# QUALITY ASSURANCE PROJECT PLAN

# FRESNO SUPERSITE - PHASE II

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# 1. PROJECT MANAGEMENT

## 1.1 Background/Introduction

The U.S. Environmental Protection Agency's (EPA) Supersites (U.S. EPA, 1998a) will operate research-grade air monitoring stations to improve understanding of measurement technologies, source contributions and control strategies, and the effects of suspended particles on health. Supersites are being established in seven urban areas within the continental United States: 1) Fresno, CA; 2) Los Angeles, CA; 3) Houston, TX; 4) St. Louis, MO; 5) Pittsburgh, PA; 6) Baltimore, MD; and 7) New York, NY. These Supersites are designed to: 1) test specific scientific hypotheses appropriate for the monitored airshed and suite of measurements; 2) provide measurements that can be compared and contrasted among the seven urban areas; 3) add value to larger monitoring networks and research studies; and 4) leverage EPA investments with contributions from other agencies. The information derived from these Supersites will complement information from $PM_{2.5}$ and $PM_{10}$ (particles with aerodynamic diameters less than 2.5 and 10 µm, respectively) measurement networks operated at Community Representative (CORE), transport, and background locations as part of the national $PM_{2.5}$ compliance and IMPROVE (Interagency Monitoring of Protected Visual Environments) networks.

Fresno is one of two prototype Supersites that were initiated during 1999, with Phase I measurements including the period of May 15, 1999, to March 31, 2001. The Phase II project enhances and extends monitoring at the existing Fresno Supersite such that a continuous record of advanced air quality measurements is available through March 31, 2003. This acquisition of nearly four years of data will accommodate the needs of simultaneous health-related studies and allow for hypothesis testing. In addition, the Fresno Supersite data set will represent large extremes in meteorology, aerosol composition, and emissions.

The objectives of the Fresno Supersite project are to: 1) test and evaluate new monitoring methods, with the intent to establish their comparability with existing methods and determine their applicability to air quality planning, exposure assessment, and health impact determination; 2) increase the knowledge base of aerosol characteristics, behavior, and sources so that regulatory agencies can develop standards and strategies that protect public health; and 3) acquire measurements that can be used to evaluate relationships between aerosol properties, co-factors, and observed health end-points.

Hypotheses for Fresno Supersite Objective 1 are: 1) $PM_{2.5}$ and $PM_{10}$ measurements by different methods are comparable; 2) mass from number count equals gravimetric mass; 3) hourly coarse particle concentrations can be reliably determined from continuous $PM_{10}$ and $PM_{2.5}$ measurements; 4) bioaerosols and endotoxins constitute a constant fraction of coarse particle mass; 5) photoionization measurements are correlated with organic particle concentrations; and 6) chemiluminescent $NO_2$ is equivalent to true $NO_2$. Hypotheses for Fresno Supersite Objective 2 are: 1) statistical aggregates of particle indicators for a single year deviate by less than sampling error from a three-year distribution; 2) continuous carbon measurements differentiate carbon sources from each other; 3) chemical, temporal, and particle size indicators of source contributions do not appreciably vary from year to year; 4) particle size, number, surface area, and major chemical component indictors are highly correlated and are equivalent indicators of health risk; and 5) $PM_{2.5}$ and $PM_{10}$ mass concentrations are higher during drought years than in years with normal precipitation. Hypotheses for Fresno Supersite Objective 3 are: 1) respiratory and cardiovascular distress are related to $PM_{2.5}$ concentrations and other indicators; 2) concentration thresholds exist for air quality indicator relationships to health effects; 3) particle characteristics have different effects on the onset and severity of short-term reductions in lung function, asthma attacks, and cardiovascular ailments; 4) animals react differently to different particle size, surface area, chemical, and mass characteristics; and 5) particles in human lungs are similar to those in urban air. Objective 3 hypotheses are to be tested in concurrent epidemiological, toxicological, exposure, and clinical studies that will use Fresno measurements in real time to conduct experiments and retrospectively to analyze the results (Watson et al., 2000).

U.S. EPA requires that projects performed by extramural organizations on behalf of or funded by the U.S. EPA that involves the acquisition of environmental data, especially data generated from direct measurement activities, shall be implemented in accordance with an approved Quality Assurance Project Plan (QAPP) (U.S. EPA, 1999). This QAPP was prepared for the Fresno Supersite project in accordance with U.S. EPA's specific requirements for form and content (U.S. EPA, 1999) and general guidelines (U.S. EPA, 1998b) in fulfillment of this requirement.

## 1.2 Project Organization

### 1.2.1 Overview of Project Organization

Figure 1-1 presents the organizational structure for the Fresno Supersite project. The Fresno Supersite Study is led by the Desert Research Institute (DRI) with collaboration from the California Air Resources Board (ARB) and the University of California at Riverside College of Engineering's Center for Environmental Research and Technology (CE-CERT). Dr. John G. Watson, a Research Professor at DRI, is the principal investigator, and Dr. Judith C. Chow, also a DRI Research Professor, is co-investigator. Mr. Peter Ouchida of ARB is the Supervisor of the Fresno site, and Mr. Scott Scheller of ARB is the site operator. These individuals interface directly with the CE-CERT and DRI personnel described below. Mr. Dennis Fitz, a Research Engineer at CE-CERT, is Quality Assurance Manager. Supersite measurements include an array of particle size measurements that are being duplicated and enhanced in a new-generation smog chamber being constructed at CE-CERT under EPA sponsorship. This chamber will include aerosol generation and detection capabilities that will provide a primary standard for particle size instrument calibration. Although QA is supervised by an independent organization, it is an integral part of the measurement process. Mr. Fitz is a continual and active participant in technical decision-making and data analysis. These principals are supported by staff specializing in instrument design and operation, chemical speciation, data management, data analysis, and air quality modeling.

Mr. Dale Crow, DRI Research Engineer, is task leader for field operations. Mr. Steve Kohl, DRI Research Chemist, supervises laboratory operations (including sample chain-of-custody, data management, and data validation). Dr. John Bowen, DRI Research Scientist, coordinates field and laboratory operations. Mr. Crow and Dr. Bowen assist ARB site operators with the installation and calibration of field equipment. Dr. Norman Robinson, DRI Associate Research Professor, in collaboration with Mr. Greg O'Brien at ARB, develops database formats and structures and assembles the project database. Dr. Douglas Lowenthal, DRI Associate Research Professor, applies Level I and Level II data validation criteria, performs data analysis, and assists in preparation of project publications.

### 1.2.2 Responsibilities of Key Individuals

**Dr. John Watson**, as Principal Investigator, oversees all project tasks and has responsibility for the successful completion of Supersite measurements and interactions with other investigators that will use the measurements. Dr. Watson monitors all phases of the study and ensures that study objectives and milestones are attained. He participates in meetings with EPA's project officer and prepares quarterly progress reports. He visits the Supersite every three to six months, organizes and conducts meetings with ARB participants, and resolves conflicts and problems as they arise. He reviews the database and ensures that Supersite data are submitted to the NARSTO Permanent Data Archive within 12 months of the end of each quarter of data collection as required by the cooperative agreement.

**Dr. Judith Chow**, as Co-Investigator, assists in project planning and facilitates field sampling, chemical analysis, data retrieval/reformatting/processing, and data analysis/modeling tasks. Dr. Chow conducts site visits and verifies instrument settings, and collaborates with other team members on quarterly to semiannual reviews, quality assurance project plan, quarterly progress reports, and final reports. Dr. Chow also participates in project planning and progress report meetings

**Dr. Norman Robinson**, as Data Manager, assembles the project database. His responsibilities include: 1) database design [structure of the database; tables used to hold data; and conventions such as names, units, flags, time conventions, etc.], 2) data processing [convert data collected from various sources in various formats and conventions to meet Fresno Supersite database conventions], 3) data traceability [design data processing procedures and documentation to provide traceability from the database back to the original data], 4) level 0 statistical checks [perform minimum and maximum checks, jump checks, and flatness checks], and 5) database documentation [assemble internal and external documentation describing database structures and data processing procedures].

**Dr. Douglas Lowenthal**, as Data Analyst, assists Drs. Watson and Chow in assembling the data and applying the validation tests described in Section 2.10. Comparisons will be made between in-situ continuous measurements and integrated filter measurements to establish equivalence and comparability.

**Mr. Dennis Fitz**, as Quality Assurance Manager, specifies primary, calibration, performance test, and audit standards and the frequency of their application. He defines data validity flags that qualify the information based on internal and external consistency tests. He uses data from performance audits, performance tests, and validation checks to define the accuracy, precision, and validity of each data point. These measurement attributes are added to the project database. Mr. Fitz also conducts on-site and laboratory system audits for each measurement. He reviews each standard operating procedure for completeness and consistency. He analyzes performance audit results, and prepares audit reports. For the entire data set, Mr. Fitz prepares data qualification statements that define the extent to which the acquired measurements attain the project's accuracy, precision, validity, and completeness objectives.

## 1.3 Project Description

The Fresno Supersite is acquiring advanced air quality measurements related to suspended particulate matter to accomplish the following objectives:

Test and evaluate non-routine monitoring methods, with the intent to establish their comparability with existing methods and determine their applicability to air quality planning, exposure assessment, and health impact determination.

Increase the knowledge base of aerosol characteristics, behavior, and sources so regulatory agencies can develop standards and strategies that protect public health.

Evaluate relationships between aerosol properties, co-factors, and observed health end-points.

The measurement emphasis at the Fresno Supersite is on in-situ, continuous, short duration measurements of: 1) $PM_{2.5}$, $PM_{10}$, and coarse ($PM_{10}$ minus $PM_{2.5}$) mass; 2) $PM_{2.5}$ sulfate, nitrate, carbon, light absorption, and light extinction; 3) numbers of particles in discrete size ranges from 0.01 to ~10 µm; 4) criteria pollutant gases ($O_3$, CO, $NO_x$); 5) reactive gases ($NO_2$, $NO_y$, $HNO_3$, PAN); and 6) single-particle characterization. Field sampling and laboratory analysis are applied for: 1) gaseous and particulate organic compounds (light hydrocarbons, heavy hydrocarbons, carbonyls, PAH, and other semi-volatiles); and 2) $PM_{2.5}$ mass, elements, ions, and carbon.

Observables common to other Supersites are: 1) daily $PM_{2.5}$ 24-hour average mass with Federal Reference Method (FRM) samplers; 2) continuous hourly and five minute average $PM_{2.5}$ and $PM_{10}$ mass with beta attenuation monitors (BAM) and tapered element oscillating microbalances (TEOM); 3) $PM_{2.5}$ chemical speciation with an EPA speciation sampler and protocol; 4) coarse particle mass by dichotomous sampler and difference between $PM_{10}$ and $PM_{2.5}$ BAM and TEOM measurements; and 5) high-sensitivity and time-resolved scalar and vector wind speed, wind direction, temperature, relative humidity, barometric pressure, and solar radiation. In addition to the Fresno Supersite, three satellite sites are selected to assess the zone of representation of the centralized Supersite. Figure 1-2 shows the location of the Fresno First Street Supersite (FSF) and the two nearby satellite sites next to a busy road near a freeway on ramp (FREM) and in a quiet residential neighborhood

(FRES). Figure 1-3 shows the central part of California's San Joaquin Valley, within which Fresno is the largest city, with the locations of other sites relevant to Supersite hypothesis testing.

### 1.3.1 Project Tasks

The Fresno Supersite study includes the following six tasks: 1) equipment procurement and installation; 2) network operations and data processing; 3) laboratory measurements; 4) quality assurance; 5) data validation and data analysis; and 6) management and reporting.

Under Task 1, Equipment Procurement and Installation, the equipment listed in Table 1-1 is specified, procured, acceptance-tested, installed, and calibrated. New instruments are configured and bench-tested in the laboratory prior to field deployment. Instrument placement, sample presentation tubing, and wiring are documented. Arrangements are made to ensure continued sampling between 1999 and the end of the first quarter of 2003. Data logging capabilities and outputs of each instrument are specified and modifications made to the digital and analogue data acquisition systems; these systems provide remote access to near real time data. This communication capability can be used by health researchers to schedule clinical and toxicological measurements of test subjects.

Watson et al. (1998a) describe the operating principles, detection limits, and expected accuracy and precision of most of the instruments specified in Table 1-1. Standard operating procedures (SOPs) relevant to most of the Fresno measurements have been developed, and are listed in Table 2-1. Criteria gas pollutants (e.g., CO, $O_3$, $NO_x$), meteorological, and other air toxic measurements are acquired by ARB as part of the NAMS, SLAMS, and PAMS networks (California Air Resources Board, 1978). $PM_{2.5}$ and $PM_{10}$ reference method sampling follows established procedures (U.S. EPA, 1998c).

Under Task 2, Network Operations and Data Processing, routine on-site operations and external QA audits are conducted. On-site activities are carried out by the ARB site operator, Mr. Scott Scheller, and directed by the Fresno site supervisor, Mr. Peter Ouchida. Mr. Scheller is assisted by local college students. On-site operations include: 1) inspection of instruments and data from the acquisition systems; 2) periodic performance tests; 3) sample receipt, changing, and storage; 4) documentation of instrument, station, and meteorological conditions; 5) preventive maintenance; 6) corrective maintenance; and 7) transmission of data, samples, and documentation.

On-site operations are supplemented with DRI air quality laboratory support that includes: 1) periodic download and examination of field data; 2) review of site documentation; 3) replenishment of consumables and supplies; 4) regular contact and operations review with field staff; 5) periodic site visits to perform calibration, repair, and maintenance; and 6) coordination with other investigators and auditors. Uploaded data are integrated into a comprehensive database that is submitted to the validation checks described in Sections 2.10 and 4.0.

Task 3, Laboratory Measurements, follows the guidelines documented by Chow and Watson (1998) for U.S. EPA's speciation network. Gravimetric (U.S. EPA, 1998c), x-ray fluorescence (Watson et al., 1999), ion chromatography (Chow and Watson, 1999), atomic absorption spectrophotometry, automated colorimetry, and thermal/optical carbon (Chow et al., 1993, 2001; Birch and Cary, 1996; Birch, 1998; NIOSH, 1996) analyses are performed on filter samples collected by Andersen FRM, Andersen RAAS (speciation sampler), and Airmetrics Minivol samplers (Chow, 1995). The specific procedures for the laboratory measurements are presented in the appropriate SOP listed in Table 2-1. Field blanks are provided with filter packs designated for sampling. Each analysis includes daily calibration, 10% replicates, standards, blanks, and re-analyses when performance tolerances or data validation criteria are not met. Remaining sample sections are archived under refrigeration for the duration of the project for potential re-analysis or analysis for other species. Averages and standard deviations of field blank concentrations are determined and incorporated into calculations of chemical component concentrations (Watson et al., 2001).

Task 4, Quality Assurance, is described in greater detail in Sections 2.5 to 2.8 and 3.1. An independent QA manager and his staff at UCR conduct systems and performance audits. Data qualification statements are produced that estimate the extent to which accuracy and precision of the acquired data can be used to test hypotheses. Audit schedules, tests, and standards are also described in Sections 2.5 to 2.7. Several of the advanced measurements do not have traceable standards; their accuracy will therefore be evaluated by comparison with collocated measurements of the same or similar quantities. Several of the measurement hypotheses presented in Table 3-1 address these comparisons. At the conclusion of the experiment a Final Quality Assurance Report (QAFR) will be issued. This report will state whether or not the project DQOs have been met.

Under Task 5, Data Validation and Analysis, a research-grade database of specified accuracy, precision, validity, and completeness has been developed. The data validation levels and techniques that will be employed are described in Section 2.10.2. The database integrates Fresno Supersite measurements with similar and complementary data from other sites in the Fresno area and other parts of California. Time series and scatterplots are examined to identify outliers. Validation levels described in Section 2.10 are assigned. After data validation and data management procedures are perfected, the continuous database is intended to be available to investigators within three months of the previous calendar quarter, and the laboratory analysis database is intended to be available within six months after the previous calendar quarter. Internet-based data management and delivery systems are being developed at the ARB (http://www.arb.ca.gov/airways/crpaqs/lookups.htm) to facilitate data distribution to all users. At project completion, Fresno Supersite data will be compiled onto a CD-ROM with project reports and publications. The available historical database of gas, particulate, and meteorological measurements for the Fresno Supersite is also included on the CD. These data are submitted to EPA's Supersite database and to applicable NARSTO data archives. Task 5 also uses data to examine hypotheses. Descriptions of these analyses and data analysis responsibilities are given in Section 4.

Under Task 6, Management and Reporting, the efforts of different project participants, including those associated with concurrent studies, are coordinated. The Principal Investigator attends national Supersite meetings each year and presents progress on measurements and hypothesis testing. This QAPP and the validated data set described in Section 2.10 are also project management and reporting responsibilities.

### 1.3.2 Project Schedule

The project schedule and milestones are shown in Figure 1-4. As shown in Table 1-1, measurements began May 15, 1999, and will continue until March 31, 2003. Additional measurements as part of the California Regional $PM_{2.5}/PM_{10}$ Air Quality Study (CRPAQS) (Watson et al., 1998b) will take place during 15 episode winter intensive days between December 1, 2000, and January 31, 2001, and at several other locations around Fresno from December 1, 1999, through January 31, 2001.

## 1.4 Quality Objectives and Criteria for Measurement Data

DRI and its cooperating groups, CE-CERT and ARB, are fully committed to an effective quality assurance/quality control (QA/QC) program for the Fresno Supersite project. DRI and its cooperating groups will ensure that all ambient air quality and research measurement data generated for internal and external use shall meet specific data quality objectives (DQOs). In some cases, such as for monitoring of criteria pollutants (including $PM_{2.5}$), data quality objectives have been established by the EPA, and are described in detail in 40CFR58, Appendix A. These DQOs have been used to establish data quality indicators (DQIs) for various phases of the monitoring process. In some instances, the performance of the state-of-the-art instruments used at the Fresno Supersite has not been reliably determined. Efforts are made to compare the same measurements on different instruments to assess the quality, reliability, and comparability of measured pollutant concentrations.

The DQIs that are used to characterize measurements at the Fresno Supersite are listed and defined below. Where applicable, the methodology described in 40CFR58, Appendix A will be utilized.

### 1.4.1 Precision

Precision represents the reproducibility of measurements as determined by collocated sampling using the same methods or by propagation of individual measurement precisions determined by replicate analysis, blank analysis, and performance tests (Watson et al., 2001). Precision, $s_M$, can thus be defined as deviations from the average response to the same measurable quantity as follows:

$$s_m = [(\sum_{i=1}^{n} (C_m - C)^2)/(n-1)]^{1/2}$$

Precision of the continuous analyzers will be determined from replicate analyses of calibration standards, span checks, and/or precision check records. For a direct-reading analyzer that provides a response that is linearly proportional to the ambient concentration, the calibration relationship between the true concentration, $C_t$, and the measured concentration, $C_m$, is:

$$C_m = aC_t + b$$

Where: a = the proportionality constant (or span)
b = the baseline or blank level

Because $C_t$ is assumed to be the true value, its precision is set equal to zero. Using derived formulas for the propagating of errors, two simple rules can be used to propagate the precisions of the measured values ($s_a$ and $s_b$) to estimate the precision of the derived value ($s_x$). This is assuming the errors are randomly distributed about the true value according to a normal distribution, and that these errors are uncorrelated with each other.

1. For addition and subtraction of the form $x = a + b$ or $x = a – b$:

$$s_x^2 = s_a^2 + s_b^2$$

2. For multiplication and division of the form $x = ab$ or $x = a/b$:

$$(s_x/x)^2 = (s_a/a)^2 + (s_b/b)^2$$

Applying these equations to the measured concentration equation ($C_m = aC_t + b$), the measurement precision, $s_m$, is:

$$s_m^2 = (s_a^2/a^2)(C_m\text{-}b)^2 + s_b^2$$

Thus, the precision for a direct-reading measurement, $s_m$, is seen to be a function of the concentration, $C_m$, the relative standard deviation of the span ($s_a/a$), and the absolute standard deviation of the baseline response, $s_b$. Each of these (Cm, $s_a/a$, and $s_b$) must be quantified to estimate the precision of the measurement Cm. The values are determined by periodic performance testing using standard concentrations and scrubbed air. Many of the direct-reading instruments at the Fresno Supersite automatically provide daily zero and span values that can be used in this equation. Other instruments require manual methods and estimations to obtain these values.

Precision for filter-based instruments are propagated from precisions of the volumetric measurements, the chemical composition measurements, and the field blank variability using the methods of Bevington (1969) and Watson et al. (1995). The following equations are used to calculate the precision associated with filter-based measurements:

$$C_i = (M_i - B_i)/V$$

$$V = F \times t$$

$$\overline{B_i} = \frac{1}{n}\sum_{j=1}^{n} B_{ij}$$

$$STD_{Bi} = [\frac{1}{n-1}\sum_{j=1}^{n}(B_{ij} - \overline{B_i})^2]^{1/2}$$

$$SIG_{Bi} = [\frac{1}{n}\sum_{j=1}^{n}(\sigma_{Bij})^2]^{1/2}$$

Case 1 . . . If $\overline{B_i} < SIG_{Bi}$
then $\overline{B_i} = 0$ and $\sigma_{\overline{Bi}} = 0$

Case 2 . . . If $\overline{B_i} > SIG_{Bi}$ and $\overline{B_i} < STD_{Bi}$
then $\overline{B_i} = 0$ and $\sigma_{\overline{Bi}} = STD_{Bi}$

Case 3 . . . If $\overline{B_i} > SIG_{Bi}$ and $\overline{B_i} > STD_{Bi}$
then $\overline{B_i} = \overline{B_i}$ and $\sigma_{\overline{Bi}} = STD_{Bi}$

$$\sigma_{Ci} = [\frac{\sigma_{Mi}^2 + \sigma_{Bi}^2}{V^2} + \frac{\sigma_V^2 (M_i - B_i)^2}{V^4}]^{1/2}$$

$$\sigma_{RMS_i} = (\frac{1}{n}\sum_{j=1}^{n}\sigma_{Ci}^2)^{1/2}$$

$$\sigma_V/V = 0.05$$

where:

$\overline{B_i}$ = average amount of species i on field blanks
$B_{ij}$ = the amount of species i found on field blank j
$C_i$ = the ambient concentration of species i
F = flow rate throughout sampling period
$M_i$ = amount of species i on the substrate
$M_{ijr}$ = amount of species i on sample j from original analysis
$M_{ijr}$ = amount of species i on sample j from replicate analysis
n = total number of samples in the sum
$SIG_{Bi}$ = the root mean square error (RMSE), the square root of the averaged sum of the squares of $\sigma_{Bij}$.
$STD_{Bi}$ = standard deviation of the blank
$\sigma_{\overline{Bi}}$ = blank precision for species i
$\sigma_{Bij}$ = precision of the species i found on field blank j
$\sigma_{Ci}$ = propagated precision for the concentration of species i

$\sigma_{Mi}$ = precision of amount of species i on the substrate
$\sigma_{RMS_i}$ = root mean square precision for species i
$\sigma_V$ = precision of sample volume
t = sample duration
V = volume of air sampled

The project goal for precision is ±10%, expressed as the coefficient of variation (CV), for values that exceed ten times their lower quantifiable limits. The precision goal for gravimetric mass is ±5% CV as determined from replicate weighings.

### 1.4.2 Bias

Bias is the systematic or persistent distortion of a measurement process that causes error in one direction. Bias is determined through performance audits and or by inter-comparisons of the performance of similar instruments. Quantifiable biases that exceed precision intervals are corrected as part of the data validation process.

Due to the unique nature of many of the measurements to be conducted, the situation will arise where primary standards are unavailable to determine bias. In addition, bias of the discrete methodologies can only be determined for the analytical instruments, and does include effects introduced by sample collection and transport. Bias will be calculated under three distinct situations:

- A primary standard does not exist to determine instrumental accuracy
- The comparison of two discrete methodologies using ambient data

- Comparison two discrete methodologies using ambient data, one of which is a reference standard.

When a primary standard method is not available, bias will be calculated using the equation:

$$\text{Bias} = 1/n \sum_{i=1}^{n} \left[(X_i–S)/S\right] \text{ x } 100$$

Where S is a non-primary standard value and $X_i$ is the instrument results of the ith measurement of the standard.

For comparison of two methodologies, neither of which is considered as a reference standard, bias will be calculated by the equation:

$$\text{Bias} = 1/n \sum_{i=1}^{n} \left[((M1_i - M2_i)/((M1_i + M2_i)/2))\right] \text{ x } 100$$

Where $M1_i$ and $M2_i$ are the ith measurement of the two methodologies (M1 and M2) being subjected to comparison. The use of the average of the two methodologies in computing bias recognizes that a primary standard is not available.

If the results of a particular methodology are being compared to a primary reference standard then the following equation will apply:

$$\text{Bias} = 1/n \sum_{i=1}^{n} \left[(M2_i – M1_i)/M1_i\right] \text{ x } 100$$

Where the denominator has been replaced with the ith measurement of the primary standard that will be used to determine bias.

### 1.4.3 Accuracy

Accuracy is the correctness of data and refers to the degree of difference between a measured value and a known or “true” value. For particulate measurements, there are no known true values. Relative accuracy may be determined by comparing a measured value with a presumed reference or standard, such as a $PM_{2.5}$ FRM sampler. Sampler accuracy will be measured by performance (flow rate) checks and audits between the sampler and a certified flow meter. The goal is ± 5% relative percent difference (RPD) or better. Since no true reference samples exist for the chemistry of airborne particulate matter, the accuracy of other speciated atmospheric components cannot be inherently determined. Analytical accuracy of the analytes will be determined by analyzing known reference materials in the laboratory.

The accuracy of the continuous analyzers will be determined from performance audits conducted by the ARB. The analyzers will be challenged with standards from an independent, NIST-traceable source not used for calibration, encompassing the operational range of the instrument. A minimum of three data points, including zero will comprise the performance audit. A linear regression analysis in the following form will be used to determine the slope, intercept and correlation coefficient:

$$y = mx + b$$

Where x the audit concentration, y is the reported analyzer response, m is the slope, and b is intercept. The deviation of the slope from unity is used as the measure of accuracy. The goal for the continuous analyzers is ± 10%, or a slope within the range of 0.900 to 1.100.

For gravimetric and speciated fine particle samplers, the accuracy will be determined by flow rate checks. The estimation of accuracy for this method is:

$$\%\text{Accuracy} = [\ (Q_m - Q_a)/Q_a] \text{ x } 100$$

Where $Q_a$ is the flow rate measured using a NIST traceable flow device, and $Q_m$ is the flow rate indicated by the sampler.

### 1.4.4 Detectability

Detectability is the low range critical value that a method-specific procedure can reliably discern. Analytical procedures and sampling equipment impose specific constraints on the determination of minimum detection limits (MDLs). For the gaseous analyzers MDLs are determined by repeatedly challenging the analyzer with zero air, and for filter-based methods the MDLs are determined by the use of field and laboratory blanks. A field blank is a filter that travels with the filters that will be utilized in sample collection and should be treated in the same manner as any other filter with the exception that it does not collect sample. A laboratory blank is a filter that is pre-weighed and processed in the same manner as all filters arriving from the field, but is kept in the laboratory. Besides providing MDL information the use of blanks provides essential field and laboratory measurement control data. Generally, the MDL for measurements on this program is determined as three times the standard deviation of field blanks or three times the standard deviation of the noise of an instrument when subjected to clean air.

The MDL for each continuous gas analyzer has been well characterized; this information can be found in the appropriate analyzer manual. This information can be verified through statistical evaluation of data from zero air checks, using the following:

$$\text{MDL} = t_{(n-1,1-a = 0.99)} * s$$

Where s is the standard deviation of the replicate zero analyses, t is the students t value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

The determination of MDLs for discrete measurements involves a different approach. The samples are collected at a location away from analysis. Standards for the determination of detection limits for the laboratory analytical instruments are prepared in the laboratory and therefore are not subjected to the same procedures and equipment as the ambient samples. This detection limit is referred to as the instrument detection limit (IDL). The IDL is indicative of the ability of the instrument to differentiate, at a specific probability, between zero and at a specific concentration. The IDL standard does not experience the same handling procedures; collection on filter medium and denuders for HPLC analysis or canister collection for GCMS analysis; and therefore does not provide information relating to the detection limit at ambient. The IDL for each HPLC and GCMS analyte will be determined through statistical evaluation as described in the equation above.

### 1.4.5 Completeness

Completeness is the percentage of valid data reported compared to the total number of samples that are scheduled to be collected during the year. For this project, in which many of the instruments are prototypes or are newer technology, the completeness objective for all species and measurements is 75% for each year. Completeness will be determined using the following:

$$\text{Completeness} = [(D_x - D_c)/D_c] \times 100$$

With regard to discrete measurements, $D_x$ is the number of samples for each species that valid results are obtained and $D_c$ is the number of samples that scheduled to be collected and analyzed during the year. Completeness for continuous methods is the percentage of valid data obtained from the total amount possible, over a given time period.

### 1.4.6 Representativeness

Representativeness is the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environment condition. For this project, spatial and temporal data representativeness are achieved by following siting criteria for particulate monitoring sites (Watson et al., 1997) and by comparing measurements at the First Street site with those from other monitoring stations in the region, including the satellite sites identified in Figures 1-2 and 1-3.

### 1.4.7 Comparability

Comparability reflects the extent to which measurements of the same observable agree among different methods. Comparability may vary by method, aerosol composition, and meteorological conditions. Several of the hypotheses tested at the Fresno Supersite include formal comparisons of measurements for different measurement configurations, aerosol compositions, and times of the year.

## 1.5 Project Training Requirements

The roles of Principal Investigators, QA manager, field and lab supervisors, operators, coordinators, database managers, and data analysts are described in Sections 1.2.1 and 1.2.2 of this QAPP. Each of these persons has substantial experience in their assigned tasks. These key project personnel should be familiar with the content of this QAPP, thus obtaining a project overview, including information on all functions of the measurement systems, from sampling to data validation and reporting. The Principal Investigators are responsible for ensuring that project participants are properly trained to perform individual tasks. Additional guidance about actual site operations for this project is provided to the site operators in the form of checklists, forms, SOPs, and other material forming part of this QAPP. In addition, all project personnel must review and understand the SOPs applicable to their respective area of responsibility.

The indoctrination of any new personnel will be accomplished through their reading of the appropriate SOPs, coupled with on-the-job training by experienced personnel. If major revisions or enhancements are made to this QAPP or SOPs, all affected individuals must review those revisions at that time.

## 1.6 Documentation and Records

This QAPP is summarizes Fresno Supersite measurements, defines data quality indicators, and specifies data quality objectives. Field and laboratory standard operating procedures developed for Fresno Supersite measurements are followed and revised as needed, for the duration of the study. Procedures for advanced monitoring methods are being developed and reviewed by the Principal Investigators. Revisions made to the SOPs during the study period are noted and archived for traceability. Remedial actions taken as a result of field, laboratory, or data audits are also documented. This information will be incorporated into the Final Quality Assurance Report as part of final project report delivery to EPA. Procedural summaries will also be published in appropriate handbooks and manuals.

A description of the data management process is presented in Section 2.10 of this QAPP. This includes the database design, data validation methodology, and eventual transmittal of the data to the NARSTO center for archiving. In addition, a records management system specifically dedicated to this program will be maintained at the DRI facility. The objective of this system is to provide efficient retrieval of all measurements and experiments performed under this program, along with all supporting documentation which includes all pertinent records, field and laboratory logs, and chain-of-custody forms for all discrete measurements. In the case where the record is in electronic format, it is stored in a set of dedicated LAN folders. Hard-copy records will be maintained in a dedicated cabinet. These records will be maintained in the program files for a period of not less than five years after the completion of Phase II.

**Table 1-1.** Fresno Supersite Measurements

| **Observable and Method** | **Operator**[h] | **Size Range** | **Ave. Time** | **Frequency** | **Period** |
|---|---|---|---|---|---|
| **Gases** | | | | | |
| Nitrogen oxides (NO/$NO_x$) (TEI 42 chemiluminescence with internal converter) [a] | ARB | Gas | 5-min | daily | 1990 onward [b] |
| $NO_2$/PAN (UC Riverside Luminol) | ARB | Gas | 5-min | daily | 12/1/00 to 3/31/03 |
| Ozone (API 400 UV absorption) [a] | ARB | Gas | 5-min | daily | 1990 onward [b] |
| Carbon monoxide (Dasibi 3008 infrared gas filter correlation) | ARB | Gas | 5-min | daily | 1990 onward [b] |
| Non-methane hydrocarbons (TEI 55C flame ionization) | ARB | Gas | 1-hr | daily | 1990 onward [b] |
| Reactive nitrogen ($NO_y$) (TEI 42C chemiluminescence with external converter) [a] | ARB | Gas | 5-min | daily | 12/15/99 to 3/31/03 |
| Nitric acid ($HNO_3$) (TEI 42C chemiluminescence with external converters and denuders) [c] | ARB | Gas | 5-min | daily | 12/1/00 to 3/31/03 |
| **Filter Mass and Chemistry** | | | | | |
| TSP mass (Andersen hivol with quartz filters) and lead | ARB | TSP | 24-hr | 12th day | 1990 onward [b] |
| $PM_{10}$ mass, sulfate, nitrate, chloride, and ammonium (Andersen hivol SSI with quartz filters) | ARB | <10 µm | 24-hr | 6th day | 1990 onward [b] |
| $PM_{2.5}$ and coarse mass (dichotomous samplers with Teflon filters) | ARB | <2.5 µm<br><10 µm | 24-hr | 6th day | 1990 onward [b] |
| $PM_{2.5}$ mass, light absorption, elements, ions, and carbon (two Andersen single-channel FRMs with Teflon and quartz filters) | ARB/DRI | <2.5 µm | 24-hr | 6th day | 7/5/99 to 6/30/01 (method evaluation) |
| $PM_{2.5}$ mass, elements, ions, and carbon (six-channel Andersen RAAS speciation sampler with denuders and backup filters) | ARB/DRI | <2.5 µm | 24-hr | 6th day | 7/5/99 to 6/30/01 (method evaluation) |
| Particle morphology (Airmetrics Minivol with polycarbonate filter for scanning electron microscopy) | ARB/DRI | < ~30 µm | 24-hr | 6th day | 7/5/99 to 6/30/01 (method evaluation) |

| **Observable and Method** | **Operator**[h] | **Size Range** | **Ave. Time** | **Frequency** | **Period** |
|---|---|---|---|---|---|
| PM$_{2.5}$ mass, elements, ions, and carbon (Airmetrics Minivol with Teflon/citric-acid-impregnated and quartz/sodium-chloride-impregnated filters) [c] | ARB/DRI | <2.5 µm | 24-hr | 6th day | 12/1/99 to 3/31/03 |
| PM$_{2.5}$ mass, elements, ions, and carbon (two-channel Met One speciation sampler) | ARB/DRI | <2.5 µm | 24-hr | 3rd day | 2001 onward [b] |
| PM$_{2.5}$ mass, elements, ions, carbon, and ammonia (two-channel DRI sequential filter sampler with nitric acid denuders and backup filters; mass on all, chemistry on 100 samples) [a] | ARB/DRI | <2.5 µm | 24-hr | daily | 12/1/99 to 1/31/01 [d] |
| PM$_{2.5}$ mass, elements, ions, and carbon (two-channel sequential filter sampler with denuders and backup filters) [a] | ARB/DRI | <2.5 µm | 3-, 5-, and 8-hr (5 samples per day) [e] | daily on episode days | 15 episode days<br>12/1/00 to 1/31/01 [d] |
| Nitric acid and ammonia (denuder difference with aluminum oxide and citric acid denuders and sodium chloride and citric acid impregnated cellulose filters) | ARB/DRI | <2.5 µm | 3-, 5-, and 8-hr (5 samples per day) | daily on episode days | 15 episode days<br>12/1/00 to 1/31/01 [d] |
| Toxic species (metals, chromium VI, aldehydes) (Xontec 920) | ARB | <~30 µm | 24-hr | 12th day | 1996 onward [b] |
| **Continuous Particle Mass and Chemistry** | | | | | |
| PM$_{2.5}$ mass (50 °C R&P 1400a TEOM with sharp-cut cyclone)) | ARB | <2.5 µm | 1-hr | daily | 7/5/99 to 3/31/03 |
| PM$_{10}$ mass (50 °C R&P 1400a TEOM) | ARB | <10 µm | 1-hr | daily | 7/5/99 to 3/31/03 |
| PM$_{2.5}$ mass (ambient temperature Met One 1020 BAM with sharp-cut cyclone) [a] | ARB | <2.5 µm | 1-hr | daily | 5/15/99 to 3/31/03 [b] |
| PM$_{10}$ mass (ambient temperature Met One 1020 BAM) [a] | ARB | <10 µm | 1-hr | daily | 5/15/99 to 3/31/03 [b] |
| PM$_{2.5}$ nitrate (R&P 8400N/ADI flash volatilization with NO$_x$ detector) [c] | ARB | <2.5 µm | 10-min | daily | 9/23/99 to 3/31/03 |
| PM$_{2.5}$ sulfate (R&P8400S/ADI flash volatilization with SO$_2$ detector) | ARB | <2.5 µm | 10-min | daily | 9/23/99 to 10/28/99<br>2/7/00 to 3/31/03 |

| Observable and Method | Operator[h] | Size Range | Ave. Time | Frequency | Period |
|---|---|---|---|---|---|
| $PM_{2.5}$ organic and elemental carbon (R&P Series 5400 thermal evolution, OC at 275 °C, EC at 600 °C) [a] | ARB | <2.5 µm | 30-min | daily | 12/15/99 to 3/31/03 |
| Individual particle size and chemistry (UC Riverside time-of-flight spectrometer) | ARB | <10 µm | 5-min | daily on episode days | 12/1/00 to 1/31/01 [d] |
| Particle-bound polycyclic aromatic hydrocarbons (PAH) (EcoChem Analytics PAS2000 UV ionization with electrometer detector) | ARB | <1 µm | 5-min | daily | 9/30/99 to 3/31/03 |
| **Organic Gases and Particles** | | | | | |
| Toxic hydrocarbons ($C_2$ to $C_{12}$) (Xontec 910 canister sampler) | ARB | gas | 24-hr | 12th day | 1995 onward |
| Carbonyls (Xontec 925 2,4-dinitrophenylhydrazine [DNPH] cartridge sampler) [a] | ARB | gas | 24-hr<br>summer (4 samples per day) [f] | 12th day<br>3rd day | 1995 onward [b]<br>1995 onward [b] |
| Carbonyls (DRI sequential sampler with DNPH cartridge) [a] | ARB/DRI | gas | 5- to 8-hr, (4 samples per day) | daily for episodes | 15 episode days 12/1/00 to 1/31/01 [d] |
| Light hydrocarbons ($C_2$ to $C_{12}$) (canister sampler) [a] | ARB/DRI | gas | 5- to 8-hr, (4 samples per day) | daily for episodes | 15 episode days 12/1/00 to 1/31/01 [d] |
| Heavy hydrocarbons ($C_{10}$ to $C_{20}$) (TENAX sampler) [a] | ARB/DRI | gas | 5- to 8-hr, (4 samples per day) | daily for episodes | 15 episode days 12/1/00 to 1/31/01 [d] |
| $PM_{2.5}$ organic compounds (DRI sequential sampler with Teflon-coated glass-fiber/PUF/XAD filters) [a] | ARB/DRI | <2.5 µm<br><2.5 µm | 5- to 8-hr, (4 samples per day)<br>24-hr | daily for episodes<br>6th day | 15 episode days 12/1/00 to 1/31/01 [d]<br>6/1/00 to 9/30/00 [d] |
| $PM_{2.5}$ organic compounds (Airmetrics Minivol with Teflon-coated glass-fiber filters) (aggregate 60 samples for organic compound analysis) [a] | ARB | <2.5 µm | 24-hr | 6th day | 2/1/00 to 1/31/01 [d] |

| Observable and Method | Operator[h] | Size Range | Ave. Time | Frequency | Period |
|---|---|---|---|---|---|
| **Continuous Light Scattering** | | | | | |
| Ambient particle light scattering (Optec NGN2 ambient-temperature nephelometer at 550 nm) | ARB | <~30 µm | 5-min | daily | 5/15/99 to 3/31/03 |
| Total particle light scattering (Radiance M903 nephelometer with smart heater at 530 nm) [a] | ARB | <~30 µm | 5-min | daily | 2/15/00 to 3/31/03 |
| $PM_{2.5}$ particle light scattering (Radiance M903 nephelometer with smart heater at 530 nm and sharp-cut cyclone) | ARB | <2.5 µm | 5-min | daily | 4/1/00 to 3/31/03 |
| Total particle light scattering (GreenTek GT640A photometer at 780 nm) | ARB | <2.5 µm | 5-min | daily | 1/1/00 to 3/31/03 |
| Total particle light scattering (TSI DustTrak 8520 photometer at 780 nm) | ARB | <2.5 µm | 5-min | daily | 5/15/99 to 3/31/03 |
| **Continuous Light Absorption** | | | | | |
| Coefficient of haze (RAC 205019-1 paper tape sampler) | ARB | <~30 µm | 2-hr | daily | 1990 onward [b] |
| Single-wavelength light absorption (McGee AE14U aethalometer at 880 nm) [a] | ARB | <2.5 µm | 5-min | daily | 5/15/99 to 3/31/03 |
| Seven-wavelength light absorption (Andersen AE30S multi-color [350, 450, 520, 590, 615, 660, 880, and 950 nm] aethalometer) | ARB | <2.5 µm | 5-min | daily | 5/15/99 to 3/31/03 |
| **Particle Sizes** | | | | | |
| Ultrafine particle number by size in 50 size fractions (TSI 3936L10 S scanning mobility particle sizer) [a] | ARB | 0.010 to 0.5 µm, 50 bins | 5-min | daily | 12/15/99 to 3/31/03 |
| Fine particle number in 8 size fractions (PMS Lasair 1003 optical particle counter) [a] | ARB | 0.1 to 2 µm (<0.1, <0.2, <0.3, <0.4, <0.5, <0.7, <1.0, and <2.0 µm) | 5-min | daily | 11/1/99 to 3/31/03 |
| Coarse particle size distribution in 16 size fractions (Climet CI-500 optical particle counter) [a] | ARB | 0.3 to 10 µm (<0.3, <0.4, <0.5, <0.63, <0.8, <1.0, <1.3, <1.6, <2.0, <2.5, <3.2, <4.0, <5.0, <6.3, <8.0, and <10 µm) | 5-min | daily | 12/15/99 to 3/31/03 |
| Mass, elements, and ion size distribution in 8 size fractions (MOUDI with Teflon filters for mass and ions) | ARB/DRI | 0.054 to 10 µm (<0.054, <0.105, <0.148, <0.37, <0.54, <1.0, <2.5, <5.6, and <10 µm) | 5- to 8-hr | daily for episodes | 15 Episode Days 12/1/00 to 1/31/01 [d] |

| **Observable and Method** | **Operator**[h] | **Size Range** | **Ave. Time** | **Frequency** | **Period** |
|---|---|---|---|---|---|
| Carbon size distribution in 8 size fractions (MOUDI with aluminum filters for organic and elemental carbon) | ARB/DRI | 0.054 to 15 µm<br>(<0.054, <0.105, <0.148, <0.37, <0.54, <1.0, <2.5, <5.6, and <15 µm) | 5- to 8-hr | daily for episodes | 15 Episode Days 12/1/00 to 1/31/01 [d] |
| **Meteorology** | | | | | |
| Wind speed/direction (Met One 05305L high-sensitivity wind vane and anemometer) [a] | ARB | NA [g] | 5-min | daily | 5/15/99 onward [d] |
| Temperature (Met One CS500L platinum resistance sensor) [a] | ARB | NA | 5-min | daily | 5/15/99 onward [d] |
| Relative humidity (Met One CS500L capacitance sensor) [a] | ARB | NA | 5-min | daily | 5/15/99 onward [d] |
| Solar radiation (Met One LI200X-L pyranometer) [a] | ARB | NA | 5-min | daily | 9/15/99 onward [d] |
| Atmospheric pressure (Met One piezofilm sensor) [a] | ARB | NA | 1-hr | daily | 9/15/99 onward [d] |
| **Data Acquisition and Processing** | | | | | |
| Campbell Scientific 24-input analogue data logger with modem dialup | ARB | NA | All times | daily | 5/15/99 onward [d] |
| PC-LABVIEW serial data logger with modem dialup [a] | ARB | NA | All times | daily | 12/1/99 onward [d] |

[a] These ground-level measurements are also acquired at the non-urban Angiola site established by the California Regional Particulate Air Quality Study (CRPAQS) from 2/1/00 through 1/31/01 and during pollution episodes. This site is located ~85 km south of Fresno in a flat area of the San Joaquin Valley surrounded by agricultural fields. Simultaneous measurements from Angiola will be used with those from the Fresno Supersite to evaluate hypotheses about measurement equivalence in the absence of fresh urban emissions and to separate urban from non-urban contributions to the concentrations of measured observables. CRPAQS episodic measurements at Angiola are taken concurrently with those acquired at Fresno.

[b] Part of the California Air Resources Board's (ARB) compliance monitoring network.

[c] At three satellite sites only (see Figures 1-2 and 1-3).

[d] Measurements from CRPAQS. Three to five wintertime episodes of three to six day duration, monitored for a total of 15 days between 12/1/00 and 1/31/01 based on a forecast of high $PM_{2.5}$ concentrations under clear sky stagnation and stagnation with fog conditions.

[e] CRPAQS winter intensive sampling periods. Five times per day (0000 to 0500, 0500 to 1000, 1000 to 1300, 1300 to 1600, and 1600 to 2400 PST).

[f] CRPAQS winter intensive sampling periods. Four times per day (0000 to 0500, 0500 to 1000, 1000 to 1600, and 1600 to 2400 PST).

[g] Not applicable.

[h] All field measurements are performed by ARB. Where indicated, the laboratory analyses are performed by DRI.

**Table 1-2.** Fresno Supersite Participants

### Project Management

| | |
|---|---|
| Dr. Richard Scheffe | U.S. Environmental Protection Agency<br>Office of Air Quality Planning and Standards (MD-14)<br>Research Triangle Park, NC 27711<br>phone 919-541-4650, fax 919-541-1903, scheffe.rich@epa.gov |
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| Mr. Dennis Mikel | U.S. Environmental Protection Agency<br>Office of Air Quality Planning and Standards (MD-14)<br>Research Triangle Park, NC 27711<br>phone 919-541-5511, mikel.dennisk@epa.gov |
| Dr. Marc Pitchford | National Oceanic and Atmospheric Administration<br>755 East Flamingo Rd.<br>Las Vegas, NV 89119<br>phone 702-895-0432, fax 702-895-0507, marcp@dri.edu |
| Dr. Paul Solomon | U.S. Environmental Protection Agency<br>Office of Research and Development<br>944 E. Harmon, Rm. 235<br>Las Vegas, NV 89118<br>phone 702-798-2280, fax 702-798-2261, solomon.paul@epa.gov |
| Dr. John Watson | Desert Research Institute<br>2215 Raggio Parkway<br>Reno, NV 89512<br>phone 775-674-7046, fax 775-674-7009, johnw@dri.edu |
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**Table 1-2.** (continued)

**External/Science Advisors**

| | |
|---|---|
| Dr. Alan Lloyd | California Air Resources Board<br>Office of the Chairman<br>1001 I St.<br>Sacramento, CA 95814<br>phone 916-322-5840, fax 916-327-5748, alloyd@arb.ca.gov |
| Dr. Shankar Prasad | California Air Resources Board<br>1001 I St.<br>Sacramento, CA 95814<br>phone 916-323-2559, fax 916-322-4737, sprasad@arb.ca.gov |

**Quality Assurance Manager**

| | |
|---|---|
| Mr. Dennis Fitz | University of California<br>Center for Environmental Research and Technology (CERT)<br>College of Engineering<br>1200 Columbia<br>Riverside, CA 92507<br>phone 909-781-5781, fax 909-781-5790, dfitz@cert.ucr.edu |

**Data Management and Validation**

| | |
|---|---|
| Dr. Norman Robinson | Desert Research Institute<br>2215 Raggio Parkway<br>Reno, NV 89512<br>phone 775-674-7045, fax 775-674-7009, normr@dri.edu |
| Mr. Greg O’Brien | California Air Resources Board<br>1001 I St.<br>Sacramento, CA 95814<br>phone 916-322-7063, gobrien@arb.ca.gov |
| Dr. Douglas Lowenthal | Desert Research Institute<br>2215 Raggio Parkway<br>Reno, NV 89512<br>phone 775-674-7047, fax 775-674-7009, dougl@dri.edu |

**Table 1-2.** (continued)

**Field and Laboratory Operations**

| | |
|---|---|
| Mr. Peter Ouchida | California Air Resources Board<br>Air Quality Surveillance Branch<br>1309 T St.<br>Sacramento, CA  95814<br>phone 916-322-3719, fax 916-327-8217, pouchida@arb.ca.gov |
| Mr. Scott Scheller | California Air Resources Board<br>3425 N. First St., Room 205B<br>Fresno, CA  93726<br>phone 559-228-1825, fax 559-228-0116, sschelle@arb.ca.gov |
| Mr. Dale Crow | Desert Research Institute<br>2215 Raggio Parkway<br>Reno, NV  89512<br>phone 775-674-7078, fax 775-674-7009, dalec@dri.edu |
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**Figure 1-1.** Organizational Chart of the Fresno Supersite Management Structure

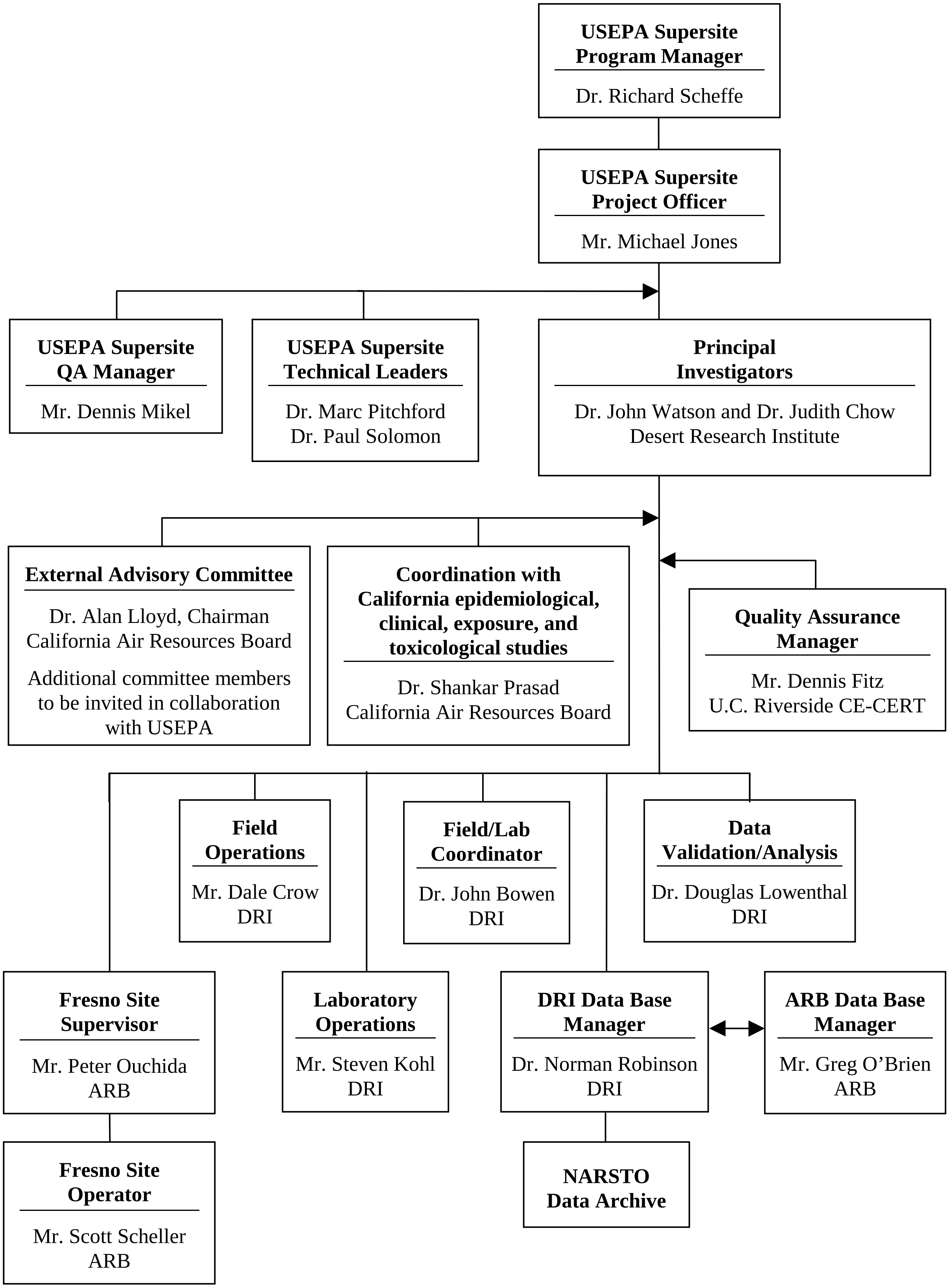


**Figure 1-2.** Location of the Fresno First Street (FSF) Supersite with Nearby Satellite Sites Near a Freeway On-ramp (FREM) and in a Nearby Residential Neighborhood.

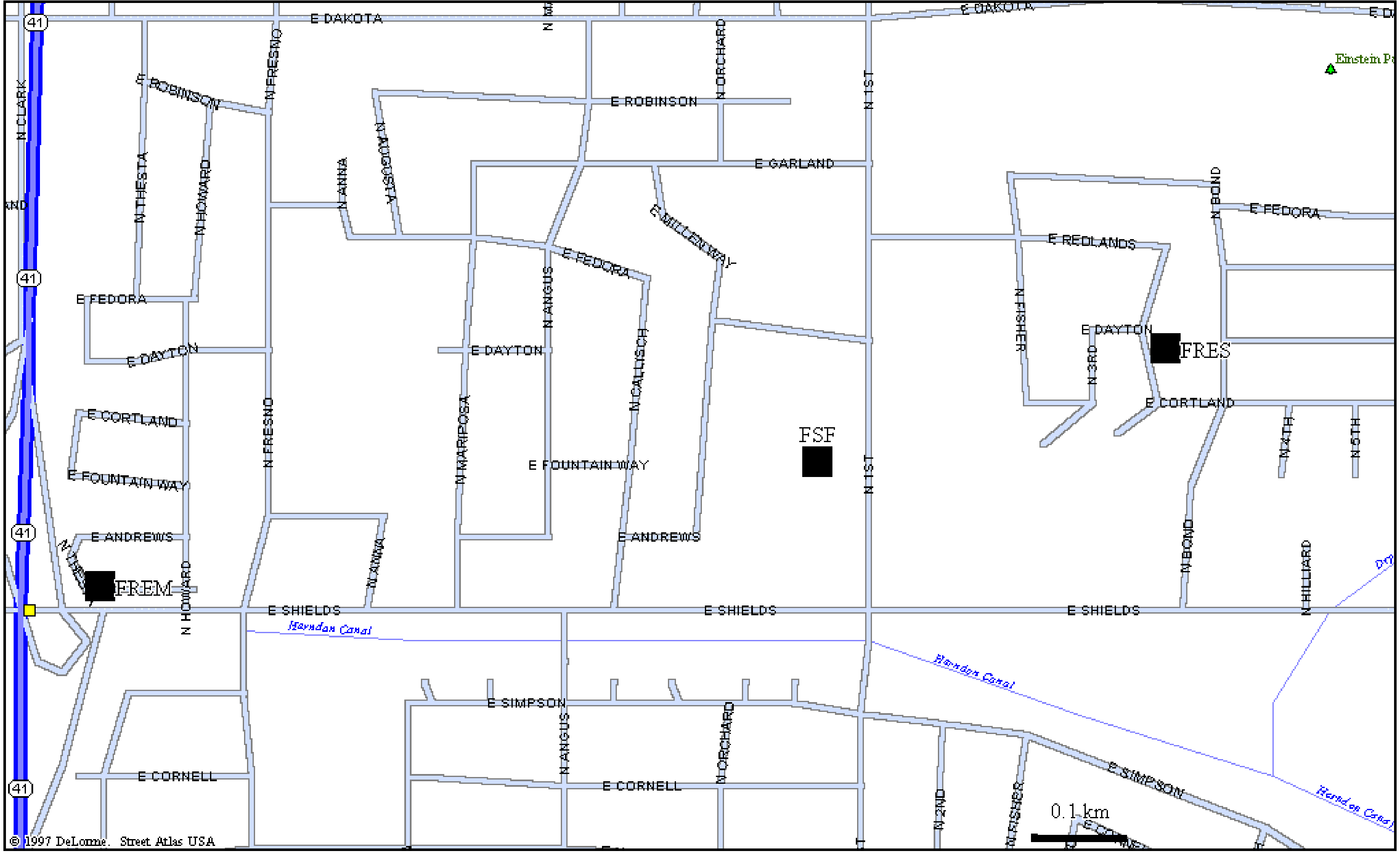


**Figure 1-3.** The Fresno Supersite's Location in California's San Joaquin Valley. Clovis (CLO) is a $PM_{2.5}$ compliance site. Selma (SELM) is a downwind transport site. Angiola (ANGI) is part of the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study, located in a non-urban area to acquire measurements similar to those at the Supersite.

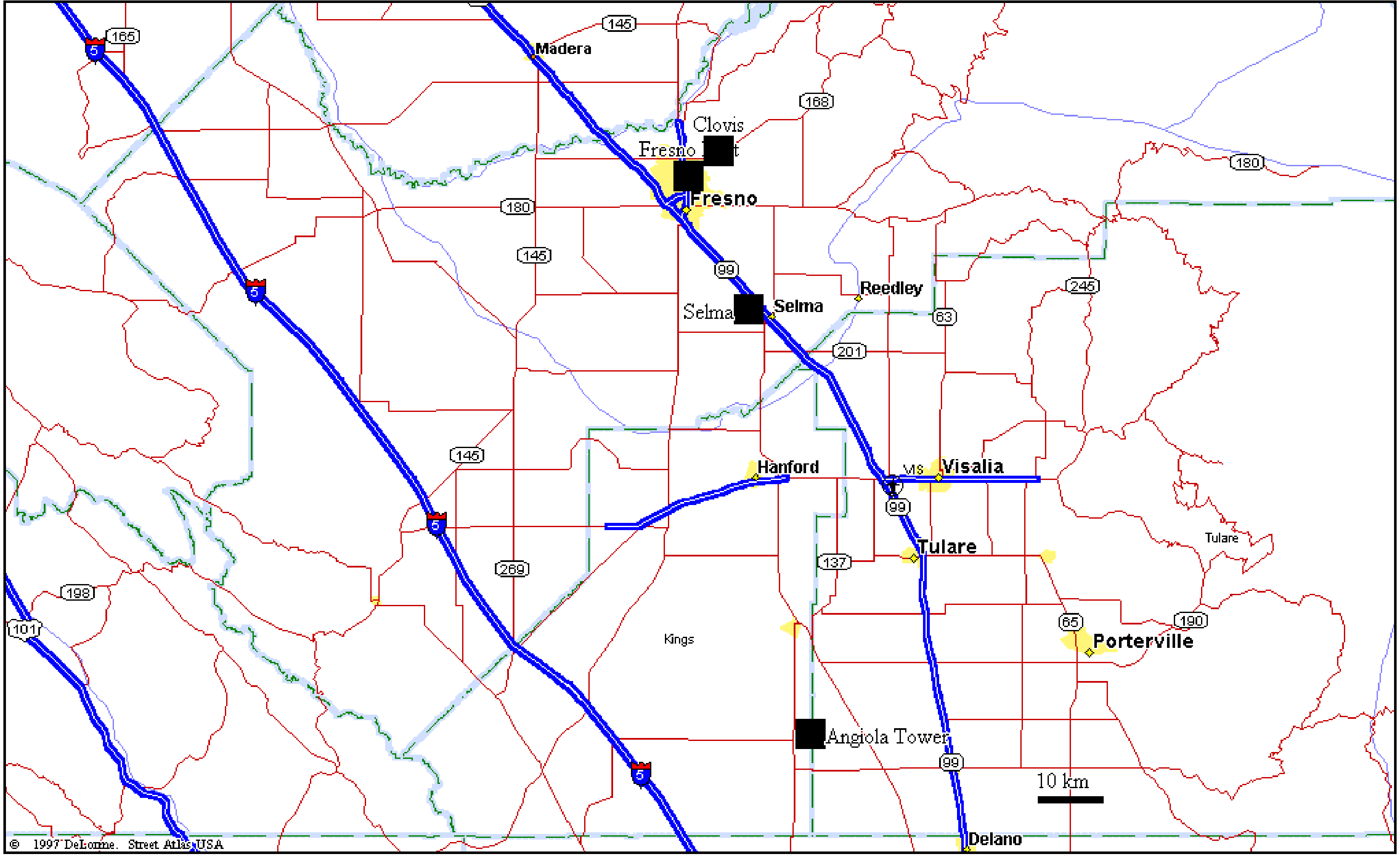
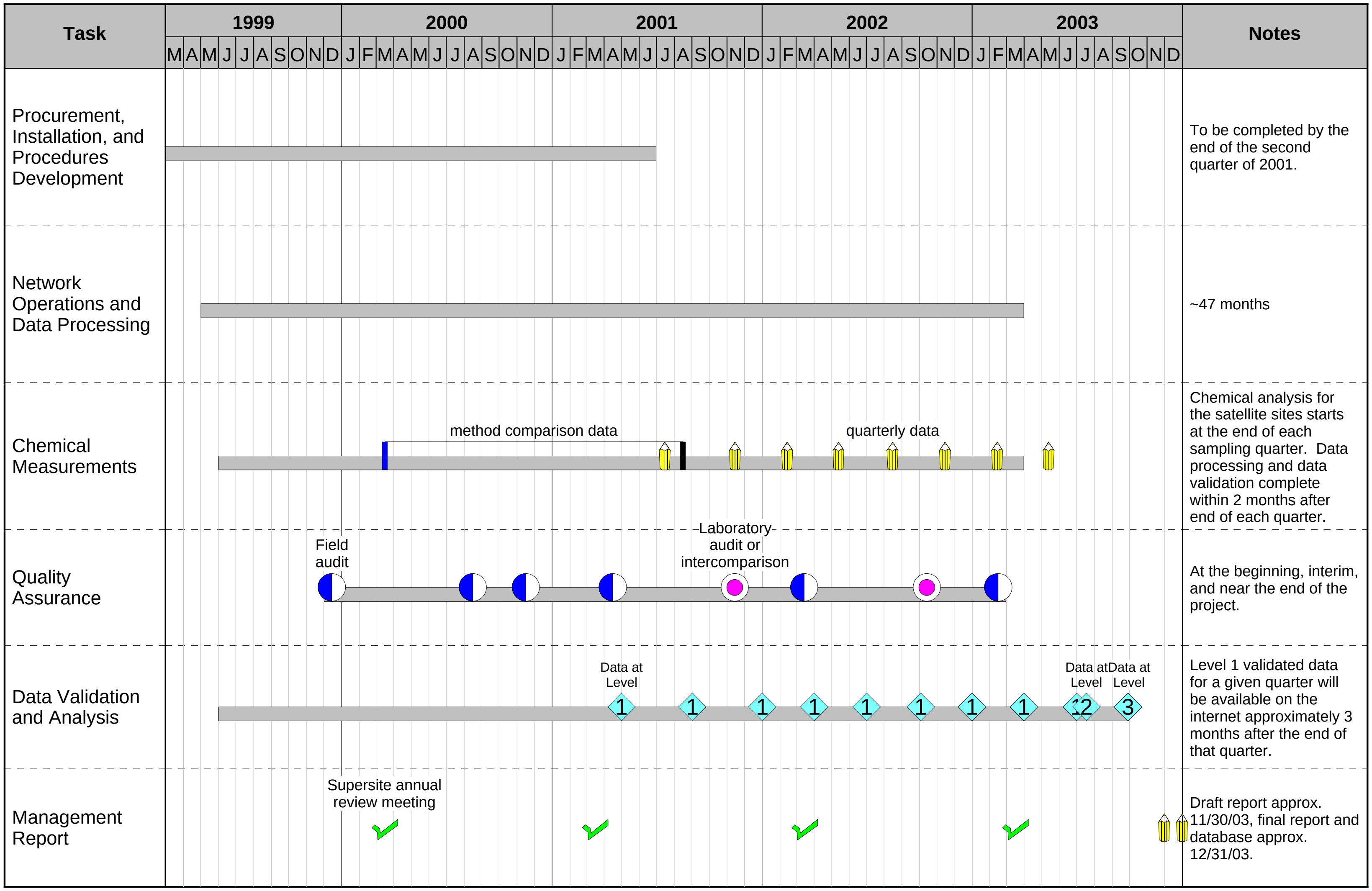


**Figure 1-4.** Project Milestones for Fresno Supersite.



| Task | Notes |
|---|---|
| Procurement, Installation, and Procedures Development | To be completed by the end of the second quarter of 2001. |
| Network Operations and Data Processing | ~47 months |
| Chemical Measurements | Chemical analysis for the satellite sites starts at the end of each sampling quarter. Data processing and data validation complete within 2 months after end of each quarter. |
| Quality Assurance | At the beginning, interim, and near the end of the project. |
| Data Validation and Analysis | Level 1 validated data for a given quarter will be available on the internet approximately 3 months after the end of that quarter. |
| Management Report | Draft report approx. 11/30/03, final report and database approx. 12/31/03. |

# 2. MEASUREMENT/DATA ACQUISITION

## 2.1 Sampling Design

The city of Fresno was selected for Supersite measurements owing to: 1) high occurrences of asthma and other respiratory distress that are the object of intensive health studies; 2) a large self-contained population (>500,000) island in regional pollution cloud; 3) an aerosol composition that varies substantially from day to day and throughout the year, and contrasts with high sulfate levels found at Midwestern and eastern Supersites; 4) a long record (since 1990) of $PM_{2.5}$ and other air quality and meteorological data; and 5) its central location in a major central California air quality study. The Fresno First Street location for the Supersite, as shown in Figure 1-2, is centrally located to represent the urban population, with several $PM_{2.5}$ compliance and satellite sites sampling simultaneously to determine how good this representation might be.

### 2.1.1 Site Selection

Fresno and its sister city of Clovis are located in the center of California's San Joaquin Valley, which encompasses nearly 64,000 $km^2$ and contains a population in excess of three million people. The Fresno metropolitan area is the largest population center for 150 km to the north and south. Figure 2-1 shows the major population centers in the Central California. The more than 500,000 population is ethnically diverse, with ~51% White, ~36% Hispanic, ~5% African-American, and ~8% Asian. The Fresno area experiences frequent hospitalizations for asthma, ranking second in California for African-American children, third for Hispanic children, and eighth for Caucasian children.

The San Joaquin Valley in which Fresno is situated is bordered on the west by the coastal mountain range and on the east by the Sierra Nevada range (Chow et al., 1993). These ranges converge at the Tehachapi Mountains in the southern end of the Valley, nearly 200 km south of Fresno. Weather changes with season throughout the year. Spring often experiences small frontal passages with low moisture content resulting in high winds. Summer meteorology is driven by heating over the Mojave Desert that creates a thermal low-pressure system and a large pressure gradient between the coast and the desert. Fall is influenced by the Great Basin High, with prolonged periods of slow air movement and limited vertical mixing. Mixing depths and ventilation are low in the morning during all seasons and remain low throughout the day during the winter. Relative humidities are highest in the winter, with low relative humidities in the summer and fall. For spring, summer, and fall, the typical winds are northwesterly, directed along the Valley axis. This is the predominant non-winter wind flow pattern both during the day and night, although it is more sluggish during fall.

Central California emission source categories include: 1) small to medium-sized point sources (e.g., power stations, incinerators, cement plants, and steam generators); 2) area sources (e.g., fires, wind blown dust, petroleum extraction operations, cooking, and residential fuel combustion); 3) mobile sources (e.g., cars, trucks, off-road heavy equipment, trains, and aircraft); 4) agricultural and ranching activities (e.g., fertilizers, herbicides, tilling, agricultural burns, and livestock); and 5) biogenic sources (e.g., oxides of nitrogen from biological activity in soils and hydrocarbon emissions from plants). Agriculture is the main industry surrounding Fresno, with cotton, alfalfa, corn, safflower, grapes, and tomatoes being the major crops. Cattle feedlots, dairies, chickens, and turkeys constitute most of the animal husbandry in the region. Oil and gas production, refining to the south, waste incineration to the northwest, electrical co-generation at various locations, transportation, commerce, local government, and light manufacturing constitute the remainder of the economy.

$PM_{2.5}$ levels measured in Fresno from 1991 to 1996 with dichotomous samplers operating every sixth day show annual averages ranging from 18 to 24 $\mu g/m^3$. The highest 24-hour averages ranged from 56 to 93 $\mu g/m^3$ during this period. These exceed the annual (15 $\mu g/m^3$) and 24-hour (65 $\mu g/m^3$) National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$. The highest $PM_{2.5}$ concentrations are typically found during winter and fall, with the lowest concentrations occurring during spring and summer. $PM_{2.5}$ constitutes ~80% of $PM_{10}$ during winter and ~50% of $PM_{10}$ during the rest of the year.

Fresno experiences high ammonium nitrate levels during winter and sometimes in fall, large geological contributions during fall and spring, and medium to high carbon concentrations throughout the year. Vegetative burning and cooking during winter when dispersion is poor enhance organic carbon concentrations. Ammonium sulfate levels average less than 2 $\mu g/m^3$ throughout the year. Strader et al. (1999) hypothesize that up to 20% of wintertime organic material during some parts of the day may be of secondary origin, owing to multiday accumulation of organic precursors, but organic to elemental carbon proportions are typically similar to those of primary emissions. This wide variability in aerosol concentration and composition found throughout the year, over multi-day episodes, and even within a day provides the contrasts and extremes needed to stress measurement methods and to evaluate changes in health end-points. The Fresno atmosphere presents substantial measurement challenges caused by multiple area sources, volatile aerosol, and fogs and rain during winter.

The ARB has operated the site at 3425 First Street (coordinates -119.7727725 °W, 36.78184232 °N), ~5.5 km north-northeast of the downtown commercial district, since 1990. Commercial establishments, office buildings, churches, and schools are located north and south of the Fresno Supersite on First St., a four-lane artery with moderate traffic levels. Medium-density single-family homes and some apartments are located in the blocks to the east and west of First St. Sampling inlets are located on a second story rooftop ~10 m above ground level and ~30 m from the west side curb of First St. Other PM sites in the Fresno metropolitan area include the Clovis residential site (W 119° 42’ 58.6”, N 36° 49’ 9.8”) located ~7 km northeast of the Supersite, and the Drummond St. ($PM_{10}$ only) industrial site (W 119° 44’ 29.0”, N 36° 42’ 19.7”) ~9 km south-southeast.

The zone of representation of the First Street Supersite is evaluated with the three surrounding satellite sites shown in Figures 1-2 and 1-3. Satellite sites are equipped with nephelometers operating continuously and with Minivol Teflon and quartz filter samplers operating for 24 hours every sixth day between 12/01/99 and 03/31/03 to quantify mass, light absorption, elemental, ion, and carbon concentrations. The Radiance Research nephelometers are equipped with “smart heaters” that operate only when the relative humidity exceeds 65%. This minimizes loss of volatile nitrate while removing interference from aerosol liquid water.

As shown in Figure 1-2, two satellite sites (FREM and FRES) are located in the vicinity of the Supersite to determine its zone of representation and the effects of local sources on chemical concentrations. A vehicle-dominated site at Shields Ave. and SR 41 is in a residential area near a four-lane arterial and a freeway onramp ~1 km west-southwest of the Supersite and will quantify incremental carbon contributions from directly emitted vehicle exhaust. A residential site near a city park is located ~0.5 km east of the Supersite on a lightly traveled neighborhood street. For most of the year this site represents a neighborhood similar to that around the Supersite. During winter, however, Schauer and Cass (2000) attributed the large increment in organic carbon near this site to neighborhood wood combustion. A third satellite site located at the Selma Airport, ~24 km south southeast of the Supersite, is outside the populated area and provides the ability to separate urban-scale from regional-scale PM contributions.

The Angiola Tower site operated between 12/01/99 and 01/31/01 as part of the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) is equipped with much of the same measurements as the Fresno Supersite. The Angiola site is located in a flat field ~85 km south-southeast of Fresno with minimal influence from non-urban sources. A 100 m tower is instrumented with micrometeorological and particle monitors to evaluate the vertical mixing and transport of pollutants between major urban areas such as Fresno and Bakersfield. Measurements at the Angiola Tower site will be compared with those from Fresno to evaluate hypotheses about urban- and regional-scale contributions to excessive $PM_{2.5}$ and $PM_{10}$ concentrations.

Figure 2-2 shows the locations of sites in the Fresno area in relation to other $PM_{2.5}$ samplers located throughout Central California during CRPAQS and for long-term $PM_{2.5}$ monitoring. This larger database will allow Supersite measurements to be contrasted with those from sites that experience different meteorological and emissions situations.

### 2.1.2 Measurements and Sampling Frequency

Measurements and samples to be acquired at the Fresno Supersite are given in Table 1-1, along with their averaging time, sampling frequency, and the period(s) during which they will be operated.

## 2.2 Sampling Method Requirements

Sampling methods and procedures are specified in Standard Operating Procedures (SOPs) that include checklists, and calibration forms for each monitoring instrument and sampler. SOPs describe monitoring or sampling requirements, acceptance testing procedures, preparation, installation, sample collection, handling and preservation, data acquisition, routine maintenance, routine service checks, calibrations, QC checks, and audit procedures.

Table 2-1 lists the 54 SOPs applicable to the Fresno Supersite measurements and their current status. Included are nine SOPs for gaseous pollutant measurements, nine for filter mass and chemistry, eight for in-situ continuous particle mass and chemistry, eight for organic gases and particles, four for particle light scattering, three for particle light absorption, five for particle size, six for meteorological measurements, and two for data base management. Summary sheets are being used for the four SOPs still in preparation, and these are being developed into full SOPs as more is learned about the instruments, their operating characteristics, and their limitations. For criteria pollutant and meteorological measurements, ARB QA procedures and SOPs are followed to assure continuity and consistency of data with the ARB network. For measurements specific to CRPAQS, DRI or other co-investigators' procedures are followed for the study period between 12/01/99 to 01/31/01. Efforts have been made to assemble measurements in the standardized Supersite format shown in Table 2-2 for all three- to four-year research-grade instruments. In addition, 24 analytical laboratory-related SOPs (Table 2-3) are assembled in DRI SOP format (Table 2-4).

### 2.2.1 Sample Preparation, Setup, and Recovery Procedures

Sample preparation, setup, and recovery procedures for field related measurements and activities are described in the SOPs given in Table 2-1. General sample handling and sample chain-of-custody procedures are discussed in Section 2.3. Similar procedures for laboratory related activities and operations are described in Section 2.4. Detailed information is contained in the SOPs.

### 2.2.2 Sampling and Measurement System Corrective Actions

Problems that arise in the field or the laboratory during the course of the project are resolved expeditiously to ensure that the project's overall data quality objectives are achieved. Detailed instructions for troubleshooting and corrective actions for each instrument are given in the SOPs. Table 2-5 provides corrective actions in response to anticipated sampling and measurement problems. Additional corrective actions are discussed in Section 2.5 on QC requirements.

## 2.3 Sample Handling and Custody

Sample handling, chain-of-custody, and archiving are specifically discussed in the SOPs. Most of the measurements specified in Table 1-1 are *in situ*, with instruments located in an environmentally controlled room. To minimize sampling losses or changes and to ensure comparability among the measurements, sample inlet lines are: 1) kept as short as possible by locating instruments close to the shelter ceiling, 2) located at a common height above rooftop level (~2.0 m), equivalent to the height of the FRM inlets, 3) made of conducting material with straight or gently curving entries to instruments to minimize particle losses, and 4) with diameters as small as possible to minimize residence time that might causes changes in temperature and humidity.

Filter packs, denuders, and absorbents from integrated aerosol samplers are prepared in clean laboratories and shipped to and from the field by overnight transport in cooled (<4°C) containers containing max/min temperature recorders. Samples are stored in refrigerators before and after sampling. Shipments are coordinated between the field and laboratory by means of a semi-automated chain-of-custody system. Sample identifiers are bar-coded to indicate sample type, analysis type, and sampling time and location. These identifiers are entered into field and laboratory data acquisition systems to track sample status at any time during the study.

## 2.4 Analytical Methods Requirements

Table 1-1 identifies the sampling and analysis methods, and the organizations responsible for each. Several common quality control activities take place for all analyses: 1) acceptance-testing for contamination of substrates, reagents, extraction vials prior to use; 2) field and laboratory blank designation and analysis to determine blank levels and variability; 3) periodic performance tests of zero and span values for field and laboratory instruments to determine reproducibility and calibration drift; 4) periodic multi-point calibrations in the range of ambient concentrations to determine linearity and concentration relationships; and 5) data validation flags for field and laboratory operations that indicate deviations from procedures. Results from these common quality control activities are compiled into a separate database and are used to develop the data qualifications statement.

Detailed requirements for analytical methods are specific to the type of sampling instrument, flow rate, sampling period, and analysis method. Laboratory-related SOPs, summarized in Table 2-3, contain detailed information for filter and substrate preparation, filter pack assembly/disassembly, shipping/receiving, chemical analysis, and QA/QC. These SOPs follow the format presented in Table 2-4.

## 2.5 Quality Control Requirements

Table 2-6 summarizes calibration standards and frequency, performance test standards and frequency, performance tolerances, and audit standards and frequency to be implemented for the Fresno Supersite. Detailed quality control and quality assurance procedures are specified in each listed SOP.

## 2.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Prior to deployment in the field, each instrument is bench-tested and inspected in the laboratory. Maintenance frequency varies (weekly, monthly, quarterly, or semiannually) depending on the instrument. Instrument and equipment testing, inspection, and maintenance requirements are discussed in detail in the SOPs.

## 2.7 Instrument Calibration and Frequency

Several types of standards are needed for calibration, auditing, and performance tests. Primary standards are well characterized and protected, with stable concentrations to which all other standards are traceable. Transfer standards are often more easily produced or commonly available and are traceable to primary standards; these are used for calibration, performance testing, and auditing. The same standards can be used for calibration and performance testing, but audit standards must be independently traceable to primary standards. Performance tests may measure instrument response rather than response to a specific value of an observable when transfer standards for the primary observable are lacking.

Table 2-6 identifies the intended primary and transfer standards and the intended frequency of application for calibration, performance testing, and auditing. The particular method for delivering these standards to the instrument depends on the instrument type.

Calibration, performance testing, and auditing methods for laboratory operations are largely based on the preparation of standard solutions from mineral salts. NIST does not provide these types of standards. However, standard solutions in a large range of concentrations will be obtained commercially for inorganic monoatomic and polyatomic ions.

## 2.8 Inspection/Acceptance Requirements for Supplies and Consumables

Field/laboratory supplies, consumables, quantities, cost, frequency of replacement, catalog number, and vendor information are listed in detail in each SOP. Lab and field coordinators are responsible for checking/replenishing supplies on a quarterly basis.

## 2.9 Data Acquisition Requirements (Non-direct Measurements)

Data from the ARB network will be integrated into the Fresno Supersite database for future data analysis. No specific data acquisition is needed for this collaborative effort.

## 2.10 Data Management

### 2.10.1 Overview

The Fresno Supersite will use the database system established for the Central California Air Quality Studies (CCAQS) to support data collection, distribution, and archiving requirements for the project. CCAQS comprise two studies – the multi-year California Regional Particulate Air Quality Study (CRPAQS) and the intensive Central California Ozone Study (CCOS). Mr. Greg O’Brien of the ARB, one of the database managers for the Fresno Supersite, is also the database manager for CCAQS. A flow diagram of the path of the data flow for this project is presented in Figure 2.3. All data from the Fresno Supersite that has passes Level 1 data validation (see below) will be sent to the ARB CCAQS database for further processing and validation. The Fresno Supersite data will adhere to all the formatting, database, naming, and other conventions established for the CCAQS database and its data will be integrated into the CCAQS database. Thus, investigators will be able to use the additional data available through CCAQS to supplement the Fresno Supersite data. The integrated Supersite data will be available through the CCAQS web site, **http:\\www.arb.ca.gov/airways/ccaqs.htm**.

In addition, the Fresno Supersite data stored as part of CCAQS will be extracted from the database and made available separately on CD-ROMs and via a DRI web server, and submitted to the NARSTO center at Oak Ridge National Laboratory for archiving and distribution through EPA and NARSTO centralized databases. Both the Fresno Supersite subset and the CCAQS data adhere to the consistent metadata requirements and data formats for NARSTO technical programs data, including the U.S. EPA PM Supersites program. The data submitted to NARSTO will contain the validity codes specified in an updated version of DRI SOP FDBM002, to be provided at a later date.

The relational database management system (RDBMS) identified for the CCAQS project is Microsoft SQL Server 2000 with a Windows 2000 DataCenter Server. Microsoft Access 2000 is used to organize and validate Supersite data prior to submission to the CCAQS database.

The CCAQS database, of which the Fresno Supersite data will form a part, is compiled, documented, evaluated, and distributed by the Modeling Support Section, Planning and Technical Support Division (TSD) of the ARB. Common data management and validation conventions have been assembled. To the extent possible, CCAQS field data structures, processing, validation, and delivery procedures are consistent with those established for the long-term database and other ARB data sets from recent air quality studies. A number of enhancements to the process flow are currently being designed.

CCAQS data management conventions and methods build upon experience from the 1990 San Joaquin Valley Air Quality Study (SJVAQS) (Blumenthal et al., 1993), the 1995 Integrated Monitoring Study (IMS-95) (Solomon and Magliano, 1999), and the 1997 Southern California Oxidant Study (SCOS-97) (Fujita et al., 1997). The following specifications are maintained by the CCAQS Data Manager and will be available to all project participants via the Internet. The “lookup” reference tables and data described below will be available at http://www.arb.ca.gov/airways/crpaqs/default.htm. The four most important reference tables for the CCAQS data providers are: Sites, Parameters, Instruments, and Methods. These tables are required for reference to properly format data files for submittal.

Monitoring Sites: Each site location for CCAQS is identified with a unique alphanumeric site ID accompanied by its name, address, coordinates, elevation, etc. To verify the coordinates and elevations for each site, the field managers use a Global Positioning System (GPS), pressure-based altimeter, and topographical maps. Coordinates are determined with GPS using map basis NAD-83 (Federal Aviation Administration convention). The GPS time stamp is recorded to correct coordinate deviations. A long-term GPS monitor at the Fresno Supersite will allow other investigators to adjust their GPS readings for drifts induced by the U.S. Department of Defense for security purposes. Immediate surroundings are recorded with a digital camera of the area around the site are to be displayed on the CCAQS web site.

Parameters: Each observed parameter is assigned a unique code that is accompanied by its definition, units, averaging time, applicable temperature and pressure adjustments, and data reporting format.

Methods: The characteristics of the method used to make the observation measurement. This is essentially how an instrument, under what conditions, an observation value (Obs_Value) was obtained. Sampling frequency and duration, parameter, instrument, units, along with other method related information is available in this lookup table.

Data Validation Flags: A table of validation flags (Study_Valid_Flags) has been developed as part of the CCAQS database.

Air Obs (observation data files): Basic air observation data are constructed into normalized table formats that have the same structure for different types of data, meteorological or air quality. Each record contains the site code, sample date, sample time, variable code, measurement value, measurement precision, validity code, and validation level. Separate tables are produced for different averaging times and for non-uniform data sets. These files are transparent to most users and can be easily manipulated into convenient data analysis forms.

The QA Manager audits the integrity of the database by randomly selecting data sets and tracing them through the data management system to their final values in the finished database. Unit conversion, sample times, site and variable codes, and data validation flags are applied manually, and the results are compared with data extracted from the internet-based data set.

### 2.10.2 Data Validation Levels

Mueller (1980), Mueller et al., (1983), and Watson et al. (2001) define a three-level data validation process for an environmental measurement study. Data records are designated as having passed these levels by entries in the column of each data file. These levels, and the validation codes that designate them, are defined as follows:

**Level 0:** These data are obtained directly from the data loggers that acquire the data in the field. Averaging times represent the minimum intervals recorded by the data logger, which do not necessarily correspond to the averaging periods specified for the database files. Level 0 data have not been edited for instrument downtime, nor have procedural adjustments for baseline and span changes been applied. Level 0 data are not contained in the Fresno Supersite database; although they are consulted on a regular basis to ascertain instrument functionality and to identify potential episodes prior to receipt of Level 1 data.

**Level 1:** These data have passed several validation tests applied by the measurement investigator prior to data submission. Level 1 criteria are currently under development for many of the new instruments. The general features of Level 1 are: 1) removal of values when monitoring instruments fail specified validation criteria; 2) flagging measurements when significant deviations from measurement assumptions have occurred; 3) verifying computer file entries against data sheets, where appropriate; 4) replacement of data from a backup data acquisition system in the event of failure of the primary system; 5) adjustment of measurement values for quantifiable baseline and span or interference biases; and 6) identification, investigation, and flagging of data that are beyond reasonable bounds or that are unrepresentative of the variable being measured (e.g., high light scattering associated with adverse weather).

**Level 2:** Level 2 data validation takes place after data from various measurement methods have been assembled in the master database. Level 2 validation is the first step in data analysis. Level 2 tests involve the testing of measurement assumptions (e.g., internal nephelometer temperatures do not significantly exceed ambient temperatures), comparisons of collocated measurements (e.g., filter nitrate and in-situ continuous nitrate), and internal consistency tests (e.g., the sum of measured aerosol species does not exceed measured mass concentrations). Level 2 tests also involve the testing of measurement assumptions, comparisons of collocated measurements, and internal consistency tests.

**Level 3:** Level 3 is applied during the model reconciliation process, when the results from different modeling and data analysis approaches are compared with each other and with measurements. The first assumption upon finding a measurement, which is inconsistent with physical expectations, is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. The Level 3 designation is applied only to those variables that have undergone this reexamination after the completion of data analysis and modeling. Level 3 validations continue for as long as the database is maintained.

A higher validation level assigned to a data record indicates that those data have gone through, and passed a greater level of scrutiny than data at a lower level. All data supplied to the CCAQS database will have undergone data validation through Level 1. As part of the CCAQS database it will be re-subjected to data validation through Level 1 and then subjected to higher levels of validation. All data in the Fresno Supersite data set will achieve Level 1 status prior to use in data analysis and modeling. The validation tests passed by Level 1 data are stringent by the standards of most air quality and meteorological networks, and few changes are made in elevating the status of a data record from Level 1 to Level 2. Since some analyses are applied to episodes rather than to all samples, some data records in a file will achieve Level 2 designation while the remaining records will remain at Level 1. Only a few data records will be designated as Level 3 to identify that they have undergone additional investigation. Data designated as Levels 2 or 3 validations are not necessarily "better" than data designated at Level 1. The level only signifies that they have undergone additional scrutiny as a result of the tests described above.

### 2.10.3 Data Transmittal

For the duration of the Fresno Supersite project, DRI and its support groups will collect, validate, and submit data to the CCAQS Data Manager for inclusion in the database system. The appropriate backup files will be generated at each stage of the data dissemination process. The Data Manager interacts with numerous data source providers to make data available as early as possible. Data transmittal file formats and transmittal file naming conventions have been established to make the job of collecting and processing data into the database more efficient and accurate. Data are submitted in electronic form using file transfer protocol (FTP) after being validated to Level 1 by DRI and its collaborators.

**Table 2-1.** Summary of SOPs Applied to Fresno Supersite Field Measurements

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| I. Gases | | | | | | |
| FGAS001 | Nitrogen Oxides (NO/$NO_x$) | (TECO) 42 w. internal TEI converter | TECO 42 Oxides of Nitrogen Analyzer | 08/01/94 | ARB SOP #W.1, W.2, and W.3 | Follow ARB procedure |
| FGAS002 | Ozone ($O_3$) | API 400 | API Model 400 Ozone Analyzer | 10/02/00 | | Follow STI procedure |
| FGAS003 | Carbon Monoxide (CO) | Dasibi 3008 | Dasibi Model 3008 Carbon Monoxide Analyzer | 01/01/92 | ARB SOP #S.1, S.2, and S.3 | Follow ARB procedure |
| FGAS004 | Non-methane Hydrocarbons (NMHC) | TEI 55C with flame ionization detector | Compendium Method TO-12 for the Determination of Non-Methane Hydrocarbons with Flame Ionization Detector | 06/01/88 | EPA | Follow EPA TO-12 procedure |
| FGAS005 | $NO_2$/PAN | UC Riverside | Routine Operation of $NO_2$/PAN GC Analyzer | 12/21/00 | CE-CERT/ DRI | in process of converting to Fresno Supersite format |
| FGAS006 | Reactive Nitrogen ($NO_y$) | TEI 42CY with external converter | Routine Operation of the TEI Model CY $NO_y$ Analyzer | 12/21/00 | CE-CERT/ DRI | in process of converting to Fresno Supersite format |
| FGAS007 | NO/$NO_y$ zero air system | Aadco Series 737R-11 | Routine operation of the AADCO Series 737R-11 Pure Air Generator | 03/08/00 | CE-CERT/ DRI | in process of converting to Fresno Supersite format |

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| I. Gases (continued) | | | | | | |
| FGAS008 | NO/NO$_y$ zero air system | Environics 9100 | Routine Operation of the Environics Series 9100 Computerized Ambient Monitoring Calibration System | 03/08/00 | CE-CERT/ DRI | in process of converting to Fresno Supersite format |
| FGAS009 | Nitric Acid (HNO$_3$) | TEI 42C with external converters and denuders | Routine Operation of the TEI Model 42CY NO$_y$-HNO$_3$ Analyzer | 12/21/00 | CE-CERT/ DRI | in process of converting to Fresno Supersite format |
| II. Filter Mass and Chemistry | | | | | | |
| FFLT001 | TSP mass and lead | Andersen Hi-Vol | High Volume Air Sampler | 11/01/93 | ARB SOP #E.1 and E.2 | Follow ARB procedure |
| FFLT002 | PM$_{10}$ mass, sulfate, nitrate, chloride, and ammonium | Andersen 1200 SSI Hi-Vol | Sierra-Andersen 1200 Size Selective Inlet PM$_{10}$ Sampler | 07/07/97 | ARB SOP #P.1, P.2, and P.3 | Follow ARB procedure |
| FFLT003 | PM$_{2.5}$ and coarse mass, elements, endotoxins, spores, molds, and fungi | Sierra-Andersen 224 dichotomous sampler | Dichotomous Sampler | 02/03/97 | ARB SOP #M.1, M.2, and M.3 | Follow ARB procedure |
| FFLT004 | PM$_{2.5}$ mass, light absorption, elements, ions, and carbon | Andersen RAAS2.5-100 single-channel FRM | Andersen Instruments RAAS PM2.5-100 for Fresno Supersite | 03/16/00 | DRI SOP #1-212.0 | Revision 0 of Fresno Supersite format |

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| II. Filter Mass and Chemistry (continued) | | | | | | |
| FFLT005 | $PM_{2.5}$ mass, elements, ions, and carbon | six-channel Andersen RAAS2.5-400 speciation sampler with denuders and backup filters | Andersen Instruments RAAS2.5-400 Chemical Speciation Monitor for the Fresno Supersite | 08/15/00 | DRI SOP #1-215.0 | Revision 0 of Fresno Supersite format |
| FFLT006 | Particle morphology | Airmetrics Minivol with polycarbonate filters) | Airmetrics Minivol PM Sampler For Fresno Supersite | 03/16/00 | DRI SOP #1-209.4 | Revision 0 of Fresno Supersite format |
| FFLT007 | $PM_{2.5}$ mass, elements, ions, carbon, and ammonia | two-channel DRI SFS with nitric acid denuders and backup filters | Sequential Filter Sampler for the Fresno Supersite | 03/16/00 | DRI SOP #1-207.13 | Revision 0 of Fresno Supersite format |
| FFLT008 | $PM_{2.5}$ mass, elements, ions, and carbon | two-channel DRI SFS with denuders and backup filters | Sequential Filter Sampler for the Fresno Supersite | 03/16/00 | DRI SOP #1-207.13 | Revision 0 of Fresno Supersite format |
| FFLT009 | Toxic species (metals, chromium VI, aldehydes) | Xontec 920 | Xontech 920 Sampler | 11/01/94 | ARB SOP #R.1, R.2, and R.3 | Follow ARB procedure |
| III. Continuous Particle Mass and Chemistry | | | | | | |
| FPCH001 | $PM_{2.5}$ mass | ambient R&P 1400a TEOM | Rupprecht & Patashnick Series 1400a TEOM $PM_{2.5}$ Operating Procedure | 10/02/00 | DRI/ARB | Revision 0 of Fresno Supersite format |
| FPCH002 | $PM_{10}$ mass | R&P 1400a TEOM | Rupprecht & Patashnick Series 1400a TEOM $PM_{10}$ Operating Procedure | 01/23/95 | ARB SOP #Z.1 and Z.2 | Follow ARB procedure |

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| III. Continuous Particle Mass and Chemistry (continued) | | | | | | |
| FPCH003 | $PM_{2.5}$ mass | ambient Met One 1020 BAM | Routine Operation of the Met One Model 1020 Beta Attenuation Monitor for Particulate Matter Mass | 03/08/00 | STI/DRI | Revision 0 of Fresno Supersite format |
| FPCH004 | $PM_{10}$ mass | ambient Met One 1020 BAM | Routine Operation of the Met One Model 1020 Beta Attenuation Monitor for Particulate Matter Mass | 03/08/00 | STI/DRI | Revision 0 of Fresno Supersite format |
| FPCH005 | $PM_{2.5}$ nitrate | R&P 8400N | Operation of the Rupprecht & Patashnick Series 8400N Ambient Nitrate Monitor | 11/26/00 | ADI/DRI | in process of converting to Fresno Supersite format |
| FPCH006 | $PM_{2.5}$ sulfate | R&P 8400S | Operation of the Rupprecht & Patashnick Series 8400S Ambient Sulfate Monitor | 06/30/01 | ADI/DRI | in preparation |
| FPCH007 | $PM_{2.5}$ organic and elemental carbon | R&P Series 5400 | Routine Operation of the Rupprecht & Patashnick Series 5400 Ambient Carbon Particulate Monitor | 08/23/00 | STI/DRI | Revision 0 of Fresno Supersite format |
| FPCH008 | Individual particle size and chemistry | UC Riverside time-of-flight spectrometer | Individual Particle Size and Chemistry by Time of Flight Spectrometer | 06/30/01 | UC Riverside | in preparation |
| IV. Organic Gases and Particles | | | | | | |
| FORG001 | Particle-bound PAH | EcoChem Analytics PAS2000 | Operation of EcoChem Analytics PAS 2000 Analyzer | 03/16/00 | DRI SOP #1-410.0 | Revision 0 of Fresno Supersite format |
| FORG002 | Toxic hydrocarbons | Xontec 910A canister sampler | Gaseous Toxic Sample Xontech Model 910A | 03/01/96 | ARB | follow ARB procedure |

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| IV. Organic Gases and Particles (continued) | | | | | | |
| FORG003 | Carbonyls | Xontec 925 DNPH sampler | Gaseous Toxic Sample Xontech Model 925. Compendium Method TO-11A for Determination of Carbonyl Samples. | 01/01/99 | EPA | follow EPA TO-11A procedure |
| FORG004 | Carbonyls | DRI sequential sampler with DNPH cartridge | DRI Carbonyl Sampler | 06/12/97 | DRI SOP #1-710.3 | follow DRI procedure |
| FORG005 | Light hydrocarbons | DRI canister sampler | Operation of DRI 6-Canister Sampler | 03/08/95 | DRI SOP #1-702c.3 | follow DRI procedure |
| FORG006 | Heavy hydrocarbons | TENAX sampler | Procedure for Collecting Tenax Samples | 09/95 | DRI SOP #1-720.2 | follow DRI procedure |
| FORG007 | $PM_{2.5}$ organic compounds | Teflon-coated glass-fiber/PUF/XAD filters and GCMS | 4-Channel Sequential FP/SVOC Sampler | 01/28/97 | DRI SOP #1-750.4 | follow DRI procedure |
| FORG008 | $PM_{2.5}$ organic compounds | Minivol with Teflon-coated glass-fiber filters and GCMS | Airmetrics Minivol PM Sampler For Fresno Supersite | 03/16/00 | DRI SOP #1-209.4 | follow DRI procedure |
| V. Continuous Light Scattering | | | | | | |
| FSCA001 | Ambient particle light scattering | Optec NGN2 | Optec, Inc. NGN-2 Nephelometer for Fresno Supersite | 08/11/00 | DRI SOP #1-260.0 | Revision 0 of Fresno Supersite format |
| FSCA002 | Dry particle light scattering | Radiance M903 heated nephelometer | Routine Operation of the Radiance Research Model M903 Nephelometer for Continuous Light Scattering Measurements in CRPAQS | 2/24/00 | STI/DRI | Revision 0 of Fresno Supersite format |
| FSCA003 | $PM_{2.5}$ total particle light scattering | Met One (GreenTek) GT-640A photometer | Met One Model GT-640A Logger Particle Counter for Fresno Supersite | 3/16/00 | DRI SOP #1-407.0 | Revision 0 of Fresno Supersite format |

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| V. Continuous Light Scattering (continued) | | | | | | |
| FSCA004 | $PM_{2.5}$ total particle light scattering | TSI DustTrak 8520 photometer | TSI Model 8520 DustTrak Aerosol Monitor for Fresno Supersite | 08/15/00 | DRI SOP #1-408.0 | Revision 0 of Fresno Supersite format |
| VI. Light Absorption | | | | | | |
| FABS001 | Coefficient of Haze (COH) | RAC 205019-1 paper tape sampler | Research Appliance Corporation AISI Tape Sampler | 09/01/83 | ARB SOP #K.1 and K.2 | follow ARB procedure |
| FABS002 | Single wavelength light absorption | Anderesen (Magee) AE14U aethalometer | Routine Operation of Andersen Instruments Aethalometers for Measurement of Black Carbon Concentrations | 03/07/00 | STI/DRI | Revision 0 of Fresno Supersite format |
| FABS003 | Multi-wavelength light absorption | Andersen AE30S multi-color aethalometer | Routine Operation of Andersen Instruments Aethalometers for Measurement of Black Carbon Concentrations | 03/07/00 | STI/DRI | Revision 0 of Fresno Supersite format |
| VII. Particle Sizes | | | | | | |
| FPSD001 | Scanning mobility particle sizer | TSI 3025AS ultrafine condensation particle counter with TSI 3936L10S scanning mobility particle sizer (0.01 to 0.5 µm, 50 bins) | Routine Operation of Ultrafine Particle Counters with TSI 3020 Ultrafine Condensation Particle Counter and TSI 3936L10S Scanning Mobility Particle Sizer | 04/01/00 | ADI/DRI | in process of converting to Fresno Supersite format |
| FPSD002 | Fine particle size distribution | PMS Lasair 1003 optical particle counter | Operation of Lasair 1003 Optical Particle Counter for Fine Particle Size Distribution | 04/01/00 | ADI/DRI | in process of converting to Fresno Supersite format |

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| VII. Particle Sizes (continued) | | | | | | |
| FPSD003 | Coarse particle size distribution | Climet CI-500 optical particle counter (0.3 to 10 µm in 16 size fractions, and 0.1 to 2 µm in 8 size fractions) | Operation of Climet CI-500 Optical Particle Counter for Coarse Particle Size Distribution | 04/01/00 | ADI/DRI | in process of converting to Fresno Supersite format |
| FPSD004 | Mass, elements, and ion size distribution | MOUDI with Teflon filters (0.054 to 5.6 µm) | Micro-Orifice Uniform Deposit Impactor (MOUDI) Field and Laboratory Operations | 10/21/92 | DRI SOP #1-208.3 | Follow DRI procedure |
| FPSD005 | Carbon size distribution | MOUDI with aluminum filters (0.054 to 5.6 µm) | Micro-Orifice Uniform Deposit Impactor (MOUDI) Field and Laboratory Operations | 10/21/92 | DRI SOP #1-208.3 | Follow DRI procedure |
| VIII. Meteorology | | | | | | |
| FMET001 | Wind speed | Met One 05305L high-sensitivity wind vane | Meteorological Parameter Procedures for Wind Speed Sensors | 07/28/95 | ARB SOP #T.1, T.2, and T.3 | Follow ARB procedure |
| FMET002 | Wind direction | Met One 05305L anemometer | Meteorological Parameter Procedures for Wind Direction Sensors | 09/30/95 | ARB SOP #V.1, V.2, and V.3 | Follow ARB procedure |
| FMET003 | Temperature | Met One CS500L | Meteorological Parameter Procedures for Inside/Outside Temperature Sensors | 06/01/96 | ARB SOP #AA.1, AA.2, and AA.3 | Follow ARB procedure |
| FMET004 | Relative humidity | Met One CS500L | Meteorological Parameter Procedures for Percent Relative Humidity Sensors | 10/01/97 | ARB SOP #U.1 and U.2 | Follow ARB procedure |
| FMET005 | Solar radiation | Met One LI200X-L | Meteorological Parameter Procedures for Solar Radiation Sensors | 06/30/00 | DRI | in preparation |
| FMET006 | Atmospheric pressure | Met One piezofilm sensor | Meteorological Parameter Procedures for Atmospheric Pressure Sensors | 06/30/00 | DRI | in preparation |

| SOP No. | Measurement(s) | Instrument | SOP Title | Date of Last Revision | Primary Source(s) | Status |
|---|---|---|---|---|---|---|
| VIII. Data Base Management | | | | | | |
| FDBM001 | Meteorological and continuous gaseous data processing | | Meteorological and Continuous Gaseous Data Processing and Validation | 12/31/94 | DRI SOP #3-109.2 | Follow DRI procedure |
| FDBM002 | Data processing and validation | | Data Processing and Validation | 12/31/94 | DRI SOP #3-003.4 | Follow DRI procedure |

**Table 2-2.** Format for SOPs for Fresno Supersite Project

| Section | Contents |
|---|---|
| 1.0 | General Information |
| 1.1 | Principles and Applicability |
| 1.2 | Summary of Method (including range, sensitivity, precision, and accuracy) |
| 1.3 | Definitions |
| 1.4 | Health and Safety Warnings (what might happen if procedure is not followed or followed incorrectly) |
| 1.5 | Cautions (activities that could result in equipment damage or sample degradation or voiding) |
| 1.6 | Interferences |
| 1.7 | Personnel Qualifications (specify required training if necessary) |
| 2.0 | Installation/Collection Procedures |
| 2.1 | Apparatus and Materials |
| 2.1.1 | Description of Apparatus/Material |
| 2.1.2 | Reagents and Gases |
| 2.1.3 | Initial Startup |
| 2.2 | Installation/Sampling |
| 2.2.1 | Power and Space |
| 2.2.2 | Probe Assembly |
| 2.2.3 | Sample Collection |
| 2.2.4 | Handling and Preservation |
| 2.2.5 | Sample Preparation and Analysis |
| 2.2.6 | Data Acquisition System |
| 2.2.7 | Troubleshooting |
| 2.3 | Instrument or Method Calibration |
| 2.3.1 | Standards |
| 2.3.2 | Calibration |
| 2.3.3 | Calculations |
| 3.0 | Quality Control and Quality Assurance |
| 3.1 | Routine Service Checks |
| 3.1.1 | General Information |
| 3.1.2 | Frequency of QC Checks (e.g., daily, weekly, monthly, annually) |
| 3.2 | Detailed Maintenance Procedures |
| 3.3 | Acceptance Testing Procedures |
| 3.3.1 | General Information |
| 3.3.2 | Physical Inspection |
| 3.3.3 | Operational Tests |
| 3.3.4 | Final Review |
| 3.4 | Quality Assurance |
| 3.4.1 | Performance Audit Procedures/Schedule |
| 3.4.2 | Systems Audit Procedure/Schedule |
| 3.4.3 | Data Validation Procedure Summary |
| 3.5 | Checklist |
| 4.0 | References |

**Table 2-3.** Summary of Laboratory-related SOPs

| DRI SOP No. | Observable/Method | Title | Date of Last Revision |
|---|---|---|---|
| 2-101.1 | TSP and $PM_{10}$ mass | Gravimetric Analysis, Processing, and Documentation of 8”X10” Glass Fiber Filters for Hi-Vol Sampling | |
| 2-102.3 | PM mass | Gravimetric Analysis Procedures | 8/30/94 |
| 2-114.1 | $PM_{2.5}$ FRM mass | $PM_{2.5}$ FRM Gravimetric Analysis | 3/1/99 |
| 2-107.2 | Light transmission | Light Transmission Analysis Procedure | 8/3/90 |
| 2-105.3 | Nylon filter pretreatment | Preparation of Nylon Filters for Nitric acid or Total Nitrate Sampling | 4th qtr 94 |
| 2-106.3 | Quartz-fiber filter pretreatment | Pre-firing of Quartz Fiber filters for Carbonaceous Material Sampling | 12/23/94 |
| 2-108.3 | Sectioning of filters | Sectioning of Teflon and Quartz Filter Samples | 2nd qtr 94 |
| 2-109.4 | Ionic species filter extraction | Extraction of Ionic Species from Filter Samples | 8/8/96 |
| 2-110.4 | Filter pack processing | Filter Pack Assembling, Disassembling, and Cleaning Procedure | 11/24/98 |
| 2-111.4 | Filter pack shipping and receiving | Sample Shipping, Receiving, and Chain-of-Custody | 11/24/98 |
| 2-112.1 | $PM_{2.5}$ FRM filter pack processing | $PM_{2.5}$ FRM Filter Pack Assembly, Disassembly, and Cleaning | 3/1/99 |
| 2-113.1 | $PM_{2.5}$ FRM shipping and receiving | $PM_{2.5}$ FRM Sample Shipping, Receiving, and Chain-of-Custody | 3/1/99 |
| 2-203.4 | $Cl^-$, $NO_3^-$, $SO_4^=$ | Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography | 4th qtr 94 |
| 2-204.4 | OC and EC in seven fractions | Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples | 6/1/00 |
| 2-205.2 | 40 elements from Na to U | X-ray Fluorescence (XRF) Analysis of Aerosol Filter Samples | 9/22/90 |
| 2-206.4 | $Na^+$, $K^+$ | Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy | 4th qtr 94 |
| 2-207.5 | $NH_4^+$ or $NH_3$ as $NH_4^+$ | Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetric Analysis | 11/20/98 |
| 2-703.1 | Volatile organic compounds ($C_2$-$C_{12}$) | Analysis of VOC in Ambient Air by Gas Chromatography with Cyrogenic Concentration | 7/2/98 |
| 2-704.1 | Volatile organic compounds ($C_2$-$C_{12}$) | Analysis of VOC in Ambient Air by Gas Chromatography and Mass Spectrometry | 7/2/98 |
| 2-710.1 | Carbonyls | Analysis of Carbonyl Compounds by High Pressure Liquid Chromatography | 7/9/98 |
| 2-720.1 | Heavy hydrocarbons ($C_8$-$C_{20}$) | Analysis of $C_8$ to $C_{20}$ Volatile Organic Compounds on Tenax by Gas Chromatography with FID or MSD/FTIR Detection | 9/21/95 |
| 2-750.1 | Semi-volatile organic compounds | Analysis of Semi-Volatile Organic Compounds by Gas Chromatography and Mass Spectrometry | 6/24/98 |

**Table 2-4**. Format for DRI Laboratory SOPs

| **Section** | **Contents** |
|---|---|
| 1.0 | General Discussion |
| 1.1 | Purpose of Procedure |
| 1.2 | Measurement Principle |
| 1.3 | Measurement Interferences and Their Minimization |
| 1.4 | Ranges and Typical Values of Measurements Obtained by This Procedure |
| 1.5 | Typical Lower Quantifiable Limits, Precision, and Accuracy |
| 1.6 | Responsibilities of Personnel for Carrying Out Portions of This Procedure |
| 1.7 | Definitions |
| 1.8 | Related Procedures |
| 2.0 | Apparatus, Instrumentation, Reagents, and Forms |
| 2.1 | Apparatus and Instrumentation |
| 2.1.1 | Description (including manufacturer and model numbers and number of items to be kept on hand) |
| 2.1.2 | Characterization (typical stability response time, idiosyncrasies) |
| 2.1.3 | Maintenance (routine maintenance, troubleshooting, references to operating manual) |
| 2.1.4 | Spare Parts List |
| 2.2 | Reagents (purity grade, supplier, storage, when to reorder) |
| 2.3 | Forms (copies of all paperwork, description of each entry, when to reorder) |
| 3.0 | Calibration Standards |
| 3.1 | Preparation of Working Standards (ranges of standard values, traceability to primary standards) |
| 3.2 | Use (what is compared to standards) |
| 3.3 | Typical accuracy of Calibration Standards |
| 4.0 | Procedures |
| 4.1 | General Flow Diagram |
| 4.2 | Start-Up |
| 4.3 | Routine Operation |
| 4.4 | Shut-Down |
| 4.5 | Checklists |
| 5.0 | Quantification |
| 5.1 | Calibration Procedures |
| 5.2 | Calculations (background subtraction, interference corrections, precision calculations) |
| 6.0 | Quality Control |
| 6.1 | Performance Testing (frequency of blanks and standards) |
| 6.2 | Reproducibility Testing (frequency of replicates) |
| 6.3 | Control Charts, Tolerances, and Actions to be Taken |
| 6.4 | Flags for Non-Standard Procedures |
| 6.5 | Data validation Feedback |
| 7.0 | Quality Assurance |
| 7.1 | Performance Audit Schedule |
| 7.2 | Systems Audit Schedule |
| 7.3 | Data Validation Procedure Summary |
| 8.0 | References |

**Table 2-5**. Typical Corrective Actions for Anticipated Sampling and Measurement Problems

| **Item** | **Potential Problem** | **Corrective Actions** | **Notification or Documentation** |
|---|---|---|---|
| Filter conditioning | Environmental chamber temperature and/or relative humidity out of specification | Check control system and reset, if necessary. If these actions do not correct the problem, check with the laboratory supervisor and/or building maintenance.<br>Wait at least 24 hours after problem has been resolved before conducting a weighing session. | Document problem in laboratory logbook and notify laboratory supervisor. |
| Filter inspection (pre-weigh) | One or more filter defects detailed in SOP observed. | Discard filter and replace it with an acceptable one. | Document problem in logbook and notify laboratory supervisor if problem persists. |
| Filter inspection (pre-weigh) | Filter dropped or contaminated by technician. | Discard filter and replace it with an acceptable one. | None |
| Filter loading (pre-sampling) | Filter defect noted, filter dropped, or filter contaminated. | Discard filter and replace it with a spare filter or use a field blank. | Document problem on field data sheet and notify field coordinator. |
| Filter unloading (post-sampling) | Filter defect noted, filter dropped, or filter contaminated. | Examine filter and flag or invalidate filter results. | Document problem on field data sheet and have field coordinator approve. |
| Denuder handling | Denuder breaks | Carefully wrap denuder in aluminum foil, label the foil, and set the unit aside. Ship the broken denuder to the laboratory. | Document potential sample losses on field data sheet. Notify field/lab coordinator to arrange for the denuder's repair or replacement. |
| Container shipment | Shipment is delayed or lost | Contact sender and obtain the shipment's tracking number. Track and locate the shipment. Use spare or field blank samples for sampling, if necessary. If shipment is subsequently never located, file claim with carrier. | Document any filter pack replacements or losses of certain sampling periods in logbook and notify field coordinator. |
| Container shipment | Shipment is damaged | Assess damage to internal components. Repair or replace if necessary and file claim with carrier. | Document problem in logbook and notify field coordinator. |
| Sampler ambient temperature and pressure measurement | Out of acceptable tolerance | Inspect electrical connections and fittings. Recalibrate sensor. Contact sampler manufacturer if problem is not resolved. | Document problem on field data sheet and notify field coordinator. |

| **Item** | **Potential Problem** | **Corrective Actions** | **Notification or Documentation** |
|---|---|---|---|
| Initial filter pack flow rate | Out of ±10% acceptable flow range | Verify connectors and fittings.  Perform leak check and total flow checks.  Use spare filter pack if necessary. | Notify field coordinator and request additional filter packs. |
| Elapsed sample time | Sampler did not run or failed to shut down as intended. | Check sampler time clock and event programming.  Contact sampler manufacturer if problem is not resolved. | Document problem on field data sheet and notify field coordinator. |
| Site power | Power interruption | Check circuit breaker and reset.  Check line voltages. | Document problem on field data sheet and notify field coordinator.  Record any sample time loss or changes in sampling duration. |
| Test results | Poor precision among collocated samplers or instrument | Check test results.  Identify samplers or instruments that appear to produce unexpected tests results.  Troubleshoot sampling or measurement subsystems most likely to cause imprecision (flow leaks, flow control problems, temperature sensor inaccuracy, pressure sensor inaccuracy, sample programming faults, etc).  Contact instrument manufacturer if problem is not resolved. | Notify site operator, field coordinator, and principal investigators.  Notify instrument manufacturer if problem is determined to be one of design, construction, or faulty component(s). |

## **Table 2-6.** Quality Assurance Activities at the Fresno Supersite

| | *Observable (Method)* | *Percent Tolerance* | *Instrument* | *Primary Standard* | *Calibration Standard* | *Calibration Frequency* | *Performance Test Standard* | *Performance Test Frequency* | *Performance Audit Standard* | *Performance Audit Frequency* | *Audit by* $^{a}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **I. Gases** | | | | | | | | | | | |
| | $NO/NO_x$ (chemiluminescence) | ±10% | TEI 42 | NIST-traceable NO mixture | Certified NO mixture and dynamic dilution | Quarterly or when out of spec | Span with certified NO and zero with scrubbed air | Daily | Certified NO mixture and dynamic dilution | Yearly | ARB |
| | $O_3$ (UV absorption) | ±10% | API 400 | ARB Primary UV Photometer | Dasibi 1003AH UV photometer | Quarterly or when out of spec | Span with internal ozone generator and zero with scrubbed air | Daily | Dasibi 1008 with temperature and pressure adjustments | Yearly | ARB |
| | CO (infrared absorption) | ±10% | Dasibi 3008 | NIST-traceable CO mixture | Certified CO mixture and dynamic dilution | Quarterly or when out of spec | Span with certified CO and zero with scrubbed air | Daily | Certified CO mixture and dynamic dilution | Yearly | ARB |
| | NMHC (flame ionization) | ±10% | TEI 55C | NIST-traceable HC mixture | Certified HC gas dilution | Quarterly or when out of spec | Span with certified HC and zero with scrubbed air | Daily | Certified HC gas dilution | Yearly | ARB |
| | $NO_y$, $HNO_3$, $NO_2$, PAN (chemiluminescence and Luminol) | ±20% | TEI 42CY $^{b}$<br>UC Riverside Lumiinol | NIST-traceable NO mixture | Certified NO mixture and dynamic dilution | Quarterly or when out of spec | Span with certified NO and $HNO_3$ perm tube and zero with scrubbed air | Daily for NO<br>Weekly for $HNO_3$ | Certified NO mixture and dynamic dilution | 3 times over 3 years | CRPAQS/ CE-CERT |
| | $NH_3$ (chemiluminescence) | ±20% | TEI 17C $^{b}$ | NIST-traceable NO mixture | Certified NO mixture and dynamic dilution | Quarterly or when out of spec | Span with certified NO and zero with scrubbed air | Daily | Certified NO mixture and dynamic dilution | 3 times over 3 years | CRPAQS/ CE-CERT |
| **II. Filter Mass and Chemistry** | | | | | | | | | | | |
| | TSP mass (high-volume sampler) | ±5% | General Metal Works | Spirometer (>1,000 L/min) | Calibrated orifice/ roots meter | Quarterly | Calibrated orifice | Monthly | Calibrated orifice/ roots meter | Yearly | ARB |
| | $PM_{10}$ mass (hivol SSI sampler) | ±5% | Andersen | Spirometer (>1,000 L/min) | Calibrated orifice/ roots meter | Quarterly | Calibrated orifice | Monthly | Calibrated orifice/ roots meter | Yearly | ARB |
| | $PM_{2.5}$ and coarse mass, elements, elements, endotoxins, spores, mold, and fungi (collocated dichotomous samplers) | ±5% | Andersen | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Calibrated bubblemeter | Monthly | Mass flowmeter | Yearly | ARB |

**Table 2-6.** (continued)

| | *Observable (Method)* | *Percent Tolerance* | *Instrument* | *Primary Standard* | *Calibration Standard* | *Calibration Frequency* | *Performance Test Standard* | *Performance Test Frequency* | *Performance Audit Standard* | *Performance Audit Frequency* | *Audit by* [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **II. Filter Mass and Chemistry (continued)** | | | | | | | | | | | |
| | $PM_{10}$ endotoxins, spores, mold, and fungi (R&P sequential filter and Burkhard samplers) | ±5% | R&P Burkhard | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Calibrated bubblemeter | Monthly | Mass flowmeter | Yearly | ARB |
| | $PM_{2.5}$ mass, light absorption, elements, ions, and carbon (2 single-channel FRM samplers) | ±5% | Andersen | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Calibrated bubblemeter (Gillibrator) | Monthly | Mass flowmeter | Yearly | ARB |
| | $PM_{2.5}$ mass, elements, ions, and carbon (6-channel RAAS speciation sampler) | ±5% | Andersen | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Calibrated bubblemeter | Monthly | Mass flowmeter | Yearly | ARB |
| | Particle morphology (Minivol portable sampler) | ±15% | Airmetrics | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Calibrated bubblemeter | Monthly | Mass flowmeter | 5 times over 3 years | CRPAQS/ CE-CERT |
| | $PM_{2.5}$ mass, elements, ions, and carbon (2-channel Met One speciation sampler) | ±5% | Met One | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Calibrated bubblemeter | Monthly | Mass flowmeter | Yearly | ARB |
| | $PM_{2.5}$ mass, elements, ions, carbon, and ammonia (2-channel sequential filter sampler with denuders and backup filters) | ±5% | DRI SFS | NIST-certified Vol-U-Met (25-200 L/min) | Dry test meter | At the beginning and end of two-month sampling episode | Calibrated dry test meter | Monthly | Dry test meter | At the beginning and end of two-month sampling episode | CRPAQS |
| | $PM_{2.5}$ mass, elements, ions, and carbon (2-channel sequential filter sampler with denuders and backup filters) | ±5% | DRI SFS | NIST-certified Vol-U-Met (25-200 L/min) | Dry test meter | At the beginning and end of two-month sampling episode | Calibrated dry test meter | Monthly | Dry test meter | At the beginning and end of two-month sampling episode | CRPAQS |
| | Trace metals, chromium VI, aldehydes (air toxic monitor and absorbent cartridge) | ±10% | Xontec 920 | NIST-certified bubblemeter (1-25 L/min) | Dry test meter | Quarterly | Calibrated dry test meter | Monthly | Mass flowmeter | Yearly | ARB |

**Table 2-6.** (continued)

| | *Observable (Method)* | *Percent Tolerance* | *Instrument* | *Primary Standard* | *Calibration Standard* | *Calibration Frequency* | *Performance Test Standard* | *Performance Test Frequency* | *Performance Audit Standard* | *Performance Audit Frequency* | *Audit by* [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **III. Continuous Particle Mass and Chemistry** | | | | | | | | | | | |
| | $PM_{2.5}$ mass (TEOM) | ±5% | R&P 1400A | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Internal flow check | Weekly | Mass flowmeter | 5 times over 3 years | CRPAQS/ CE-CERT |
| | | ±10% | | Certified laboratory weights | Factory calibration | When out of spec | Weighed filter stubs | Quarterly | Weighed filter stubs | 5 times over 3 years | |
| | $PM_{10}$ mass (TEOM) | ±10% | R&P 1400A | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Internal flow check | Weekly | Mass flowmeter | 5 times over 3 years | CRPAQS/ CE-CERT |
| | | ±10% | | Certified laboratory weights | Factory calibration | When out of spec | Weighed filter stubs | Quarterly | Weighed filter stubs | 5 times over 3 years | |
| | $PM_{2.5}$ mass (BAM) | ±10% | Met One 1020 | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Internal flow check | Weekly | Mass flowmeter | 5 times over 3 years | CRPAQS/ CE-CERT |
| | | ±10% | | Certified laboratory weights | Factory calibration | When out of spec | Weighed thin films | Quarterly | Weighed thin films | 5 times over 3 years | |
| | $PM_{10}$ mass (BAM) | ±10% | Met One 1020 | NIST-certified bubblemeter (1-25 L/min) | Mass flowmeter/ bubblemeter | Quarterly | Internal flow check | Weekly | Mass flowmeter | 5 times over 3 years | CRPAQS/ CE-CERT |
| | | ±10% | | Certified laboratory weights | Factory calibration | When out of spec | Weighed thin films | Quarterly | Weighed thin films | 5 times over 3 years | |
| | $PM_{2.5}$ nitrate (ambient particulate nitrate monitor by flash volatilization) | ±15% | ADI/R&P | NIST-traceable NO | Certified NO with dynamic dilution and nitrate solution | Quarterly | Span with certified NO and zero with scrubbed air | Weekly | Certified NO with dynamic dilution and nitrate solution | 5 times over 3 years | CRPAQS/ CE-CERT |
| | $PM_{2.5}$ sulfate (ambient particulate sulfate monitor, flash volatilization with $SO_2$ detector) | ±15% | ADI/R&P | NIST-traceable sulfate | Certified $SO_2$ with dynamic dilution and sulfate solution | Quarterly | Span with certified $SO_2$ and zero with scrubbed air | Weekly | Certified $SO_2$ with dynamic dilution and sulfate solution | 5 times over 3 years | CRPAQS/ CE-CERT |

**Table 2-6.** (continued)

| | *Observable (Method)* | *Percent Tolerance* | *Instrument* | *Primary Standard* | *Calibration Standard* | *Calibration Frequency* | *Performance Test Standard* | *Performance Test Frequency* | *Performance Audit Standard* | *Performance Audit Frequency* | *Audit by* [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **III.** | **Continuous Particle Mass and Chemistry (continued)** | | | | | | | | | | |
| | $PM_{2.5}$ organic and elemental carbon (ambient carbon particulate by thermal evolution) | ±15% | R&P 5400 | NIST-certified $CO_2$ | Certified $CO_2$ with dynamic dilution | Quarterly | Span with certified $CO_2$ and zero with nitrogen | Weekly | Certified $CO_2$ with dynamic dilution | 5 times over 3 years | CRPAQS/ CE-CERT |
| | $PM_{2.5}$ organic and elemental carbon (ambient carbon particulate monitor, thermal optical ) | ±15% | GreenTek | NIST-certified $CO_2$ canister | Carbon dioxide | Quarterly | Collocated comparison with continuous thermal analyzer | Weekly | Mass flowmeter | 5 times over 3 years | CRPAQS/ CE-CERT |
| | Individual particle size and chemistry (time-of-flight mass spectrometer) | ±20% | U.C. Riverside | Not available | Under development | Under development | Under development | Under development | Under development | Under development | CRPAQS/ CE-CERT |
| | Particle-bound polycyclic aromatic hydrocarbons (PAHs) (photo oxidation) | ±20% | EcoChem PAS2000 | Compounds under development | Factory calibration | When out of spec | Internal electronic checks | Weekly | Collocated comparison with filter/PUF/XAD samples | Under development | CRPAQS/ CE-CERT |
| **IV.** | **Organics** | | | | | | | | | | |
| | Hydrocarbons (canister) | ±10% | Xontec 910 | NIST-certified Vol-U-Met | Calibrated rotameter | At the beginning and end of two-month sampling period | Calibrated rotameter | Monthly | Dry test meter | During sampling period | ARB |
| | Carbonyls (absorbent cartridge) | ±10% | Xontec 925 | NIST-certified Vol-U-Met | Calibrated rotameter | At the beginning and end of two-month sampling period | Calibrated rotameter | Monthly | Dry test meter | During sampling period | ARB |
| | Light hydrocarbons (canister and GC/FID) | ±10% | CRPAQS | NIST-certified Vol-U-Met | Calibrated rotameter | At the beginning and end of two-month sampling period | Calibrated rotameter | Monthly | Dry test meter | During sampling period | CRPAQS |

**Table 2-6.** (continued)

| | *Observable (Method)* | *Percent Tolerance* | *Instrument* | *Primary Standard* | *Calibration Standard* | *Calibration Frequency* | *Performance Test Standard* | *Performance Test Frequency* | *Performance Audit Standard* | *Performance Audit Frequency* | *Audit by* [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Heavy hydrocarbons (Tenax and GC/TSD/FID) | ±10% | CRPAQS | NIST-certified Vol-U-Met | Calibrated rotameter | At the beginning and end of two-month sampling period | Calibrated rotameter | Monthly | Dry test meter | During sampling period | CRPAQS |
| | Aldehydes (DNPH and HPLC) | ±10% | CRPAQS | NIST-certified Vol-U-Met | Calibrated rotameter | At the beginning and end of two-month sampling period | Calibrated rotameter | Monthly | Dry test meter | During sampling period | CRPAQS |
| **IV. Organics (continued)** | | | | | | | | | | | |
| | PM$_{2.5}$ organic compounds (Teflon-coated glass fiber/PUF/XAD and GCMS) | ±20% | DRI organic sampler | NIST-certified Vol-U-Met | Calibrated rotameter | At the beginning and end of two-month sampling period | Calibrated rotameter | Monthly | Dry test meter | During sampling period | CRPAQS |
| | PM$_{2.5}$ organic components (Teflon-coated glass fiber) | ±20% | Airmetrics | NIST-certified bubblemeter | Mass flowmeter/ bubblemeter | Quarterly | Calibrated rotameter | Monthly | Mass flowmeter | 5 times over 3 years | CRPAQS |
| **V. Light Scattering** | | | | | | | | | | | |
| | PM$_{2.5}$ Dry Particle Nephelometer (530 nm) [b] | ±10% | Radiance M903 | HFC-134a refrigerant | HFC-134a, pure CO$_2$, and particle-free air | When out of spec | Pure CO$_2$ and particle-free air | Weekly | HFC-134a, pure CO$_2$, and particle-free air | 5 times over 3 years | CRPAQS/ CE-CERT |
| | PM$_{2.5}$ Open-Air Nephelometer (550 nm) | ±10% | Optec NGN-2 | HFC-134a refrigerant | HFC-134a, pure CO$_2$, and particle-free air | When out of spec | Pure CO$_2$ and particle-free air | Weekly | HFC-134a, pure CO$_2$, and particle-free air | 5 times over 3 years | CRPAQS/ CE-CERT |
| | Ambient Particulate Monitor (photometer) [b] | ±20% | GreenTek GT640A and DUSTRAK 8520 | HFC-134a refrigerant | HFC-134a, pure CO$_2$, and particle-free air | When out of spec | Pure CO$_2$ and particle-free air | Weekly | HFC-134a, pure CO$_2$, and particle-free air | 5 times over 3 years | CRPAQS/ CE-CERT |

**Table 2-6.** (continued)

| | *Observable (Method)* | *Percent Tolerance* | *Instrument* | *Primary Standard* | *Calibration Standard* | *Calibration Frequency* | *Performance Test Standard* | *Performance Test Frequency* | *Performance Audit Standard* | *Performance Audit Frequency* | *Audit by* [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **VI. Light Absorption** | | | | | | | | | | | |
| | Coefficient of Haze | ±20% | RAC 205019-1 | Neutral density filter | Factory calibration | Quarterly | Internal electronic checks and neutral density filters | Weekly and monthly | Neutral density filter | Yearly | ARB |
| | Aethalometer (880 nm) | ±5% | Magee AE14U | Neutral density filter | Factory calibration | Quarterly | Internal electronic checks and neutral density filters | Weekly and monthly | Neutral density filter | 5 times over 3 years | CRPAQS/ CE-CERT |
| | Seven-wavelength Aethalometer [b] | ±5% | Andersen AE30S | Neutral density filter | Factory calibration | Quarterly | Internal electronic checks and neutral density filters | Weekly and monthly | Neutral density filter | 5 times over 3 years | CRPAQS/ CE-CERT |
| **VII. Particle Sizes** | | | | | | | | | | | |
| | Scanning Mobility Particle Sizer (0.01 to 1.0 µm) | ±15% | TSI 3936L10 | Collocated differential mobility analyzer | Factory calibration | Yearly | Internal electronic checks and collocated comparison | Daily and monthly | Certified particle sizes and voltage tests | 5 times over 3 years | CE-CERT |
| | Optical Particle Counter (0.5 to 10 µm) | ±15% | Climet CI-500 | Vibrating orifice aerosol generator | Polystyrene latex suspension | Yearly | Internal electronic checks and collocated comparison | Daily and monthly | Polystyrene latex suspension | 5 times over 3 years | CE-CERT |
| | Optical Particle Counter (0.1 to 2 µm) | ±15% | PMS LASAIR 1003 | Vibrating orifice aerosol generator | Polystyrene latex suspension | Yearly | Internal electronic checks and collocated comparison | Daily and monthly | Polystyrene latex suspension | 5 times over 3 years | CE-CERT |
| | Aerosol Particle Sizer [c] (0.3 to 10 µm) | ±20% | TSI 3296 | Vibrating orifice aerosol generator | Polystyrene latex suspension | Yearly | Internal electronic checks and collocated comparison | Daily and monthly | Polystyrene latex suspension | 5 times over 3 years | CE-CERT |
| | Rotating MOUDI with accessories (4 units) for mass, ions, and carbon size distributions | ±10% | MSP 100 | NIST-certified Vol-U-Met | Calibrated rotameter | At the beginning and end of two-month sampling period | Calibrated rotameter | Monthly | Dry test meter | During sampling period | CRPAQS |
| **VIII. Meteorology** | | | | | | | | | | | |
| | High-Sensitivity Anemometer (wind speed) | ±0.3 m/s | MetOne 05305L | Certified wind tunnel | Factory calibration | Yearly | Visual check, synchronize motor when out of spec | Daily and when needed | Synchronized motor | Yearly | ARB |
| | High-Sensitivity Wind Vane (wind direction) | ±5° at all points | MetOne 05305L | Surveyor compass, solar azimuth | Surveyor compass, solar azimuth | When out of spec | Visual check, realignment when out of spec | Weekly | Surveyor compass, solar azimuth | Yearly | ARB |

## **Table 2-6.** (continued)

| | *Observable (Method)* | *Percent Tolerance* | *Instrument* | *Primary Standard* | *Calibration Standard* | *Calibration Frequency* | *Performance Test Standard* | *Performance Test Frequency* | *Performance Audit Standard* | *Performance Audit Frequency* | *Audit by* [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | High-Accuracy Temperature by Platinum Resistance | ±0.1 °C | MetOne CS 500L | NIST thermometer and water bath | Factory calibration | When out of spec | On-site psychrometer | Weekly | NIST thermometer and water bath | Yearly | ARB |
| | High-Accuracy Relative Humidity by Capacitance | ±2% | MetOne CS 500L | NIST thermometer and dew cups | Factory calibration | When out of spec | On-site psychrometer | Weekly | Collocated chilled mirror sensor | Yearly | ARB |
| | Solar Radiation Sensor / Pyranometer | ±20 $w/m^2$ | MetOne LI200XL | NIST standard luminance | Factory calibration | When out of spec | Visual inspection of max and min | Weekly | Collocated pyranometer | Yearly | CE-CERT |
| | Barometric Pressure Sensor / Barometer | ±3 mm Hg | MetOne | Mercury barometer | Mercury barometer | Quarterly | Visual inspection of max and min | Weekly | Mercury barometer | Yearly | CE-CERT |
| **IX. Laboratory Chemical Analysis** | | | | | | | | | | | |
| | Mass (electrobalance) | ±10% | Mettler MT5 | Class 1.1 weights | Class 1.1 weights | Each weighing session | Class 1.1 weights, replicates, and blanks | Every 10 samples | NIST Class 1.1 weights | Yearly | CE-CERT |
| | Total elements (x-ray fluorescence) | ±5% | Kevex 700/800 | EPA polymer films, NIST impregnated glass | Micromatter film deposits | 6 months or when out of spec | NIST impregnated glass, replicates, and blanks | Every 15 samples | Micromatter film deposits and interlaboratory comparison | Yearly | CE-CERT |
| | Soluble metals (ICPMS) | ±0.005 to ±0.05 μg/mL | Varian Ultramass 700 | Mineral salt solutions | Mineral salt solutions | Each analysis session | Mixed salt solutions, replicates, and blanks | Every 10 samples | Mixed salt solutions and interlaboratory comparison | Yearly | CE-CERT |
| | Anions and cations (ion chromatography) | ±0.05 μg/mL | Dionex 500DX | Mineral salt solutions | Mineral salt solutions | Each analysis session | Mixed salt solutions, replicates, and blanks | Every 10 samples | Mixed salt solutions and interlaboratory comparison | Yearly | CE-CERT |
| | Carbon (thermal/optical reflectance or thermal/optical transmission) | ±0.2 $\mu g/cm^2$ | DRI/Met One thermal/ optical analyzer | NIST $CO_2$ and $CH_4$ | Pthalate and sucrose solutions | 3 months or when out of spec | $CH_4$, replicates, and blanks | Every sample<br>Every 10 samples | Pthalate and sucrose solutions on filters $CO_2$ and $CH_4$ and interlaboratory comparison | Yearly | CE-CERT |

[a] ARB: Audited as part of California Air Resources Board's QA program for compliance network.
CRPAQS: Audited as part of California Regional Particulate Study Air Quality Study special study between 11/15/99 and 1/31/01.
CE-CERT: Audited by Fresno Supersite QA group at University of California, Riverside, between 2/1/01 and 3/31/03.

[b] Under development and evaluation.

[c] Available during Phase II (4/1/01 to 3/31/03).

**Figure 2-1.** Major Population Centers in Central California

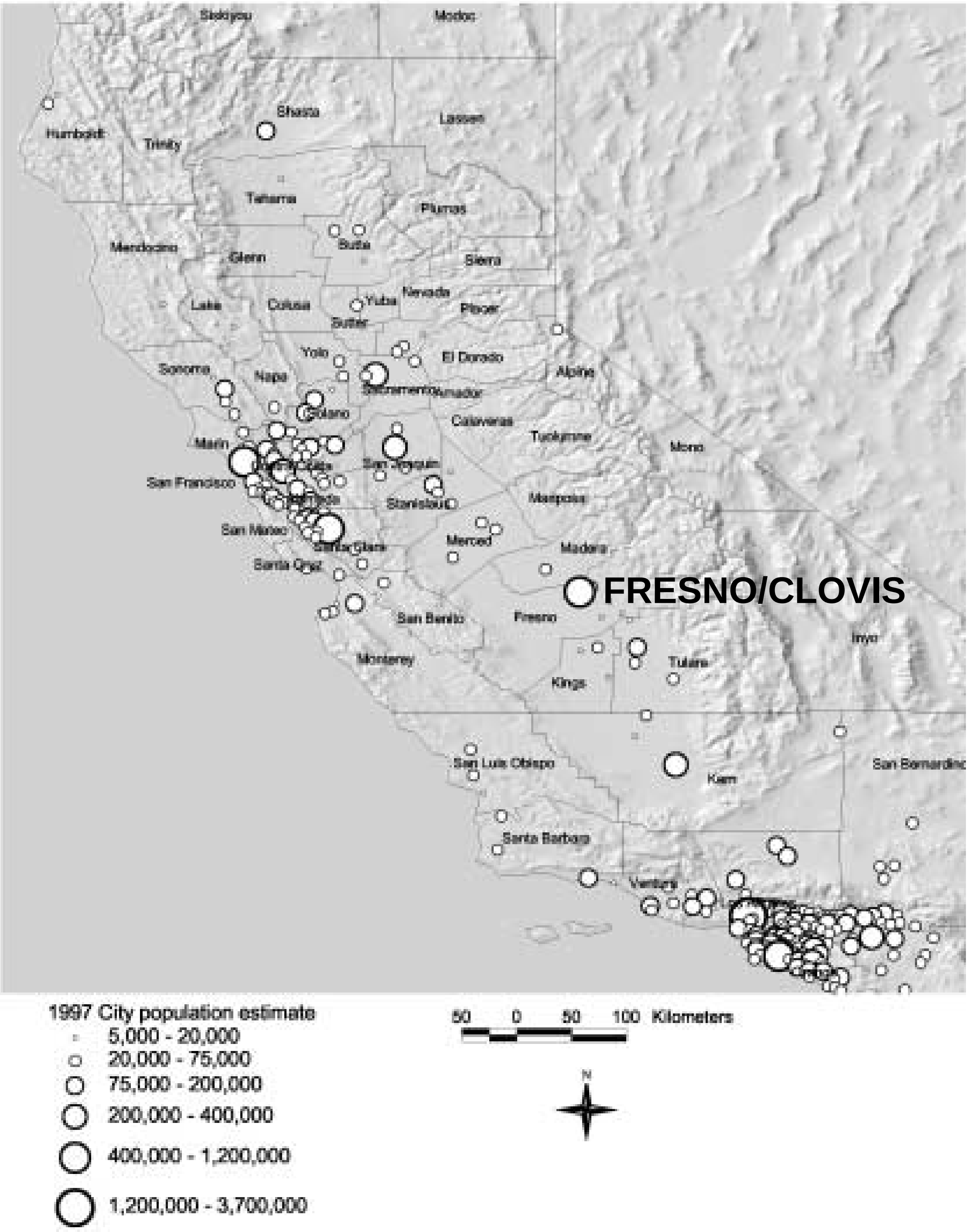


**Figure 2-2.** Related Measurements at CRPAQS Monitoring Locations

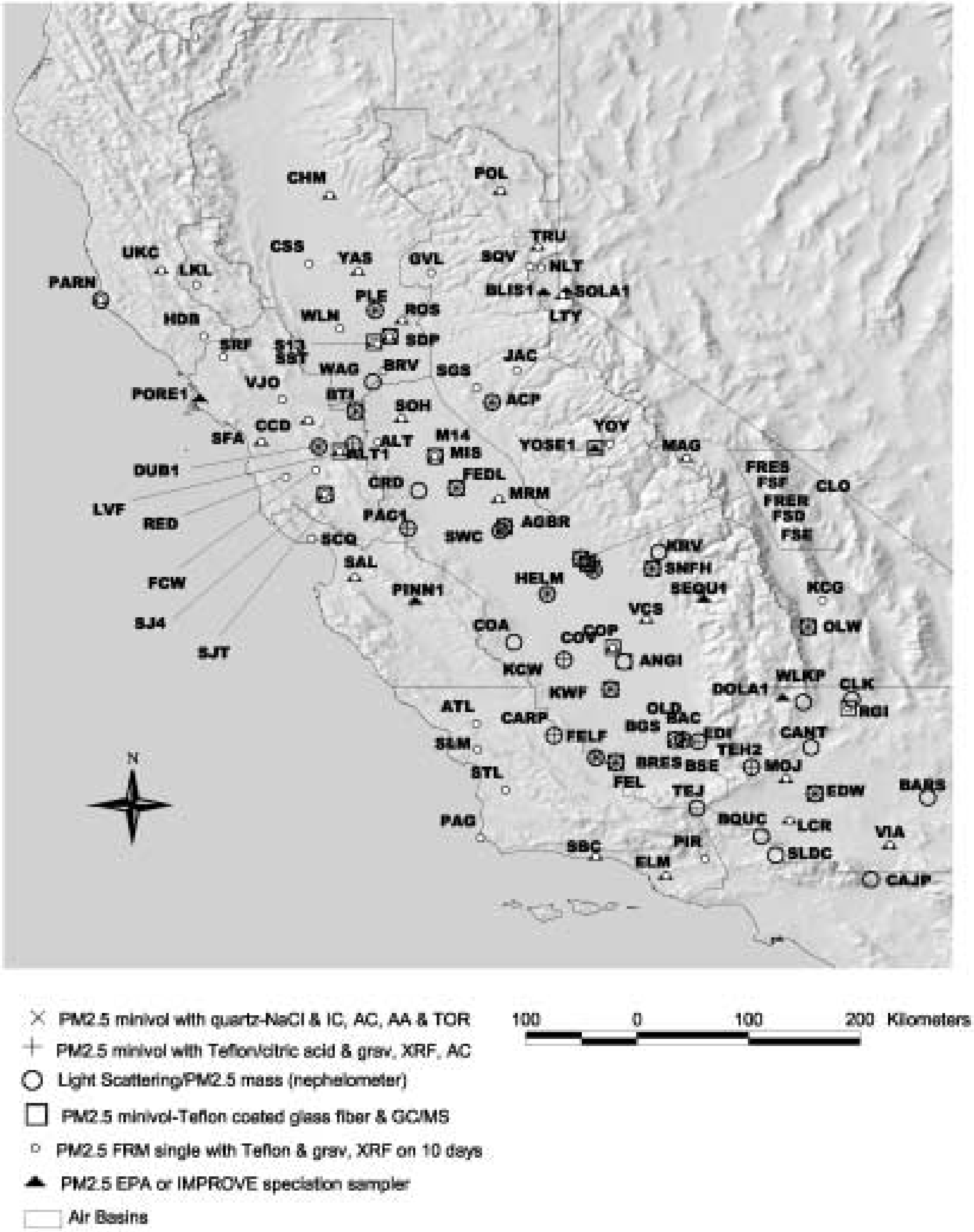
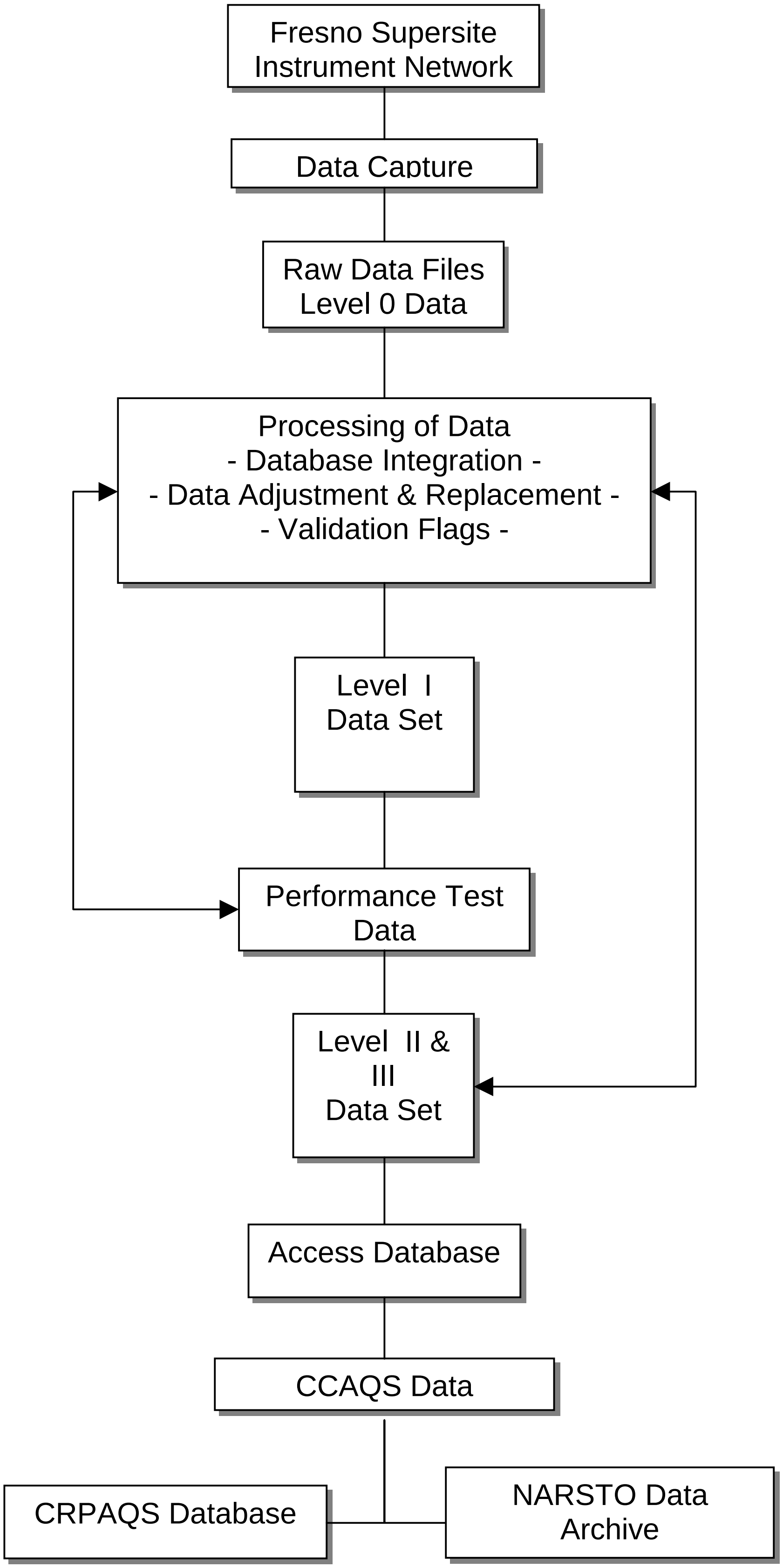


**Figure 2-3. Flow Diagram of the Database Management System**



# 3. ASSESSMENT AND OVERSIGHT

## 3.1 Assessment and Response Actions

Success of the project will be evaluated in terms of: 1) accuracy, precision, validity, and completeness of acquired data; 2) extent to which data can be used to test stated hypotheses; 3) confidence of conclusions regarding hypotheses; 4) consistency of Fresno Supersite measurements with those from other California sites and other Supersites; 5) integration with other monitoring networks and research studies; 6) leveraging of Supersite resources with those from other agencies; and 7) relevance of study conclusions to Supersite program objectives. Periodic publications and a final report by the Principal Investigator will present accomplishments within each of these areas.

The first area will be assessed by the data qualification statements presented in Section 1.4, and detailed further in Table 2-6, which also lists some of the types and frequencies of the performance evaluations. Assessment tools include systems audits, performance audits, database integrity audits, interlaboratory comparisons, comparisons with results from other Supersites, external review by a peer review panel, and peer review as part of the publication process. Common procedures and standards have been developed for the auditing of the gaseous criteria pollutants and meteorological instruments. Independent ARB staff performs these audits at the Fresno Supersite each year. Conversely, some of the novel measurements in Table 1-1 will be evaluated by comparison with other measurements that have traceable standards and audit trails.

The QA Manager will conduct field and laboratory systems audits, a laboratory performance audit and/or oversee interlaboratory comparisons, and three field performance audits. Systems audits examine all phases of measurement and data processing to determine that the SOPs are followed and that operational staff is properly trained. The systems audit is intended to be a cooperative assessment resulting in improved data, rather than a judgmental activity. Performance audits establish the extent to which data specifications are being achieved in practice and evaluate measurement accuracy against independent standards. The field systems audit is conducted at the beginning of the project after all equipment is installed and operating. It will be followed by the first field performance audit. These audits will identify deficiencies and implement remedial actions. Subsequent field performance audit results will be used to define the accuracy of the field measurements.

The laboratory audits that will be performed will consist of presenting standards with known concentrations to each laboratory process. These standards will be analyzed according to routine procedures and the results will be compared with the standard values. As shown in Table 2-6, reliable transfer standards can be obtained for mass, elements, ions, and total carbon. However, common standards are not available for organic and elemental carbon.

Interlaboratory comparisons will be performed by exchanging portions of the same filters or sample extract with selected laboratories. Mass, elemental, ion, and carbon analysis will be performed on portions of the same filter. DRI routinely conducts such interlaboratory comparisons with laboratories at the ARB and the South Coast Air Quality Management District.

The evaluation of some of the non-routine measurements in Table 2-6 involves the application of non-standardized methodologies. In these areas the QA Manager will continue to remain current on emerging technologies and methods, and will apply them to performance evaluations at a future date, if practical.

For example, testing real-time particle size analyzers is impractical under field conditions. However, methods for conducting performance audits of real-time particle size analyzers are being developed at CE-CERT and elsewhere. The CE-CERT method consists of challenging the analyzer with synthetically generated aerosol. These standards will be characterized at the CE-CERT environmental chamber facility. As currently conceived, particles less than 1 µm may be generated with a nebulizer using a dilute solution of ammonium sulfate. A differential mobility analyzer (DMA) (Liu and Pui, 1974) can then select specific monodisperse size cuts with removal of multiply charged particles in the upper end of the sub-micron diameter size range (Romay-Novas and Pui, 1988; Gupta and McMurry, 1989). The size of the classified particles depends on flow rates, classifying voltage, and geometrical factors (Knutson and Whitby, 1975), as confirmed by electron microscopic measurements at the National Institute of Standards and Technology (NIST) as part of a 0.1 µm particle standard reference method (Kinney et al., 1991). Particles produced with a DMA typically vary by ±5% about a mean size that is accurate to within ±2%.

A Vibrating Orifice Aerosol Generator (VOAG) (Berglund and Liu, 1973) generates monodisperse spherical droplets in the 1-to 10-µm diameter range from an oleic acid in ethanol solution. Particle size is determined by flow rate of the liquid through the vibrating orifice, vibration frequency, and the concentration of nonvolatile solute. Microscopic analysis (Berglund and Liu, 1973) shows that particles by the VOAG are uniform to within ±1.4% and are routinely within ±2% of the expected size.

Particles generated by these instruments are delivered to the field instruments and simultaneously monitored by a laboratory Condensation Particle Counter (CPC) and an aerosol electrometer. CPC counting efficiencies are close to 100% (Stolzenburg and McMurry, 1991; Zhang and Liu, 1991) for the size ranges and concentrations expected at the Fresno Supersite. At least 1,000 particles for each measurement are counted so that statistical counting errors are <3% (square root of count number).

The second area will be assessed by the data analysts as they use the acquired measurements to test the hypotheses presented in Table 3-1. Part of the success in using the data will be the ratio of data manipulation vs. data analysis time. The web-based data delivery system must allow all analysts to quickly integrate measurements that are most convenient for their tasks. Data quality information must be quickly available for consultation when inconsistencies with conceptual models are found.

The third area, confidence in study conclusions, will be evaluated according to the following criteria: 1) high confidence: low uncertainty in the data or data analysis approach, or more than one independent analysis approach, each of which has moderate uncertainties; 2) medium confidence: moderate uncertainty in the data or data analysis approach and independent analysis approaches were not applied; and 3) low confidence: large uncertainty in the data or data analysis approach and independent analysis approaches were not applied or were contradictory. These ratings were applied by each investigator and modified under scrutiny by all investigators in the Northern Front Range Air Quality Study (Watson et al., 1998c). Decision-makers found it useful for scientists to express their own levels of belief in the outcome of their study.

The fourth area, consistency of the Fresno Supersite measurements with those from other Supersites, will be included in the data qualification statement. This will include a table of overlapping observables and measurement periods acquired at the different sites that will facilitate generalization of Fresno findings to those of other locations.

The next two areas, integration and/or leveraging with other monitoring networks and research studies, is discussed in Section 4.3. The extent to which these opportunities are realized will be evident in the project reports and publications. The final area, relevance of study conclusions to Supersite program objectives, will be addressed in the final report. Each hypothesis under the three program objectives listed in Section 1.1 will be thoroughly addressed in order to assess how well each objective was met.

As shown in Figure 1-1, measurements from the Fresno Supersite will be closely coordinated with concurrent epidemiological, clinical, exposure, and toxicological studies. External advisors, ARB’s study coordinator, and the site supervisor will review this and other project plans and provide recommendations on how data quality might be enhanced, the extent to which Supersite measurements can be used for planning purposes and health studies, and evaluation of study findings. Scientific papers will be submitted to external peer review, and the resulting comments will be addressed in published papers. The principal investigators and/or selected task leaders will report on progress and results at annual meetings of Supersite investigators. These presentations will be structured to obtain feedback and experience from similar projects taking place in other U.S. cities.

## 3.2 Reports to Management

Figure 1-4 shows the schedule for project deliverables and reports to management. These deliverables and reports include: 1) this Quality Assurance Project Plan and its revisions; 2) quarterly progress reports; 3) a draft final report, including the QAFR (11/30/03); and 4) a final report and database (12/31/03). Presentations and technical meetings and publications in peer-reviewed journals will be produced throughout the project. In addition to these written documents, there will be annual review meetings to discuss the progress of the project and quality of the data.

**Table 3-1.** Fresno Supersite Hypotheses and Testing Methods

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **1. Measurement Method Evaluation Hypotheses** | | |
| 1.1 Mass and chemical (elements, ions, and carbon) measurements from compliance filter samplers with a Teflon-membrane filter (from Federal Reference Method [FRM] or Minivol monitors) represent $PM_{2.5}$ mass within the spatial zone of representation of the Fresno Supersite. | Community representative (CORE) sites, such as Fresno First Street, that meet $PM_{2.5}$ siting criteria (Watson et al., 1997), are intended to approximate the exposure of many people to $PM_{2.5}$ in outdoor air. There are few empirical measurements to verify that these criteria are adequate to accomplish this objective. | Compare mass and elemental concentrations measured on the $PM_{2.5}$ FRM filter with those derived from the different channels of the speciation monitor. Compare data pairs with high and low nitrate loadings, high and low temperature, and high and low relative humidities during sampling. Examine the correlation between light absorption on FRM filters and organic, elemental, and total carbon on the speciation sampler to determine the conditions under which absorption can be used as a predictor of different carbon fractions. Compare differences with propagated measurement uncertainties and with the spatial coefficient of variation of $PM_{2.5}$ mass and chemical concentrations derived from simultaneous measurements at sites surrounding the Fresno Supersite. |
| 1.2 Elemental analysis of Teflon-membrane filters under helium and vacuum atmospheres does not result in a significant (>10%) loss of volatile nitrate. | Particle analysis in EPA's speciation network is considering x-ray fluorescence analysis under a helium atmosphere rather than under the conventional vacuum. A potential advantage of this modification is that volatile species, such as ammonium nitrate, may experience less evaporation than under vacuum. If so, then FRM Teflon-membrane filters might also be used after XRF for nitrate analysis. Disadvantages are less sensitive detection limits, added cost of helium vented between each sample batch, and degraded performance and lifetime of x-ray detectors as helium diffuses through the beryllium window. Heating of the sample by x-ray bombardment may cause losses of volatile species regardless of the surrounding atmosphere. | Compare elemental and nitrate measurements from the FRM filter analyzed by x-ray fluorescence (XRF) under vacuum with those from the collocated speciation sample analyzed under helium, and quantify losses of potentially volatile species. Compare nitrate levels from both of these Teflon-membrane filters with the nitrate measured by a speciation monitor on a quartz-fiber filter, non-volatilized nitrate from a front quartz-fiber filter, and volatilized nitrate from a backup sodium-chloride-impregnated cellulose-fiber filter with preceding nitric acid denuder. Quantify any advantages to be gained from the extra expense and lower sensitivity afforded by XRF analysis under a helium atmosphere. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **1. Measurement Evaluation Hypotheses (continued)** | | |
| 1.3 Gaseous organic carbon absorbed on quartz-fiber filters are a small (<15%) fraction of organic carbon measured on these filters. | Previous studies in central California have found organic carbon on backup quartz filters that is 10% to 50% of that on the front filters (Chow et al., 1996; Chow and Egami, 1997). This absorption on the backup filter was smaller when a quartz fiber denuder preceded the filter pack (Chow et al., 1993). When this backup carbon is added or subtracted to the front filter carbon, measured mass is grossly overestimated or underestimated. The extent to which this backup carbon is a significant particle or gas artifact is currently unknown. Carbon measurements taken at other sites without denuders and backup filters can be considered more precise if this hypothesis is proven | Compare organic carbon from the quartz-fiber backup filter with and without organic carbon denuding and quantify the maximum potential artifact that might be expected under routine speciation monitoring. Plot the ratio of backup filter carbon to front filter carbon for both channels as a function of front filter carbon and $PM_{2.5}$ mass. Estimate potential biases to the highest and annual-average $PM_{2.5}$ and carbon concentrations determined from common speciation monitoring. Examine variations with respect to temperature and source contributions, especially vegetative burning. |
| 1.4 Volatilized particulate nitrate is a minor (<10%) part of particle nitrate during winter, but a major fraction of particle nitrate during other seasons. | Substantial savings in sampling and analysis costs can be attained if it can be shown that nitrate measurements taken at other sites without denuders and backup filters (during cool winter and fall months when nitrate levels are high) can be considered more precise. | Plot nitrate and ammonium concentrations from the denuded front filter as a function of total nitrate, stratified by temperature and relative humidity during sampling. Compare nitrate from FRM and from continuous monitors with total particulate nitrate from the denuded quartz-fiber front filters and sodium-chloride-impregnated backup filters. Specify the sampling and analysis conditions under which nitrate from non-denuded samples without backup filters can reasonably represent particulate nitrate in the atmosphere. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **1. Measurement Evaluation Hypotheses (continued)** | | |
| 1.5 Volatilized particulate nitrate is a minor (<10%) part of actual $PM_{2.5}$ during all seasons. | Although larger fractions of nitrate may be lost during sampling for non-winter periods, this may be a small fraction of $PM_{2.5}$ mass under certain conditions. | Plot volatilized nitrate and ammonium concentrations as a function of $PM_{2.5}$ from different monitors, including the heated Tapered Element Oscillating Microbalance (TEOM). Determine the nature of those situations under which volatilization is more than 10% of measured mass. Add particle nitrate and ammonium to the heated TEOM mass, and compare the results with filter-based $PM_{2.5}$ to determine the extent to which TEOM volatilization is specific to ammonium nitrate. |
| 1.6 PM2.5 mass concentrations estimated from particle size, weighted sums of chemical components, light scattering, light absorption, and light extinction, are equivalent to gravimetric mass of samples taken with a $PM_{2.5}$ FRM sampler. | These measures have been found to be highly correlated in previous studies, but their relationships change with aerosol composition and environmental conditions. Knowing the conditions under which equivalence can be expected will expand the utility of different continuous $PM_{2.5}$ surrogate measurements taken at other sites and lessen the need for extensive collocated measurements. | Estimate $PM_{2.5}$ mass concentrations from particle size data using reasonable assumptions about particle shape and density. Estimate $PM_{2.5}$ mass from light scattering, light absorption, or light extinction based on reasonable assumptions about particle shape, density, index of refraction, size distribution, and liquid water uptake. Estimate $PM_{2.5}$ mass based on reasonable assumptions about unmeasured hydrogen and oxygen associated with measured chemical components. Compare these mass estimates with $PM_{2.5}$ mass measured by FRMs and by the speciation monitor with volatilized components added. Explore the nature of discrepancies to determine the potential causes, in terms of particle climatology, deviations from mass estimation assumptions, or measurement limitations. Compare differences among these estimates with differences due to collocated measurement uncertainty, climatology, and filter-based sampler differences. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **1. Measurement Evaluation Hypotheses (continued)** | | |
| 1.7 PM2.5 and $PM_{10}$ mass measurements are comparable for all measurement methods during spring and summer when the sampled aerosol is stable. Mass measurements diverge during winter and part of the spring when volatile nitrate and organics constitute a large mass fraction. | These comparisons between diverse measures of $PM_{2.5}$ and $PM_{10}$ are needed because other sites do not have the Fresno Supersite's full range of instruments. Consistent relationships between $PM_{2.5}$ FRM and light scattering, even ones stratified by relative humidity and aerosol composition, will be needed to evaluate the conditions under which diverse measures are comparable and under which they diverge. This is especially relevant to measurement methods that heat the sample, such as the TEOM. | Apply statistical equivalence measures to $PM_{2.5}$ and $PM_{10}$ mass measurements from $PM_{2.5}$ FRMs, $PM_{10}$ dichotomous samplers, high-volume $PM_{10}$ samplers with size-selective inlets (hivol/SSI), beta attenuation monitors (BAM), and tapered element oscillating microbalances (TEOM). Stratify comparison data sets by season, temperature, relative humidity, and nitrate concentration and determine changes with aerosol composition. Calculate linear regression estimates of $PM_{2.5}$ from light scattering and absorption measurements and examine how these differ with changing aerosol composition and environmental variables. |
| 1.8 Particle number counts in integrated sub-ranges of the 0.01 to ~10 µm size distribution are comparable to $PM_{2.5}$ and $PM_{10}$ mass measurements assuming constant particle shape and density. | This will allow different particle size measurement devices to be evaluated as potential equivalent methods for estimating $PM_{2.5}$ concentrations. The added information of particle number concentration would provide a useful long-term database for health studies and source identification. | Examine chemical compositions from speciation measurements and compile densities for particle compositions expected in different size ranges. Assuming spherical geometry, calculate total volumes for each bin and sum to obtain mass equivalents. Apply comparison measures to determine the extent to which these estimates relate to mass measurements. |
| 1.9 Differences between continuous $PM_{10}$ and $PM_{2.5}$ monitors are comparable to coarse particle mass concentrations on dichotomous samplers. | Continuous measurements of coarse particle mass provide better time resolution and more frequent samples than dichotomous samplers. If biases in BAM and TEOM measurements affect the $PM_{10}$ and $PM_{2.5}$ samples in the same way, the coarse mass fraction may be comparable to that of a dichotomous virtual impactor filter measurement. | Calculate hourly time series of differences between $PM_{10}$ and $PM_{2.5}$ for BAM and TEOM and compare them with each other. Compare 24-hour averages of these differences with dichotomous sampler coarse mass concentrations. Examine time series plots of these differences, with propagated uncertainties, and identify periods for which agreement is good and poor. Explain disagreements in terms of aerosol composition and meteorological changes. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **1. Measurement Evaluation Hypotheses (continued)** | | |
| 1.10 The $PM_{2.5}$ geological component is comparable to the difference between continuous $PM_{2.5}$ mass measurements and the sum of continuous nitrate, sulfate, and carbon concentrations (adjusted for ammonia, hydrogen, and oxygen). | Practical technology is still under development for the *in situ* quantification of soil-related elements, but it is available for the other major components of $PM_{2.5}$ and $PM_{10}$. Mass can usually be reconstructed to within ±10%, however, with weighted sums of sulfate, nitrate, carbon, and elements when humidities are not excessive (Chow et al., 1996). If this holds true for the short-term measurements, then the geological component could be inferred from the other continuous measurements, providing complete characterization of major components at ~30 min intervals. | Calculate the difference between hourly $PM_{2.5}$ mass and weighted sums of sulfate, nitrate, and carbon for all available measurements. Propagate errors and evaluate the extent to which this difference exceeds its precision. Compare 24-hour averages of this difference with the geological fraction determined from the collocated $PM_{2.5}$ dichotomous and speciation monitors. |
| 1.11 Bioaerosol (e.g., endotoxin, pollens, spores, and molds) constitute a constant fraction of coarse particle mass. | Aluminum, silicon, calcium, titanium, iron, and other elements have been found in reasonably uniform proportions in soils throughout the San Joaquin Valley (Houck et al., 1989). Bioaerosols are less likely to exhibit constant proportions to coarse particle mass and elemental concentrations. | Calculate mass ratios of elemental, bioaerosol (pollen, molds, spores), and endotoxin concentrations for coarse particle samples. Examine how these fractions vary in space and time. Identify periods for which there is substantial variation from a constant ratio and relate these to meteorological and plant-growing conditions. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **1. Measurement Evaluation Hypotheses (continued)** | | |
| 1.12 Photoionization and wavelength-specific light absorption are correlated with organic compound concentrations. | These methods have shown good correlations with aggregates of certain organic compounds. There is good evidence that polycyclic aromatic hydrocarbons (PAHs) on particles can be specifically photoionized (Burtscher and Schmidt-Ott, 1986; Wilson et al., 1994), although instrument response is specific to the aerosol composition. Simultaneous continuous and time-integrated PUF/XAD measurements of PAH and other organic substances can be used to evaluate this relationships during the winter of 2000-2001. | Create sums of different particulate organic compound concentrations, including PAHs from the PUF/XAD measurements, and compare these with continuous photoionization methods measured over the same time periods. Apply comparison measures to determine predictability or equivalence. Identify samples for which a general relationship does not apply, and explain them in terms of differences in aerosol composition, environmental conditions, and meteorology. |
| 1.13 Nitrogen dioxide ($NO_2$) determined by standard chemiluminescence methods is an accurate measure of $NO_2$ concentrations for health assessments. | Winer et al. (1974) showed substantial biases in $NO_2$ concentrations reported by compliance-based chemiluminescence monitors, especially in the eastern Los Angeles basin during summer afternoons. These biases have not been evaluated for Fresno conditions, and the presence of several detailed nitrogen measurements, including real $NO_2$, will allow these biases to be assessed. | Apply comparison measures of compliance-based chemiluminescence-method measurements of oxides of nitrogen ($NO_x$, defined as the sum of NO and $NO_2$) with direct $NO_2$ measurements and reactive nitrogen measurements, and $NO_y$ (defined as all products of atmospheric oxidation of $NO_x$ such as $HNO_3$, HONO, $NO_3$ radicals, $N_2O_5$, $HNO_2$, and peroxyacetyl nitrate [PAN]). Identify periods for which $NO_x$, $NO_y$, and $NO_2$ measurements are comparable, and explain aerosol composition and meteorology during these periods. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses** | | |
| 2.1 Short duration (~5 min) spikes in particle measurements represent contributions from nearby (<500 m) emitters. | If this hypothesis is proven, it will provide new methods to determine the zone of influence of specific emitters. These zones of influence need to be known so that the spatial extent for applying emissions reductions can be determined. | Examine time series of shortest time averaged data available from continuous particle size, light scattering, light absorption, mass, and chemical specific measurements. Determine the extent to which integrating nephelometers used at surrounding satellite sites show corresponding short-duration peaks. Create pollution roses (average concentration as a function of wind direction) for these averages and examine them for source directionality. Use time series analyses and frequency distributions to determine the need for more frequent and shorter duration sampling than is current practice. Calculate spatial correlations among sampling spikes of 5-min, 1-hr, 3-hr, 5-hr, 8-hr, and 24-hr measurements of light scattering using CRPAQS[a] nephelometer measurements from satellite sites surrounding the Fresno Supersite. Calculate spatial correlations of 5-min spikes over longer-term averages to evaluate zone of influence of nearby sources. |
| 2.2 The majority of ultrafine particles are from nearby (<500 m), fresh emission sources. | Small particles with aerodynamic diameters <0.1 µm ($PM_{0.1}$ or “ultrafine” particles) are believed to coagulate into larger particles within a short distance of their emissions. If this is true, their numbers should increase in short duration spikes and be consistent with wind directions favoring nearby emitters, such as highly traveled First Street. | From 5-min spikes over longer-term averages of ultrafine particles as small as 0.003 µm measured with the Condensation Particle Counter, estimate the incremental mass contributed by nearby sources. Plot these increments as a function of $PM_{2.5}$ and $PM_{10}$ mass concentrations over 1-hr, 3-hr, 5-hr, 8-hr, and 24-hr periods. Describe the particle climatology for those situations under which nearby sources are a large fraction of CORE site concentrations. Compare ultrafine particle concentrations at the Fresno Supersite with CRPAQS non-urban background site (Angiola) to examine spatial variabilities of ultrafine particles. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses (continued)** | | |
| 2.3 Nearby emitters represent a small (<15%) fraction of $PM_{2.5}$ measured at a community-representative (CORE) sampling site. | If a CORE site is representative, the spikes caused by nearby emitters should be a small proportion of the $PM_{2.5}$ contributed by sources with urban- and regional-scale zones of influence. | From 5-min spikes over longer-term averages, estimate the incremental mass contributed by nearby sources. Plot these increments as a function of $PM_{2.5}$ and $PM_{10}$ mass concentrations over short-term (1-, 3-, 5-, and 8-hr) and 24-hr periods. Describe the particle climatology for those situations under which nearby sources are a large fraction of CORE site concentrations. Determine how much $PM_{2.5}$ and $PM_{10}$ and their chemical components change during the day and from day to day. Examine the day-to-day (24-hr average and diurnal) variations of $PM_{2.5}$ and $PM_{10}$ and their chemical components and PM precursors species. Where available, examine the short-term average mass and chemical concentrations. Plot PM mass, chemical composition, and precursor species concentrations as a function of time for sites collecting data at a frequency greater than once per day (i.e., < 24-hr average) and for sites collecting 24-hr data. Note similarities and differences between: (1) diurnal patterns for $PM_{2.5}$ and $PM_{10}$ and their chemical components and (2) episode and non-episode days for $PM_{2.5}$ and $PM_{10}$ and their chemical components, and assess dominant species in each size fraction by time of day for high vs. low values. Plot spatial pie charts and describe spatial patterns as a function of time of day and over a 24-hr average period (midnight to midnight). Compare episode periods to periods of lower PM concentrations as a function of the time of day and location by site type or site environment. State and justify conclusions concerning: (1) differences between sites, (2) chemical composition as a function of time of day, (3) chemical composition on episode vs. non-episode days, (4) differences between $PM_{2.5}$ and $PM_{10}$ and precursor species as a function of the time of the day and for episode vs. non-episode days. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses (continued)** | | |
| 2.4 Ammonium nitrate reductions are limited by available nitric acid rather than available ammonia in urban areas during all seasons and all hours of the day. | Limited measurements of ammonium nitrate and precursors indicate that this is the case in California's San Joaquin Valley. Existing measurements do not represent short enough sample durations or all seasons of the year to determine the need for ammonia or oxides of nitrogen emission reductions. | Using continuous measurements for particle sulfate and nitrate, gaseous ammonia and nitric acid, temperature, and relative humidity, determine the conditions under which reducing ammonia concentrations will result in reductions of ammonium nitrate or reduce the neutralization of sulfuric acid in Fresno. Apply an aerosol equilibrium model using 1-hr average total ammonia and total nitrate concentrations (Watson et al., 1994; Blanchard et al., 1997). State and justify conclusions about where and when ammonium nitrate concentrations are limited by levels of ammonia or nitrate, with special attention to time of day and time of year. Compare calculated ammonium nitrate concentrations with measurements and evaluate how well the equilibrium model applies in the San Joaquin Valley. Examine model sensitivities to changes in temperature and relative humidity over available sampling intervals. Determine the extent to which conclusions drawn from previous measurements for longer averaging periods and shorter sampling periods are valid under a wider variety of conditions. Plot isopleths of constant ammonium nitrate concentrations as functions of total ammonia and nitrate. Identify the location of typical measurements on these plots and determine the amounts of ammonia or nitrate precursors that must be reduced before significant changes in ammonium nitrate concentrations would be observed. Classify each sample as ammonia or nitrate limited. For each sample, reduce each ammonium sulfate concentration by half, and to zero, examining the changes in ammonium nitrate with these reductions. Determine the extent to which further sulfate reductions might result in increases in ammonium nitrate concentrations. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses (continued)** | | |
| 2.5 Advanced gas and particle organic speciation measurements, coupled with elements, ions, and organic and elemental carbon fractions, consistently and accurately distinguish contributions from different types of suspended dust, secondary sulfate and nitrate, vegetative burning (wood and field burning, and meat cooking), gasoline engine exhaust (cold starts, high emitters, and hot stabilized operations), diesel exhaust, and primary industrial emissions. | Watson et al. (1998c), Schauer et al. (1996), and Schauer and Cass (2000) show the possibility that this may be the case in Denver, CO; Los Angeles, CA; and in wintertime Fresno, CA. A more extensive evaluation of these approaches, combining gas and particle organic and inorganic speciation, is needed. | Using CRPAQS gas and particle organic and inorganic speciation of source and receptor samples, calculate source contribution estimates with the Chemical Mass Balance (CMB) modeling approach. Examine the temporal and spatial variation of source contribution estimates with respect to known spatial and temporal distributions of emissions and determine consistencies and inconsistencies. Plot these contributions for each sample as stacked bar charts and compare the apportionments among sampling sites and sampling periods and for episode and non-episode days. Summarize the magnitudes of source contributions at each sampling site in frequency tables. Conduct sensitivity and randomized data tests to evaluate the magnitudes of uncertainties in apportionments. Compare source contributions among nearby sites for consistencies and inconsistencies. Classify each available sample by its major contributors and determine how many cases of excessive PM concentrations are dominated by a single source type versus those that represent a superposition of sources. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses (continued)** | | |
| 2.6 Commonly measured elements, ions, and organic and elemental carbon fractions consistently and accurately distinguish contributions from suspended dust, secondary sulfate and nitrate, vegetative burning (wood and field burning and meat cooking), gasoline engine exhaust (cold starts, high emitters, and hot stabilized), diesel exhaust, and primary industry contributions. | Watson et al. (1998c) showed that this is the case in Denver by comparing apportionments from conventional measurements that will be available from USEPA's $PM_{2.5}$ speciation networks with more detailed source contribution estimates using detailed organic compounds. This needs to be generalized to another environment such as central California. | Calculate CMB source contributions using commonly measured components without the enhanced organic speciation. Compare source contribution estimates with those derived from the detailed measurements and draw conclusions about which source categories must be combined to minimize colinearity. For these categories, apply the CMB to the chemically speciated measurements taken at the Supersite and nearby sites in the urban area. Use these source contribution estimates to corroborate the zone of influence of different source types examined under previous hypotheses. |
| 2.7 Gasoline engine cold starts and high emitters are the major causes of gasoline-fueled vehicle contributions to $PM_{2.5}$, and they cause gasoline exhaust contributions to exceed diesel exhaust contributions. | Current emission inventories do not explicitly represent contributions from high-emitting vehicles, and inventoried diesel emissions exceed gasoline vehicle emissions. Receptor model and emissions testing evidence from wintertime Denver (Watson et al., 1998c) indicates that cold starts and poorly maintained gasoline vehicles may constitute the bulk of gasoline exhaust emissions. This finding needs to be evaluated in other environments such as central California. If this hypothesis is true, then current inspection and maintenance programs may need to be modified. | Compare the proportional contributions from different source categories with similar proportions in emission inventories, using results from the enhanced and common CMB receptor modeling. Identify discrepancies between receptor contributions and inventory estimates, taking diurnal and seasonal variations and source zones of influence into account. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses (continued)** | | |
| 2.8 Statistical aggregates of concentration indicators for a single year deviate by less than sampling error from a three-year distribution. | Arithmetic averages, seasonal averages, maximum 24-hour concentrations, maximum 1-hour concentrations, and various percentiles may vary substantially from year to year. In particular, the ______ 2000 data set that will be used for Central California air quality planning needs to possess statistical indicators that are similar to previous and subsequent years to produce robust emission reduction strategies. If the hypothesis is true, then shorter-term studies can be used to reliably represent the three years needed to determine compliance with the $PM_{2.5}$ NAAQS. | Calculate statistical indicators and their standard errors for each year and each observable. Apply parametric statistical tests for normal and long-normal distributions to evaluate the significance of year-to-year differences. |
| 2.9 Concentrations in continuously measured carbon fractions can be associated with different proportions of gasoline vehicle exhaust, diesel vehicle exhaust, and wood burning. | Multiwavelength absorption and photoionization methods might provide indicators of different carbon sources, especially when associated with short-duration pulses dominated by a single, nearby plume. Ratios of PAH, carbon, and light absorption measurements may differ for different sources and allow their discrimination at receptors. Testing this hypothesis will make use of source characterization studies currently planned for CRPAQS and in future studies. | Plot ratios of measurements from continuous carbon, PAH photoionization, single- and multiple-wavelength light absorption, and light scattering. Determine how these ratios change when short-term spikes that might originate from nearby sources are seen. Compare ambient ratios with ratios from similar measurements in plumes from carbon emitters such a diesels, gasoline vehicles, wood stoves, and cooking. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses (continued)** | | |
| 2.10 Annual average, seasonal average, and 98th percentile source contributions from fugitive dust, wood burning and cooking, vehicle exhaust, secondary ammonium sulfate, and secondary ammonium nitrate differ by less than ±10% over a three year period. | Daily chemical speciation permits source apportionment receptor modeling. Source contributions can be aggregated as statistical indicators corresponding to $PM_{2.5}$ and $PM_{10}$ concentrations that exceed the NAAQS. | Calculate source contributions to 24-hour average $PM_{2.5}$ from daily speciation monitor measurements using CMB receptor modeling. Calculate statistical indicators for the resulting source contributions and test the statistical significance of year-to-year differences. |
| 2.11 Indicators of particle concentrations (particle size fractions, number, surface area, and major chemical components) are highly correlated; one indicator is equivalent to other indicators that might be specified by future air quality standards. | If all of these indicators are highly correlated, then one will be as good as another in estimating air quality. High correlations also demonstrate cllinearity that make epidemiological relationships to individual variables uninterpretable. | Calculate the correlation coefficients between concentrations for data subsets stratified by time period, aerosol composition, and meteorological variables. Calculate singular values and eigenvectors for this matrix and apply colinearity measures (Henry, 1992) to determine the extent to which regression models using one or more of these variables will be biased. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **2. Aerosol Characterization and Control Strategy Hypotheses (continued)** | | |
| 2.12 Large reductions in $PM_{2.5}$ and $PM_{10}$ mass concentrations in Central California after 1992 are due to the end of a seven-year drought rather than due to emissions reductions. | Alexis et al. (1999) show a downward trend in annual geometric average $PM_{10}$ for the San Joaquin Valley, from a high of 70 $\mu g/m^3$ in 1988 to a low of 44 $\mu g/m^3$ in 1997. There is a precipitous drop between 1992 and 1993 when a seven-year drought ended. Examination of the 3-year Supersite record will permit relationships to meteorology to be examined that can be applied to the long-term data record. | Examine wintertime changes in particle measurements for multi-day episodes between storms. Tabulate the frequency and duration of these episodes from meteorological recorded from 1990 through 2002. Construct weighted wintertime averages for $PM_{2.5}$ mass and chemical composition and compare these for each year of record. |
| **3. Health and Exposure Related Hypotheses** | | |
| 3.1 PM2.5 mass concentration, surface area, and number counts are highly correlated ($R^2$>0.8) and a measure of one is a good indicator of the other two. | It will not be possible to evaluate epidemiological effects of individual indicators if they are always highly correlated. It is more probable that there are emissions and meteorological conditions under which these indicators are correlated and other conditions under which the correlation is low. | Calculate temporal correlation coefficients stratified by particle climatology variables such as time of day, temperature, relative humidity, wind sector, ultrafine particle concentration, and $PM_{2.5}$ concentration. Determine the conditions under which good and poor agreement will be found and the frequency of occurrence of these situations. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **3. Health and Exposure Related Hypotheses (continued)** | | |
| 3.2 The soluble fraction of transition metals, especially those with specific valence states such as Cr(VI) and Fe(III) which are believed to have adverse health effects, is a small fraction (<15%) of total metal concentrations in $PM_{2.5}$. | The soluble fraction of transition metals, especially with specific valence states such as Cr(VI) and Fe(III), is believed to be the portion that causes adverse health effects. This fraction may not be accurately quantified by total elemental analysis methods that are usually applied to aerosol samples. | Plot the concentrations of soluble transition metals and total transition metals (e.g., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg). Compare the ratios of soluble vs. total metals as a function of $PM_{2.5}$ mass. Examine the correlations among the soluble fraction of transition metals, total transition metals, and $PM_{2.5}$ mass. |
| 3.3 Hospital and physician diagnoses of respiratory and cardiovascular ailments are as equally sensitive to changes in $PM_{2.5}$ mass concentrations as they are to other air pollution indicators. | Current air quality standards are based on associations that can be further classified by age, race, and history of previous respiratory ailment. A variety of indicators will be available at Fresno that can be associated with different end-points. | Apply advanced statistical analysis methods to quantify relationships between health end-points and air quality indicators, taking into account inter-correlated co-factors. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **3. Health and Exposure Related Hypotheses (continued)** | | |
| 3.4 Measurements at a community representative sampling site, such as the Fresno Supersite, represent the minimum to which people are exposed in their neighborhoods within an urban area. | Nearby emitters, such as wood stoves and fireplaces or freeways, may add to outdoor exposure levels. These contributions have high spatial gradients that add to the urban-scale concentrations intended for quantification at the Fresno Supersite. | Determine how well the existing PM monitoring sites represent human exposure, maximum PM concentrations, and maximum source impacts by comparing measurements from nearby urban and non-urban sites with those at the Fresno Supersite. Determine spatial homogeneity and zones of representation for specific chemical components such as sulfate, nitrates, ammonium, organic and elemental carbon, and geological material (e.g., Si, Fe). Describe aerosol and precursor species sampling sites and their surroundings. Classify the spatial scale of sites (neighborhood to regional) and site types (agricultural to commercial). Evaluate the adequacy of monitoring networks for representing human exposure, maximum PM concentrations, and source influences. Use statistical analyses (e.g., spatial correlation analysis, cluster analysis, empirical orthogonal functions, and analysis of variance) as well as activities as a function of distance to obtain a better understanding of the relationships between/among sites and their surroundings. Plot long-term and research sites on maps with population distributions and locations of major source types/land-use types. Evaluate adequacy of site coverage and recommend new sites or site classification changes for long-term measurement sites. |
| 3.5 There is a discernible lower threshold for single and combined air quality indicators, below which no relationships with health end-points are statistically significant. | There are some indications that adverse health effects are detectable at levels lower than those specified for current air quality standards. More precise and spatially homogenous measures are needed to determine what this threshold might be for different aerosol characteristics and exposure periods. | Apply advanced statistical analysis methods to quantify relationships between health end-points and air quality indicators, taking account for inter-correlated co-factors. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **3. Health and Exposure Related Hypotheses (continued)** | | |
| 3.6 Different particle chemical characteristics have different and identifiable immuno-enhancing properties that affect the symptom onset and severity of short-term reductions in lung function, asthma attacks, and cardiovascular ailments. | Elevated levels of endotoxins, bioaerosols, may aggravate asthma in children PAH, or diesel exhaust to a greater extent than it is by number, surface, or volume concentrations (Gielen et al., 1997). | Compare measured responses in test subjects with similar and different histories of exposure to air quality. Relate these responses to differences in air quality indicators associated with the onset and severity of distress. |
| 3.7 Coarse particle concentrations and biologically active components show relationships to health end-points. | Since $PM_{2.5}$ is often a large fraction of $PM_{10}$, their levels are highly correlated. Coarse particles are not as highly correlated with $PM_{2.5}$ and they may have different and detectable harmful effects. | Apply advanced statistical analysis methods to quantify relationships between health end-points and air quality indicators, taking into account inter-correlated co-factors. |
| 3.8 Animal (rat) exposures to different combinations of concentrated amounts of particle size, surface area, chemical, and mass characteristics result in similar indications of respiratory and cardiovascular distress. | Aerosol concentrators (Sioutas et al., 1995) are used to vary the exposure of test subjects to a variety of aerosol compositions and levels (Pinkerton et al., 1996). Reactions are often different from laboratory-generated aerosols. | Compare physiological changes between rats exposed to different compositions but similar $PM_{2.5}$ mass concentrations. Identify most active agents in causing changes in cardiopulmonary response. |

**Table 3-1.** (Continued)

| Hypotheses | Background | Data Analysis, Methods, and Data Used |
|---|---|---|
| **3. Health and Exposure Related Hypotheses (continued)** | | |
| 3.9 Particles found in healthy human lungs have characteristics similar to those found in urban air over long periods of exposure. | Examination of autopsied lungs from healthy Fresno residents after accidental death shows particulate accumulations (personal communication, Dr. Kent Pinkerton, UC Davis). These particles, their location of deposit, and potential adverse affects need to be related to the actual particle characteristics that influence transfer and deposition in human airways. | Compare characteristics between autopsied human lung and ambient particles. |

[a] CRPAQS: California Regional Particulate Air Quality Study.

# 4. DATA VALIDATION AND USABILITY

## 4.1 Data Review and Validation Process

Continuous data are uploaded and examined daily at DRI's laboratory to ensure data are acquired within the specified range. Corrective action is taken if errors or anomalies are found. Detailed information on data processing and validation is given in the specific SOPs listed in Table 2-1.

## 4.2 Data Validation Requirements

The data validation procedures for the data acquired at the Fresno Supersite is discussed in Section 2.10 and in the appropriate SOPs. Field and lab validation flags applied at each level of the data validation process will be part of the final data base to establish the validity of each measurement.

## 4.3 Reconciliation with User Requirements

Table 3-1 summarizes the hypotheses to be tested at the Fresno Supersite. These hypotheses take advantage of the longer than three-year record that will be available. $PM_{2.5}$ and $PM_{10}$ NAAQS require at least a three-year record to determine attainment. While the CRPAQS monitoring and data analysis will provide detailed understanding of source contributions, meteorology, and atmospheric chemistry for one year and several multi-day episodes, they cannot provide the multi-year perspective needed to evaluate compliance with current NAAQS. The application and evaluation of advanced, continuous measurement technology over this extended period will provide knowledge needed by regulators when they consider particle health indicators and candidates for future Federal Reference Methods.

Measurement methods evaluation hypotheses (1.1 to 1.12) are based on evidence that there is climatology for the validity and comparability of measurements acquired by the same instruments. Meteorological conditions, source contributions, and aerosol chemical composition in central California are known to change substantially over a year and even between different parts of the day. Long-term measurements for a year or more are needed to evaluate the feasibility, practicality, and equivalence of different measurement techniques. Evaluation of these measurements will determine where and when less complex, more convenient, or more widely available measurements can be used in place of the advanced methods implemented at the Supersite.

Several empirical and statistical measures are applied to evaluate predictability and equivalence (Mathai et al., 1990). Linear regression is most commonly used and is the requirement for federal equivalent method (FEM) relationships with FRMs. Regression slopes and intercepts with effective variance weighting (Watson et al., 1984) for each set of paired measurements are evaluated with their standard errors. The effective variance weighting includes the precisions of both variables in the calculation and bases the standard errors on them. When the slope equals unity within three standard errors, when the intercept does not significantly differ from zero within three standard errors, and when the correlation coefficient also exceeds 0.9, the measurements are considered comparable. When the correlation coefficient exceeds 0.9 but the slope and intercept criteria are not met, the dependent variable is predictable from the independent variable.

Other comparison measures include average ratios and standard deviations, ratios of averages, and the distribution of differences (X minus Y) for $<1\sigma$, $1\sigma$ to $2\sigma$, $2\sigma$ to $3\sigma$, and $>3\sigma$ precision intervals. These measures indicate the extent to which long-term averages are more or less equivalent than individual values and whether or not the majority of differences are within stated uncertainty intervals.

Emissions reduction plans need to determine source contributions to primary particles and the limiting precursors for secondary particles. Conclusions drawn from special, short-term studies need to be generalized over at least the NAAQS three-year period, and over a longer period (~10 years) during which control strategies are implemented. Hypotheses 2.1 to 2.12 examine how well conclusions from special studies such as CRPAQS stand up during subsequent years. They also place the Supersite monitoring period within a long-term record by comparison with historical $PM_{2.5}$, $PM_{10}$, light scattering, coefficient of haze, and meteorological measurements from 1990 onward.

For example, different measurements vary over the course of a day. Variations in absolute and relative concentrations may be related to different emissions, vertical mixing, and horizontal transport that change throughout the day. Mass indicators may exhibit maxima at both midday and late evening. The compositional data may show that the midday maximum coincides with the nitrate maximum while the late evening peak coincides with increased black carbon and PAHs. The PAH to BC ratio may change throughout the day, with a substantial decrease in the afternoon. Since PAH is highly reactive, especially in sunlight, this may indicate an aged rather than fresh source of black carbon. These variations have implications for understanding sources and interpreting health data.

Mauderly et al. (1998) identify several indicators for adverse health effects: 1) PM mass; 2) PM surface area; 3) PM number (i.e., ultrafine concentration); 4) transition metals (especially the soluble fraction); 5) acids (especially sulfuric acid); 6) organic compounds; 7) bioaerosols; 8) sulfate and nitrate compounds (typically neutralized in whole or in part by ammonia or sodium); 9) peroxides and other free radicals that accompany and help to form PM; 10) soot (elemental carbon and associated PAH); and 11) correlated co-factors (other pollutants and variation in meteorology). Long-term data records of these variables are needed to examine relationships to health end-points and to determine the range of concentrations to which humans might be exposed. Owing to the complexity and expense of measurement technology, such long-term records are lacking.

Measurements at the Fresno Supersite can be acquired to support health studies related to all but category 9, peroxides and free radicals. Although sulfuric acid (category 5) could be quantified, there is sufficient evidence that available sulfate anions are completely neutralized by ammonia and alkaline species in Central California. Nitric acid could be related to health endpoints, and attempts at its continuous measurement are needed.

Hypotheses 3.1 through 3.9 in Table 3-1 require measurements from other studies related to human respiratory health in the Fresno area and Central California. The Fresno Asthmatic Children's Environment Study (FACES) sponsored by ARB at UC Berkeley will test panels of children for four years, with a variety of lung function tests and clinical examinations made throughout the period. Indoor and outdoor samples will be acquired and personal exposure monitors will be used to develop long-term exposure estimates. These will be correlated with Supersite measurements.

The Health Effects of Concentrated Ambient Particles from the Central Valley of California sponsored by U.S. EPA at UC Davis will expose rats to different levels of Central Valley aerosol, then sacrifice the rats and examine damage to their respiratory system. Portable particle concentrators for ultrafine, fine, and coarse fractions will be located near the Supersite to take advantage of its measurements. Extremes will be sought in particle number, composition, surface area, and other variables by selecting times of day and times of the year where contrasts are largest. Real-time access to Supersite measurements will be used to schedule experiments.

The Indoor Exposure from Ambient Concentrations Study sponsored by U.S. DOE at Lawrence Berkeley National Laboratory will develop a mechanistic model for infiltration of outside air into buildings. The model requires a detailed understanding of particle size and chemical characteristics, infiltration characteristics of various buildings, resident behavior, and outdoor meteorological conditions. Indoor and outdoor measurements are taken for a year to represent seasonal variations and to test the model. Supersite measurements will be used for detailed characterization and to extrapolate limited and integrated indoor/outdoor measurements to a range of aerosol characteristics and weather conditions.

For QA purposes, substantial comparisons among measurements will be made to determine their predictability, comparability, and equivalence. Although the different observables measured are quite diverse, it is possible that they may be highly correlated owing to their quantification of related particle properties or to large fluctuations caused by emissions and meteorology. Relationships between variables will depend on the composition of the aerosol as well as meteorological conditions. Measures of predictability, comparability, and equivalence are applied to data sets stratified by aerosol composition and season. Predictability requires a consistent and reliable relationship between measurements, even if they are of different quantities. Light scattering or light absorption measurements are examples of continuously measured particle properties from which $PM_{2.5}$ concentrations might be predicted. Comparability can be established between monitors that ostensibly measure the same observable, but with different principles. $PM_{2.5}$ mass acquired from the BAM, TEOM, FRM, dichot, and speciation monitors are expected to be comparable, and if they are shown to be so, they can be used interchangeably in data analysis. Equivalence is a regulatory term that allows a method to be designated as FEM applicable to compliance monitoring. Equivalence is more demanding than predictability or comparability in that it requires demonstration of comparability within high tolerances over a wide range of concentration loadings and measurement environments.

As discussed in Section 1.3.1, the project database will be available to investigators within three months of the previous calendar quarter, and the laboratory analysis database will be available within six months after the previous calendar quarter. Internet-based data management and delivery systems are being developed at the following web site to facilitate data distribution to all interested users:

http://www.arb.ca.gov/airways/crpaqs/lookups.htm

At project completion, Fresno Supersite data will be compiled onto a CD-ROM with all related project reports and publications. The available historical database of gas, particulate, and meteorological measurements for the Fresno Supersite will also be included on the CD. These data are also submitted to EPA’s Supersite database and to applicable NARSTO data archives.

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