalized Bias Error** similar to equation (A-2) but normalized with respect to the observation.

$$MNBE = \frac{1}{N} \sum_{i=1}^N \frac{(c_e(x_i, t) - c_o(x_i, t))}{c_o(x_i, t)} \times 100\%$$

**Error:**

**Equation A4:** Mean Gross Error where, N is the number of valid hourly observation-estimation pairs drawn from all valid monitoring data on the simulation day of interest. Summing the absolute values of the difference prevents cancellation of errors.

$$MAGE = \frac{1}{N} \sum_{i=1}^N |(c_e(x_i, t) - c_o(x_i, t))|$$

**Equation A5:** Mean Normalized Gross Error, similar to equation (A-4) but normalized with respect to the observation.

$$MNBE = \frac{1}{N} \sum_{i=1}^N \frac{|(c_e(x_i, t) - c_o(x_i, t))|}{c_o(x_i, t)} \times 100\%$$

**Variance**

**Equation A6:** Variance is measure of spread of data. If the variance is low, then the difference between observations and estimation is small and vice versa.

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^N |(c_e(x_i, t) - c_o(x_i, t))|^2$$

**Receptor Modeling**

Model output and performance measures will be analyzed both individually and in aggregate to determine the applicability of the source profiles. Preliminary sets of source profiles will consist of at least one source profile from each source category. Final profile selection results from interactive application of the CMB with evaluation of the performance measures. Calculated contributions will be compared to measured ambient concentrations. Reasonable agreement between calculated contributions and measured ambient concentrations would indicate that all major source categories were included in the calculations, ambient and source profile measurements were fairly accurate, and source profiles were reasonably representative of actual emissions.

Sensitivity matrices were constructed to determine the source profiles with the most influence on species apportionment. Final analysis includes comparison to regional activities and current emission inventories, and is done in conjunction with meteorological and climatological analysis.

The CMB8 model provides a statistical diagnostic evaluation of correspondence of the CMB source identification to the observed sample. The basic statistical performance evaluations include  $R^2$  -  $R^2$  error analysis, Chi<sup>2</sup> - Chi<sup>2</sup> distribution, and Pmass - percent of mass accounted for by the sum of masses attributed to identified sources. The following performance measures will be used to assess the adequacy of the CMB model runs:

Source Contribution Estimate (SCE) This is the contribution of each source type to the PM mass. Each SCE should be greater than its standard error.

Standard Error (STDERR) This is an indicator of the uncertainty of each SCE. The STDERR should be much less than the SCE.

T-Statistic (TSTAT) This is the ratio of the SCE to the STDERR. A value greater than 2.0 indicates the precision of the SCE is high and that the source is a significant contributor.

R-Square (R SQUARE) This measures the variance in the sample concentrations, which is explained by the model calculated species concentrations. A value less than 0.8 indicates that the selected sources do not account for the variance in the sample.

Chi Square (CHI SQUARE) This is a measure of goodness of fit, which is inversely proportional to the squares of the uncertainties in the source profiles and the receptor data. A CHI SQUARE greater than 4.0 indicates that one of the calculated species concentrations differs from the measured value by several uncertainty intervals.

Percent of Mass Accounted For (PERCENT MASS) This is the ratio of the sum of the SCEs to the measured mass of the sample. PERCENT MASS should be within 80% to 120%.

Uncertainty/Similarity Clusters (U/S CLUSTERS) This is an indicator of groups of source profiles which are either collinear or which have very high uncertainties.

Sum of Combined Sources (SUM OF CLUSTER SOURCES) This represents the sum of the SCEs in the U/S CLUSTER with the standard error of the sum. When the standard error is low, it suggests that a composite profile can be created to represent the cluster.

Ratio of Residual to its Standard Error (RATIO R/U) This indicates the difference between the calculated and measured species concentration (residual) divided by the

uncertainty of the residual. An R/U value greater than +/- 2.0 indicates that one or more source profiles are contributing too much or too little to the species concentration.

Ratio of Calculated to Measured Species (RATIO C/M) This is the ratio of the calculated species concentration to the measured species concentration along with the standard error of the ratio. The ratio should be near 1.0.

### SANDWICH Calculation Procedure

The measured Sulfate, Adjusted Nitrate, Derived Water, and Inferred Carbonaceous mass approach (SANDWICH) was developed to attribute portions of the bulk FRM mass to different components. Nitrates are often lost from the FRM filter along with semivolatile organics, and water bound to the inorganics also comprises a portion of the FRM mass.

The main steps in estimating the PM<sub>2.5</sub> composition are as follows:

- (1) Calculate the nitrate retained on the FRM filter using hourly relative humidity and temperature alongside STN nitrate measurements,
- (2) Calculate quarterly averages for retained nitrate, sulfate, elemental carbon, ammonium (or sulfate degree of neutralization,  $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ , if not using ammonium measurements directly),
- (3) Calculate particle bound water using the concentrations of ammonium, sulfate, and nitrate, using an equilibrium model like the Aerosol Inorganic Model (or a polynomial equation derived from model output), and
- (4) Calculate organic carbon mass (OCM<sub>mb</sub>) by difference, subtracting all inorganic species (including blank mass) from the PM<sub>2.5</sub> mass.

Total PM<sub>2.5</sub> mass is given by

$$\text{PM}_{2.5 \text{ FRM}} = [\text{SO}_4^{2-}] + [\text{NO}_3^-]_{\text{FRM}} + [\text{NH}_4^+]_{\text{FRM}} + [\text{EC}] + [\text{Other}] + [\text{OCM}_{\text{mb}}] + [\text{H}_2\text{O}] + [\text{blank mass} = 0.5 \mu\text{g}/\text{m}^3]$$

Where all concentrations have units of  $\mu\text{g}/\text{m}^3$  and

- $[\text{SO}_4^{2-}]$  = measured sulfate
- $[\text{NO}_3^-]_{\text{FRM}}$  = nitrate retained on the FRM filter
- $[\text{NH}_4^+]_{\text{FRM}}$  = ammonium associated with FRM filter nitrate and sulfate
- $[\text{EC}]$  = measured Elemental Carbon
- Other = other inorganic mass; e.g., crustal material or sea salt
- $[\text{OCM}_{\text{mb}}]$  = organic carbon mass calculated by difference by adding all inorganic species and subtracting from the FRM PM<sub>2.5</sub> mass. Organic carbon

measurements may also be used if it seems that the OC by mass balance is clearly under or overestimated.

- [H<sub>2</sub>O] = water bound to the hygroscopic species, dependent on the concentrations of sulfate, nitrate, and ammonium. Calculated using a polynomial equation dependent on the concentrations of sulfate, nitrate, and ammonium or using an inorganic aerosol equilibrium model or use alternative linear estimation where water bonded to ammonium nitrate is approximated as equivalent to twelve percent of the mass and water bonded to ammonium sulfate is approximated as 26 percent of that mass.
- Blank mass represents the mass passively collected on the filter, represented in the equation by an average value of 0.5 mg/m<sup>3</sup> (assumed constant)

### **District evaluation of filter blank mass for SANDWICH**

The SANDWICH procedure recommended by EPA guidance calls for setting aside 0.5 ug/m<sup>3</sup> as a filter blank artifact, to be kept as a constant and not be reduced for future year considerations. EPA identified the source of the artifact as sample handling contamination by inference but not by demonstrated measurement or detection. The District has identified through review of CRPAQS research that the sampling artifact has a different cause than suggested by EPA and will process the artifact accordingly.

CRPAQS research provides analysis and documentation of the source of the artifact as the difference between VOC carbon adsorbed on the filter, partially offset by carbon particulate desorbed from the filter. This material is not a handling contaminant and is related to ambient precursors and pollutants. Therefore, the mass set aside for this calculation should not be considered to be static in future years. Current receptor modeling has a very small mass identified as unassigned and mapped against total PM<sub>2.5</sub> inventory change. Prior discussion indicates that in addition to the VOC adsorbed artifact there are other inorganic filter artifacts identified by prior research and technical literature. The analysis for CRPAQS determined the source of the artifact but qualified the determination of exact mass magnitude. EPA has set a default value of 0.5 micrograms for the filter blank hypothesis, but this value is too low for the identified adsorbed carbon and inorganic artifacts. The District will review establishing appropriate mass consideration for both artifacts and will revise receptor speciated rollback methods and assumptions accordingly.

Documentation of the filter artifact analysis performed for CRPAQS can be found in sections of the document:

#### **Initial Data Analysis of Field Program Measurements**

DRI Document No. 2497, July 29, 2005

Judith C. Chow, L.-W. Antony Chen, Douglas H. Lowenthal, Prakash Doraiswamy, Kihong Park, Steven D. Kohl, Dana L. Trimble, John G. Watson, DESERT RESEARCH INSTITUTE, Division of Atmospheric Sciences, 2215 Raggio Parkway, Reno, NV 89512

#### **Organic Carbon Artifacts (Task 1.1.4)**

Several denuding and backup filter sampling systems were applied to evaluate the OC artifacts. Based the analyses, the following were concluded:

- The OC concentration on the quartz-fiber backup filter to a quartz-fiber front filter (QQ2) in an undenuded stream was concluded to be the most appropriate estimate of positive artifact (i.e., adsorption of organic gases onto the filters). The adsorption of organic gases onto the filters was, on average, 14.4% (i.e., QQ2/QPOC) of the particle OC concentration during CRPAQS. The positive artifact was lower during winter than the summer season (12.3% in winter versus 22.8% in summer).
- The OC on backup quartz-fiber filter to a front quartz-fiber filter in a carbon-denuded stream (DNQQ2) may be used as an indication of the amount of carbon that was desorbed from the particles on the front quartz-fiber filter (i.e., as an estimate of the negative artifact). The desorption of organic vapors from the particles on the filter was, on average, 4.9% (i.e., DNQQ2/DNPOC) of the particle OC concentration and ranged from 2.3% in winter to 11% in summer.
- The accuracy of using QQ2 as an estimate of the positive artifact depends on whether equilibrium was reached between the VOC in the sample stream and both filters in the QQ pair, which is highly questionable, given the difference in sampling periods and the diurnal variations in VOC concentrations. More research is needed to resolve these issues, especially the specific characterization of compounds responsible for the positive and negative artifacts and the conditions under which equilibrium is reached under different sampling conditions.

#### **Spatial scales of influence on compliance (backbone) (Task 4.4.3)**

- The comparison between measured and CMB-predicted PM<sub>2.5</sub> and PM<sub>10</sub> mass indicates that the CMB reached a good mass closure for the most part. Although the slope was within 10% of unity, large intercepts were found for both PM<sub>2.5</sub> (3.2 µg/m<sup>3</sup>) and PM<sub>10</sub> (1.24 µg/m<sup>3</sup>). This intercept most likely resulted from the organic sampling artifact.

### **SMAT Calculation Procedure**

The SMAT procedures for receptor and regional modeling will be slightly different due to the differences between the modeling methods. The general procedure to establish a Speciated Modeled Attainment Test (SMAT) is to perform calculations that consider the differences between FRM samples and the processes and quantities predicted by the model.

Step 1. Calculate the observed quarterly mean bulk PM<sub>2.5</sub> concentration and composition for each measurement site. The quarterly mean species concentrations can be calculated by multiplying the observed percentage contribution of each species against the quarterly mean bulk PM<sub>2.5</sub> design value. This design value is calculated from the bulk FRM concentrations averaged over a number of years (generally three but can be a weighted average spanning 5 years), one of which should be the modeled

base year. The procedure to speciate this bulk design value is described in the "SANDWICH" discussion.

Step 2. Calculate the RRFs for each quarter and measurement site. Relative response factors are calculated using model results. For species  $i$ , site  $j$ , and quarter  $k$  is given by the following equation:

$$RRF_{ijk} = ([C_{i, \text{quarter } k \text{ of future year}}] / [C_{i, \text{quarter } k \text{ of the base year}}])_j$$

$C_i$  represents the quarterly modeled concentration (often averaged over a number of model cells near the location of the measurement site) for the base year and the future year attainment target. The number of model cells recommended for use in the average depends on the size of the grid cell and is justified by the long  $PM_{2.5}$  sampling times, the representative spatial scale of the monitors, and the desire to offset any potential errors stemming from the geometry of the superimposed grid system. For a 12-km cell, it is recommended that RRFs be calculated from a 3x3 cell array.

Step 3. Multiply the quarterly, site-specific model-based RRFs of step 2 and speciated observations of step 1 to estimate future quarterly species concentrations.

Step 4. Sum the future quarterly species concentrations estimates of step 3 to estimate a future quarterly  $PM_{2.5}$  estimate at each monitoring site and then average these for a projected future year annual  $PM_{2.5}$  concentration for each monitoring site.

Step 5. Compare the future year annual average  $PM_{2.5}$  concentrations of step 4 to the annual  $PM_{2.5}$  standard of  $15.0 \mu\text{g}/\text{m}^3$ . If all sites have projected  $PM_{2.5}$  concentrations below the standard, the attainment test is passed.

## Determining Attainment for All Cases

The program of analysis specified in the Protocol will provide a complete attainment demonstration by assessment of all exceedances to the  $PM_{2.5}$  annual standard that have been detected by the monitoring network and establish the San Joaquin Valley to be classified as nonattainment. The demonstration will show that the proposed emission control program will successfully lower  $PM_{2.5}$  emissions to the extent that exceedances of the federal  $PM_{2.5}$  standards will be eliminated and that such conditions will be achieved at the earliest practical date consistent with the requirements of the Clean Air Act. The Protocol addresses the annual standard as the primary focus for evaluation due to compliance with the 24-hour standard in effect for this SIP. The revision of the 24-hour standard will be addressed in subsequent evaluation according to schedules promulgated by EPA.

Procedures for analysis have been selected to establish objective and reliable conclusions that have the highest confidence that can be established to establish the SIP as comprehensive and sufficient for the entire Valley in all cases. Although the best



available data will be utilized, uncertainties and limitations of the data affect results of analyses and may produce confirming and contradictory indications that must be reconciled by knowledgeable evaluation to establish reliable conclusions. The SIP control plan will establish an attainment demonstration of the PM<sub>2.5</sub> annual and 24-hour standards by successfully addressing all identifiable exceedances that classify the District as nonattainment. The Protocol includes receptor-modeling evaluation of monitoring sites that do not comply with the annual standard as well as regional modeling. Regional modeling will assess the entire SJVAB and will allow review of areas without monitors.

Supporting analyses to confirm the projection of attainment by weight of evidence include:

- Examination of historical monitoring data,
- Evaluation of source zone of influence,
- Demonstration of spatial representativeness of monitored episodes
- Assessment of control strategy impact via rollback analysis (chemical mass balance modeling with speciated rollback and enhanced analysis of secondary particulates for appropriate episodes) with application to the design value by SMAT, and
- Regional modeling used in a relative sense to establish a speciated projection of attainment (SMAT).

The combination and comparison of results provides a weight of evidence analysis to establish the adequacy of the SIP to achieve attainment. Examining historical data provides context for design value observations and an assessment of whether the design values are consistent with previous experience. Evaluation of source zone of influence is necessary for prediction of effects of control strategies with receptor and rollback techniques. Evaluation of the spatial representativeness of monitored episodes is important to determine which episodes are dominated by local sources and which have significant contributions from larger portions of the region. Response observed in the monitoring data and design values should be consistent with the technical analyses and modeling results. Examining this correlation is important to determine if modeling or other analysis provides an accurate representation of expected change, to determine that the control program is sufficient to achieve attainment of the PM<sub>2.5</sub> standards and is not excessive in its requirements

## Attachments

The following documents are attached and incorporated as elements of the Protocol, providing additional discussion of the analysis and modeling process:

- A1 SJV PM Conceptual Model 1998 (64 pages) – Conceptual description of PM<sub>10</sub> and PM<sub>2.5</sub> episode dynamics. Performed for the CRPAQS study as part of an integrated monitoring study (IMS-

- 95) designed to evaluate conceptual issues. Based on 1995 data collected in the San Joaquin Valley.
- A2 Modeling Domain –Domain map annotated with model basic operating parameters
  - A3 Modeling Boundary Conditions – Average annual surface boundary conditions
  - A4 PMF procedure (5 pages) – Methodology for the Positive Matrix Factorization approach to identify key contributing sources
  - A5 Receptor Modeling Analysis Layout (4 pages) – Documentation of receptor rollback revisions and conversion from analysis of PM10 to PM2.5
  - A6 Regional Air Quality Modeling Methodology – Model selection, emissions and meteorology for PM2.5 annual modeling

Additional documentation will accompany the submittal of the PM2.5 Plan but is not included as part of the Protocol. The District and ARB will retain modeling documentation at their respective offices for public access. Materials to be submitted as a part of the Plan approval process, either with the Plan submittal or by separate transmittal, are expected to include:

- The PM2.5 Plan, resolution of adoption and other required transmittal documents
- The PM2.5 Modeling Protocol and Attachments
- Modeling analysis results summary documentation
- Other appendices to provide supporting information for the plan
- Other documentation identified as required by EPA

## ATTACHMENT A1

To the

### San Joaquin Valley Air Pollution Control District

State Implementation Plan PM2.5 Modeling Protocol

Reference Document Title:

**“Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley,”** Document Number CP045-1-98, 8 September 1998. Prepared by: Betty Pun & Christian Seigneur, Atmospheric and Environmental Research, Inc., 2682 Bishop Drive, Suite 120, San Ramon, CA 94583. Prepared for: Mr. Eugene Shelar, Jr., Technical and Ecological Services, Pacific Gas and Electric Company, 3400 Crow Canyon Road, San Ramon, CA 94583.

#### **Referred to in the Protocol as:**

A1 SJV PM Conceptual Model 1998 (64 pages)

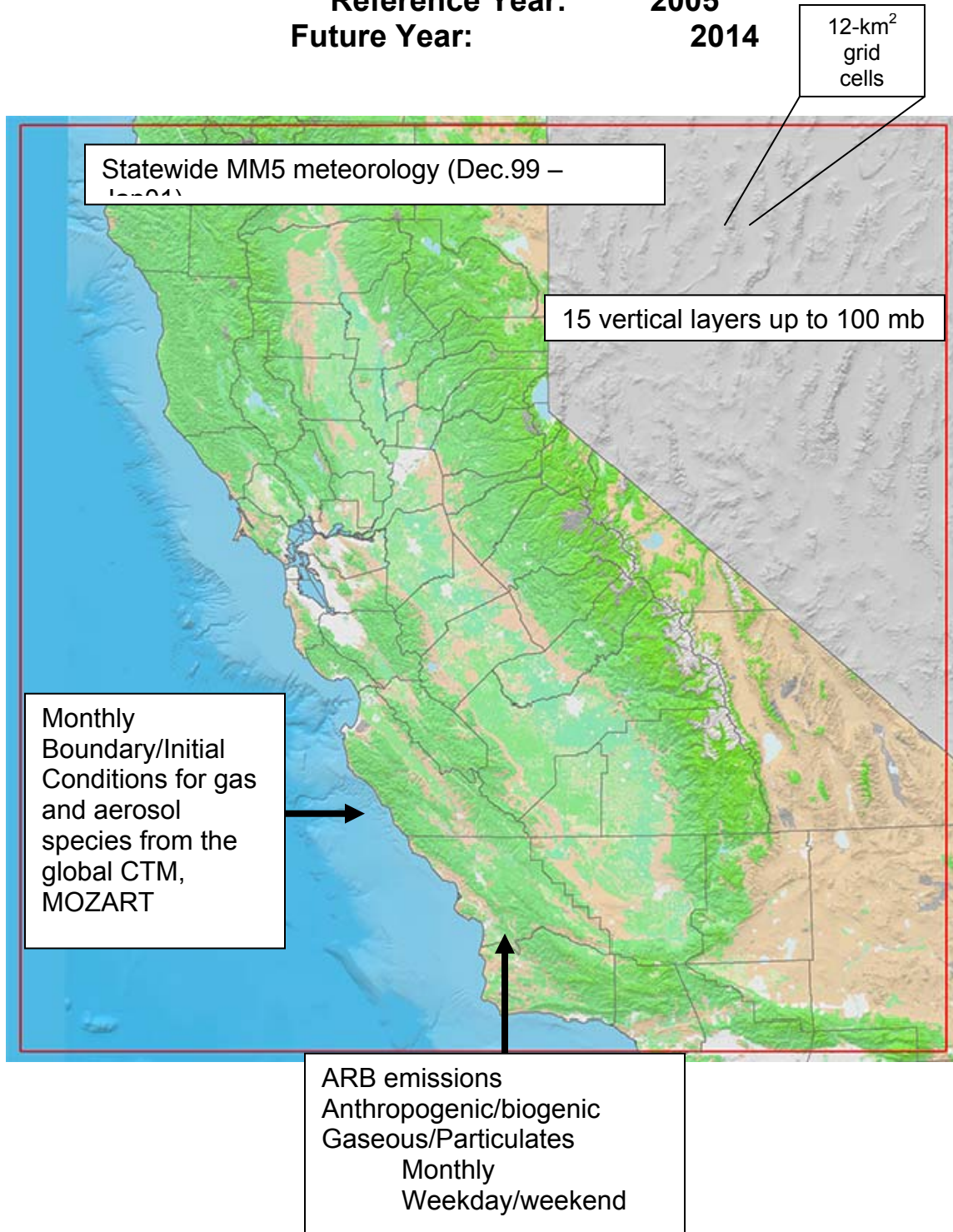
**Conceptual description of PM10 and PM2.5 episode dynamics. Performed for the CRPAQS study as part of an integrated monitoring study (IMS-95) designed to evaluate conceptual issues. Based on 1995 data collected in the San Joaquin Valley.**

For printing purposes this attachment is included by reference rather than being attached in its entirety. A copy of this document is available for review and/or purchase from the San Joaquin Valley Unified Air Pollution Control District. An electronic copy may be obtained at: <http://www.arb.ca.gov/airways/Documents/reports/sjvpmc~1.pdf>

## ATTACHMENT A2

### Modeling Domain

Model Performance: 2000  
Reference Year: 2005  
Future Year: 2014



**ATTACHMENT A3***To the***San Joaquin Valley Air Pollution Control District***State Implementation Plan PM2.5 Modeling Protocol***Average Annual Surface Boundary  
Conditions**

	North	East	South	West
<i>VOC (ppb)</i>	6.6	8.0	5.7	2.9
<i>NOx (ppb)</i>	0.7	1.5	3.6	0.1
<i>O<sub>3</sub> (ppb)</i>	38	42	39	36
<i>SO<sub>2</sub> (ppb)</i>	0.1	0.3	0.5	0.04
<i>NH<sub>3</sub> (ppb)</i>	0.2	0.2	0.2	0.01
<i>HNO<sub>3</sub> (ppb)</i>	0.2	0.5	0.8	0.1
<i>NH<sub>4</sub>NO<sub>3</sub> (μg/m<sup>3</sup>)</i>	0.2	0.2	0.2	0.02
<i>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (μg/m<sup>3</sup>)</i>	1.3	1.5	1.6	1.1
<i>OC (μg/m<sup>3</sup>)</i>	1.2	1.7	1.3	0.2
<i>EC (μg/m<sup>3</sup>)</i>	0.2	0.3	0.4	0.0

**ATTACHMENT A4**

To the

**San Joaquin Valley Air Pollution Control District***State Implementation Plan PM<sub>2.5</sub> Modeling Protocol***Summary of PM<sub>2.5</sub> Source Apportionment Procedure using PMF2**

Positive matrix factorization (PMF) is a statistical method used for deducing factors. Program PMF2 is used for the source apportionment of airborne particulate matter using PMF method. PMF2 decomposes measured data matrix into source profile and source contribution matrices simultaneously. By analyzing measured data at the receptor, PMF2 provides source profiles and source contributions at the receptor side. EPA Speciation Trends Network data measured at Fresno and Bakersfield will be analyzed separately using PMF2.

**Prepare Input Data**

Since a carbon denuder that minimizes positive sampling artifact caused by adsorption of gaseous organic materials was not included upstream of quartz filter in the Speciation Trends Network (STN) samplers, and none of the reported STN data were blank collected, an integrated organic carbon (OC) artifact is estimated utilizing the intercept of the regression of OC concentrations against PM<sub>2.5</sub> mass concentrations suggested by Tolocka et al. (2001). Samples for which the PM<sub>2.5</sub> or OC data were missing are excluded from the regression analysis between PM<sub>2.5</sub> and OC concentration. Comparing co-located PM<sub>2.5</sub> data measured by STN and Federal Reference Method (FRM), outliers are censored. As shown in Figure 1, the intercept in PM<sub>2.5</sub> regression against OC concentration is considered to be the OC artifact concentration. The STN OC concentrations are corrected by subtracting the OC artifact concentration.

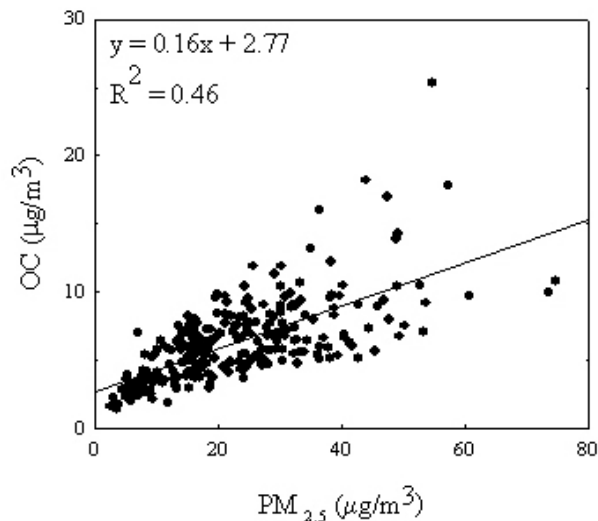


Figure 1. PM<sub>2.5</sub> mass concentrations vs. OC concentrations

For the PMF2 analysis, samples for which the PM<sub>2.5</sub> or OC data were not available or below zero, or for which PM<sub>2.5</sub> or OC mass concentration had an error flag are excluded from the data set. Outliers in comparing co-located STN PM<sub>2.5</sub> data and FRM data are excluded. The samples that contain fireworks particles which have unusually high concentrations of OC, K, As, Ba, Cu, and Pb are excluded.

X-Ray Fluorescence (XRF) S is excluded from the analyses to prevent double counting of mass concentrations since XRF S and Ion Chromatography (IC) SO<sub>4</sub><sup>2-</sup> are highly correlated in STN data. Due to the higher analytical precision compared to XRF Na and XRF K, IC Na<sup>+</sup> and IC K<sup>+</sup> are included. Chemical species below MDL values more than 90% are excluded. As recommended by Paatero and Hopke (2003), the species that have Signal-to-Noise (S/N) ratio below 0.2 (bad variable) are excluded.

PMF2 analysis requires two input data matrices: concentration data matrix and uncertainty matrix. To assign input data, the procedure of Polissar et al. (1998) is used. The measurement values are used for the input concentration data, and the sum of the analytical uncertainty and one-third of the detection limit value is used as the input uncertainty data assigned to each measured value. Concentration values below the detection limit are replaced by half of the detection limit values, and their input uncertainties are set at five-sixth of the detection limit values. Missing values are replaced by the geometric mean of the measured values for each species, and to down-weight these replaced data and then to reduce their influence on the solution, their accompanying uncertainties are set at four times of this geometric mean value. The input uncertainties are increased by a factor of thirty for the data which have error flags. The measured STN PM<sub>2.5</sub> mass concentration is included in the input data as an independent variable in the PMF2 analysis to directly obtain the mass apportionment (Kim et al, 2003).

### **Run Model**

PMF2 requires users to decide number of sources. To determine the appropriate number of sources, it is useful to look at the changes in source profiles as a function of the number of sources since after an appropriate number of sources are included in the fit, additional sources will not be physically interpretable. Because rotational ambiguity exists in factor analysis, the parameter FPEAK is used for the PMF2 to control the rotations. PMF2 is run with different FPEAK values to determine the range within which the modeling residual remains relatively constant. The optimal solution should lie in this FPEAK range.

The profiles of real pollution sources vary because of changing feed stocks, atmospheric processing, etc. Thus, PMF2 analysis needs to find an appropriate average source profile, but it will not be as tight a fit as would occur if the profiles were fixed. Thus, for various species involved in more variable composition profiles, the uncertainty space is needed to expand to obtain sensible solutions. As recommended by Paatero and Hopke (2003), which is to down-weight the variable in the analysis so

that the noise does not compromise the solution, it is possible to increase the input uncertainties of several species to obtain physically interpretable PMF2 results (i.e., source profiles and contributions) The final PMF2 solutions are determined by experiments with different numbers of sources, different FPEAK values, and different species down-weight with the final choice based on the evaluation of the resulting source profiles as well as the quality of the species fits. For example, Figure 2, a comparison of the reconstructed PM2.5 mass contributions resolved by PMF2 with measured PM2.5 mass concentrations shows that the resolved sources well reproduce the measured values and account for most of the variation in the PM2.5 mass concentrations. Figures 3 and 4 show source profile and contribution, respectively, of PMF2 resolved secondary nitrate at LA-North main site.

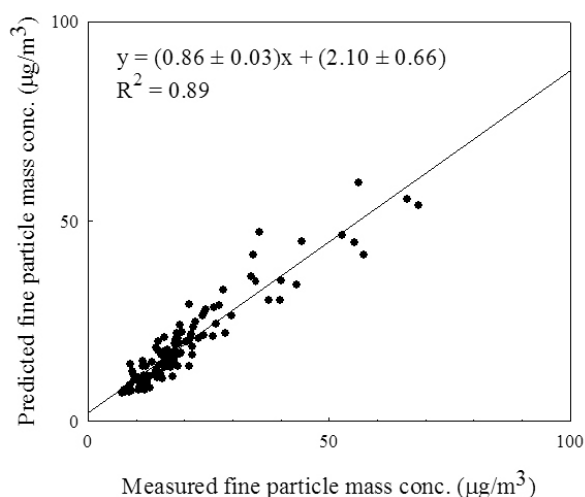


Figure 2. Measured versus PMF reconstructed PM2.5 mass concentrations.

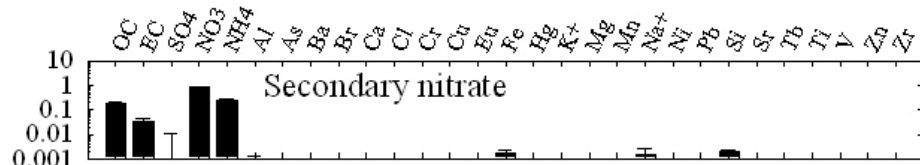


Figure 3. Source profile deduced from PM2.5 samples measured at LA-North main (prediction standard deviation).

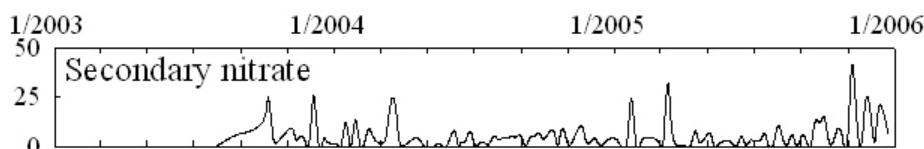


Figure 4. Source contribution deduced from PM2.5 samples measured at LA-North main.

**Interpret Sources**



To interpret PMF2 results, the identified source profiles are compared with published measurements: For example, Lowenthal et al. (1994) and Watson et al. (1994, 2001a, 2001b) for the diesel exhaust; Small et al. (1984) and EPA SPECIATE version 4.0 (2007) for industrial sources. Also, source contributions extracted by PMF2 are analyzed by temporal analyses to decide whether or not the sources are physically interpretable. The temporal variations shown in Figures 5 and 6 indicate the PMF2 deduced secondary nitrate has winter-high trend and no weekday/weekend variation that physically make sense.

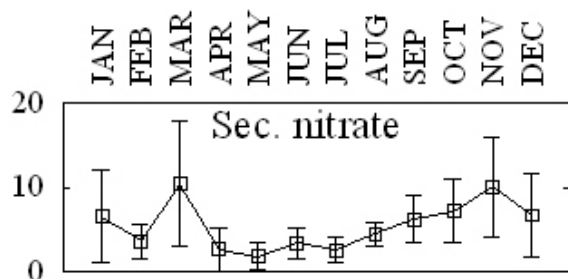


Figure 5. The monthly variations of source contributions to PM2.5 mass concentration at LA-North main (mean 95 % distribution).

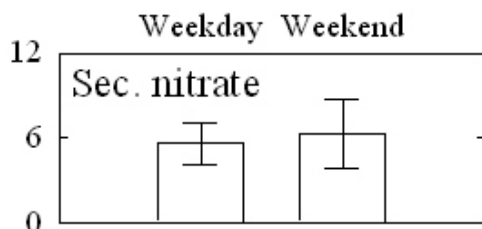


Figure 6. Weekday/weekend variations at LA-North main (mean 95 % distribution).

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Watson, J.G., Chow, J.C., Houck, J.E.. PM<sub>2.5</sub> chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in northwestern Colorado during 1995. *Chemosphere* 43, 1141–1151, 2001.

**ATTACHMENT A5**

*To the*

**San Joaquin Valley Air Pollution Control District**

*State Implementation Plan PM2.5 Modeling Protocol*

**Receptor Modeling Analysis Layout**

**ATTACHMENT A6***To the***San Joaquin Valley Air Pollution Control District***State Implementation Plan PM<sub>2.5</sub> Modeling Protocol***Regional Air Quality Modeling Methodology****Referred to in the Protocol as:**

A6 Regional Air Quality Modeling Methodology

Model selection, emissions and meteorology for PM<sub>2.5</sub> annual modeling

**The Selection of Air Quality Models:** As stipulated in the EPA Modeling Guidance, a grid-based photochemical model is necessary to perform the modeled attainment test for PM<sub>2.5</sub> (EPA, 2007). Such models offer the best available representation of important atmospheric processes and are an essential tool in analyzing the impacts of proposed emissions controls on pollutant concentrations. The EPA recommends guidelines for choosing a model for use in the attainment test. For example, the model source code should be free or low cost, modeling elements should have undergone rigorous scientific peer-review, and it should have been shown to perform well in the past for similar applications.

The Community Multiscale Air Quality Modeling System (CMAQ) has been selected for use in the PM<sub>2.5</sub> modeled attainment demonstration for the San Joaquin Valley Air Pollution Control District. CMAQ is a state-of-the-science “one-atmosphere” system that treats major atmospheric and land processes (e.g., advection, diffusion, gas phase chemistry, gas-particle mass transfer, nucleation, coagulation, wet and dry deposition, aqueous phase chemistry, etc.) and a range of species (e.g., anthropogenic and biogenic, primary and secondary, gaseous and particulate) in a comprehensive framework (EPA, 1999; CMAS, 2007).

CMAQ has been extensively peer-reviewed, is well-documented, and is regularly updated to reflect the latest changes in scientific understanding. CMAQ has been applied successfully in a range of environments and on many spatial and temporal scales. Given that CMAQ has also been applied successfully to episodic modeling in Central California, this modeling system has been selected for use in support of the PM<sub>2.5</sub> modeled attainment demonstration.

**Choice of Chemical Mechanism:** There are a number of gas-phase chemical mechanisms readily available for application in CMAQ (e.g., CB-IV, CB-V, SAPRC-99). The user has the additional option of whether to couple the chosen gas phase mechanism with aerosol and/or aqueous phase chemical processes. In order to simulate the complex mixture of PM<sub>2.5</sub> species in the San Joaquin Valley, SAPRC99 coupled with CMAQ aerosol code version 4 and aqueous phase chemistry has been

chosen for this application. SAPRC-99, a complete update of SAPRC-90, is a detailed mechanism describing the gas-phase reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO<sub>x</sub>) (Carter, 2000). AE4-AQ, the fourth-generation CMAQ aerosol code with aqueous phase chemistry, when coupled with a gas phase mechanism, represents such phenomena as gas-aerosol/aqueous phase mass transfer, chemical transformation of particulate species and their gas phase precursors, and the evolution of the aerosol size distribution.

### **Model Inputs and Setup:**

Domain Structure: The modeling domain covers the Central Valley and its surroundings with nearly 60,000 12x12 km<sup>2</sup> grid cells. The domain extends from the Pacific Ocean in the west to the Mojave Desert and western Nevada in the east and runs from the northern Sacramento Valley to the Tehachapi Mountains in the south. The vertical structure is composed of 15 layers of varying thickness up to 100 mb. The finest resolution belongs to those layers closest to the surface and is determined largely by the vertical structure of the meteorological inputs. The surface layer is approximately 30 meters thick.

Initial and Boundary Conditions: Boundary conditions were taken from the global chemical transport Model for Ozone And Related chemical Tracers (MOZART). Model boundary conditions for major species were extracted for the Central California modeling domain from MOZART results representative of the year 2000. In addition to VOCs and inorganic gases, boundary conditions were extracted for ammonium, nitrate, sulfate, and organic and elemental carbon. Initial conditions were estimated as an average of the extracted boundary conditions for each species. The impact of initial conditions will be minimized by 8-day spin up periods preceding the simulation of each month of the year 2000.

Emissions: A spatially, temporally, and chemically resolved emissions inventory of combined area, mobile, and point sources was generated using the California Emissions Forecasting System (CEFS) version 1.06 with offline adjustments. The inventory includes emissions estimates for gaseous and particulate species of anthropogenic and biogenic origin. Gridded hourly emissions were developed for the CMAQ modeling domain for December 1999 through January 2001.

Meteorological Inputs: The meteorological input fields to CMAQ were generated with the Meteorology-Chemistry Interface Processor (MCIP) version 3.0. MCIP serves as a link between meteorological models like MM5 or WRF with CMAQ and generates model-ready meteorological inputs like the wind and temperature fields necessary to drive the transport and chemistry calculations in CMAQ. Inputs to MCIP were generated using the mesoscale meteorological model (MM5) (Grell et al., 1994). PBL and radiation characteristics were calculated in MCIP, and the Models-3 dry deposition routine (Pleim - with chlorine and mercury species) was chosen to represent dry deposition.

**Model Years:** CMAQ will be run from December 1999 – January 2001 to provide the basis for the model performance evaluation. Two or more subsequent years will also be simulated. It is necessary to execute simulations for a model reference year and a future year to perform the recommended modeled attainment demonstration. These attainment runs will use meteorological inputs for 2000 and emissions for the model reference year (2005) and future year (e.g., 2014).

**Model Performance Evaluation:** To assure that the modeling system (emissions, meteorology, and air quality) is a satisfactory representation of the period modeled, the estimated emissions, meteorology, and air quality of the base-case simulation need to be compared with observations. Satisfactory performance of the model in simulating observed conditions and responses is a prerequisite for use of the modeling system to evaluate control strategies.

The rigorous comparison of model estimates with observations is termed model performance evaluation. Such a rigorous model performance evaluation for a long-term simulation requires the availability of a temporally and spatially extensive dataset. The California Regional PM<sub>10</sub>/ PM<sub>2.5</sub> Air Quality Study (CRPAQS) was an extensive and intensive measurement campaign designed to characterize the important chemical and physical processes involved in the formation and evolution of particulate matter in Central California (Chow et al. 2006). The CRPAQS measurement campaign extended from December 1999 through January 2001 and provided a wealth of data from diverse areas for model evaluation.

Following the quality assurance testing and technical review of the emissions and meteorological models, air quality model evaluation will be performed using CRPAQS data. Typical statistics for use in quantifying the differences between modeled and observed concentrations include metrics like Normalized Mean Error (NME) and Normalized Mean Bias (NMB) (Boylan and Russell, 2006):

$$MNE = \frac{\sum |C_m - C_o|}{\sum C_o}$$
$$MNB = \frac{\sum (C_m - C_o)}{\sum C_o}$$

where  $C_m$  refers to modeled concentrations,  $C_o$  refers to observed concentrations, and the summations are over all model-observation pairs of a given species at stations/time-periods of interest. Additional statistical metrics typically used for model evaluation are further documented in the Protocol.

There are hourly and daily concentration data for a range of gaseous and particulate species at numerous sites available for comparison with CMAQ modeled concentrations. These data will be used to assess model performance temporally and spatially, with a focus on monthly average performance, as recommended for long-term model simulations. Appropriate goals for model performance will be based on the EPA Modeling Guidance and recommendations in the scientific literature on appropriate measures of model performance for long term PM simulations (EPA, 2007; Boylan and

Russell, 2006). In addition to calculating monthly error statistics for a range of species (e.g., total PM<sub>2.5</sub> mass and its components such as sulfate, nitrate, ammonium, EC, and OC) at various sites in the modeling domain, time series plots will be reviewed qualitatively to determine how well the model performs spatially and on a shorter time scales.

### References:

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- Chow, J.C., Chen, L.W.A., Watson, J.G., Lowenthal, D.G., Magliano, K.A., Turkiewicz, K., and D.E. Lehrman (2006) PM<sub>2.5</sub> chemical composition and spatiotemporal variability during the California Regional PM10/PM2.5 Air Quality Study (CRPAQS). *J. Geophys. Res.*, 111, D10S04, doi:10.1029/2005JD006457.
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	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	<b>Draft Fresno analysis provided as template for receptor modeling methodology documentation.</b>													
2	Microbiology uses PM10 receptor analysis, modified to adjust species to information available for PM2.5.													
3	Receptor model analysis method has been reviewed for technical modifications appropriate for PM2.5, see Revision worksheet.													
4	<b>Fresno - Annual 2000-2001 species mass = 21.5 2005 Design value = 17.2</b>	General Note	Geologic and Construction	Mobile Exhaust	Tire and Brake Wear	Organic Carbon	Vegetative Burning	Ammonium Nitrate including associated water	Ammonium Sulfate	Marine	Unassigned			
5	Line 1 Line 1 Natural and Transport Contribution, see "Background" sheet	From CMB monthly analysis Feb 2000 to Dec 2000, adding January 2001 episode for chemistry equivalent to annual design value	From CMB	From CMB	From CMB	Estimated portion of mass included in Vegetative Burning ~30%	From CMB minus estimated Organic Carbon from other sources	From CMB	From CMB	From CMB, if present	Unaccounted mass from CMB, if any.			
6	Line 2 Line 2 Net for Rollback	22.45	0.95	4.14	0.35	0.28	4.75	7.48	2.20	0.00	0.581			
7	Line 3 Line 3 Local Contribution PM2.5-PM10 Area of Influence	18.53	0.9	4.1	0.4	1.6	3.3	6.5	1.2	0.0	0.6			
8	Line 4 Line 4 Local Contribution Area of Influence of PM2.5	7.03	0.234	0.8	0.169	0.8	0.892	2.662	0.514		0.119			
9	Line 5 Line 5 Sub regional Contribution	3.84	0.179	0.82	0.071	0.31	0.815	1.320	0.284		0.076			
10	Line 6 Line 6 Regional Contribution	3.56	0.214	0.88	0.048	0.36	0.954	1.063	0.203		0.193			
11	Line 7 Associated Emissions Categories	4.00	0.226	0.88	0.062	0.42	0.646	1.435	0.229		0.184			
12	Line 8 What Row to use for Lookup Function	2	5	7	8	9	10	14	15	N/A	16			
13	Line 9 2000 Emissions Inventory	Area of influence emissions inventory, each on a separate line for automated calculations)										INDEX		
14	Line 10 PM10	L= Area 3	2,110	1,300		0,102	1,544		2,136		3,410	3-F		
15	Line 11 Fresno, Madera	L= Areas 3,4	5,388	1,850		0,143	2,760		6,556		7,288	Sum 3,4		
16	Line 12 NOx	R= SJV	12,890	2,737		0,195	5,325		15,242		36,970	Fresno + Madera		
17	Line 13 NOx	L= Area 3	40,682	12,272		0,746	22,401		30,963		111,522	SJV Total		
18	Line 14 ROG	L= Areas 3,4							62,380		62,380	3-F		
19	Line 15 SOx	R= SJV							103,071		103,071	Sum 3,4		
20	Line 16 PM10 with new controls	L= Area 3	1,882	0,799		0,150	1,291		1,665		2,682	3-F		
21	Line 17 PM10 with new controls	L= Areas 3,4	4,885	1,225		0,219	2,432		5,566		6,109	Sum 3,4		
22	Line 18 PM10 with new controls	R= SJV	11,672	1,771		0,300	4,637		13,609		32,814	Fresno + Madera		
23	Line 19 NOx with new controls	L= Area 3	37,776	7,748		1,115	18,373		26,911		96,883	SJV Total		
24	Line 20 NOx with new controls	L= Areas 3,4							38,170		38,170	3-F		
25	Line 21 NOx with new controls	R= SJV							67,481		67,481	Sum 3,4		
26	Line 22 ROG without new controls	L= Area 3	10,391				19,845		40,943		104,709	Fresno + Madera		
27	Line 23 ROG without new controls	L= Areas 3,4							69,716		174,428	SJV Total		
28	Line 24 ROG without new controls	R= SJV							236,701		236,701	3-F		
29	Line 25 ROG with new controls	L= Area 3	10,391				19,845		40,943		104,709	Fresno + Madera		
30	Line 26 ROG with new controls	L= Areas 3,4							69,716		174,428	SJV Total		
31	Line 27 SOx without new controls	R= SJV							236,701		236,701	3-F		
32	Line 28 SOx without new controls	L= Area 3							4,396		4,396	3-F		
33	Line 29 SOx without new controls	L= Areas 3,4							7,201		7,201	Sum 3,4		
34	Line 30 SOx with new controls	R= SJV							11,419		11,419	Fresno + Madera		
35	Line 31 SOx with new controls	L= Area 3							4,296		4,296	3-F		
36	Line 32 SOx with new controls	L= Areas 3,4							7,201		7,201	Sum 3,4		
37	Line 33 SOx with new controls	R= SJV							11,419		11,419	Fresno + Madera		
38	Line 34 2014 Rollback Projection								26,491		26,491	SJV Total		
39	Line 35 Local Contribution PM2.5-PM10 Area of Influence	+2014 L1(2000 L1) * LINE 4	0.2	1.0	0.1	0.2	0.4	0.1	0.7	2.0	0.6	0.1		
40	Line 36 Local Contribution Area of Influence of PM2.5	+2014 L2(2000 L2) * LINE 5	0.2	0.4	0.1	0.1	0.2	0.0	0.7	1.0	0.3	0.1		
41	Line 37 Sub regional Contribution	+2014 S1(2000 S2) * LINE 6	0.2	0.3	0.0	0.1	0.2	0.0	0.9	0.8	0.2	0.2		
42	Line 38 Regional Contribution	+2014 R(2000 R) * LINE 7	0.2	0.5	0.1	0.1	0.3	0.1	0.6	1.1	0.2	0.2		
43	Line 39 Natural Background contribution	+ LINE 2	0.1	0.0	0.0	0.0	0.4	0.1	1.4	1.0	0.0	0.0		
44	Line 40 2014 projected Annual Result	18.56	0.9	2.2	0.3	0.9	1.6	0.2	5.9	2.2	0.9	0.9		
45	Line 41 2014 Rollback Projection with additional controls								5.9		5.9	3-F		
46	Line 42 Local Contribution PM2.5-PM10 Area of Influence	+2014 L1(2000 L1) * LINE 4	0.2	1.0	0.1	0.2	0.4	0.1	0.7	2.0	0.6	0.1		
47	Line 43 Local Contribution Area of Influence of PM2.5	+2014 L2(2000 L2) * LINE 5	0.2	0.4	0.1	0.1	0.2	0.0	0.7	1.0	0.3	0.1		
48	Line 44 Sub regional Contribution	+2014 S1(2000 S2) * LINE 6	0.2	0.3	0.0	0.1	0.2	0.0	0.9	0.8	0.2	0.2		
49	Line 45 Regional Contribution	+2014 R(2000 R) * LINE 7	0.2	0.5	0.1	0.1	0.3	0.1	0.6	1.1	0.2	0.2		
50	Line 46 Natural Background contribution	+ LINE 2	0.1	0.0	0.0	0.0	0.4	0.1	1.4	1.0	0.0	0.0		
51	Line 47 2014 projected Annual Result	18.56	0.9	2.2	0.3	0.9	1.6	0.2	5.9	2.2	0.9	0.9		
52	Line 48 2014 projected Annual Result	17.76 linear nitrate projection							1.6		1.6	3-F		
53	Line 49 Modeling comparison	18.56 IMS95 nitrate modeling							0.9		0.9	3-F		
54	Line 50 Current 2005 Design value = 17.2	18.47 CMAQ nitrate modeling							0.7		0.7	3-F		
55	Line 51 2005 Design value = 17.2	18.66 Average of all three							0.8		0.8	3-F		
56	Line 52 2005 Design value = 17.2	18.51 Average of CMAQ and IMS95							4.1		4.1	3-F		
57	Line 53 CMAQ								1.8		1.8	3-F		
58	Line 54 CMAQ								1.0		1.0	3-F		
59	Line 55 CMAQ								0.8		0.8	3-F		
60	Line 56 CMAQ								4.5		4.5	3-F		



## **Revisions to receptor modeling rollback method**

### **Design value and species for Fresno and Kern provided from both 2000 PM10/PM2.5 species and 2005 PM2.5 species**

#### **2005 PM species processed with CMB receptor analysis**

Adjustments: 0.6 microgram for unassigned subtracted from organic carbon estimate

#### **2000 Design value and species determined from evaluation of PM10 receptor analysis and review of PM2.5 data**

From this process, an approximate match was made to calculate species for the observed concentration of PM2.5

Used Species data for PM2.5 for columns C, J, K and M

MV CMB adjustment PM10 to PM2.5 by EI ratio 90%

MV Kings adjusted to 55% of Tulare

T&BW CMB adjustment PM10 to PM2.5 by EI ratio 50%

T&BW CMB Kings adjusted to 55% of Tulare

Organic carbon- vegetative burning - adjustment ratio PM10 to PM2.5 75% Kern, Kings, Tulare

Organic carbon- vegetative burning - adjustment ratio PM10 to PM2.5 ratio 90% Fresno -representing 2000 OC/EC

Fresno uses 2001 PM2.5 nitrates from PM2.5 species data, 2000 not available

Kern uses 2002 speciation data for PM2.5 nitrates, 200 and 2001 not available

Tulare and Kings both use the Tulare 2002 speciation data for PM2.5 nitrates, 2000 and 2001 not available

#### **Methodology Improvements and corrections**

Revise background estimates for geologic , nitrate and sulfate to dynamic 10% rather than set value used for PM10

Correct background percent for Organic Carbon to %20

Revision of TOG to ROG for technical basis linking particle formation to reactive species, columns D-E and G-H

Revised primary secondary ratio to 85% 15% based on CRPAQS results, columns D-E and G-H

Revised intrabasin transport calculations based on mass relationship

Updated emissions inventory used for base and future years

Added model comparison rows and headings

Added RRF SMAT calculation fields on appropriate worksheets