

FRESNO SUPERSITE INSTALLATION, OPERATION, AND DATA ANALYSIS

**A Research Proposal
for the
Cooperative Institute for Atmospheric Sciences and Terrestrial Applications (CIASTA)**

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1. INTRODUCTION

This proposal presents the rationale, description, and statement of work for an air quality Supersite to be operated at the Fresno First Street monitoring site in California's Central Valley. This is one of five to seven Supersites that are to be established in urban areas within the United States by the U.S. Environmental Protection Agency (EPA) to better understand the measurement, sources, and health effects of suspended particulate matter (PM). The information derived from these Supersites is expected to complement information from PM_{2.5} and PM₁₀ (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} monitoring network (Watson et al., 1997a). The Fresno Supersite will be designed and operated to provide data for studies related to control strategy development and health assessment in central California. Relevant data from other measurement programs will be integrated into the Fresno Supersite data base to support data analyses that test specific hypotheses.

1.1 Background

National Ambient Air Quality Standards (NAAQS) apply to PM_{2.5} and PM₁₀ mass concentrations and are described as follows (U.S. EPA, 1997):

- Twenty-four-hour average PM_{2.5} not to exceed 65 µg/m³ for a three-year average of annual 98th percentiles at any community-representative site in a monitoring area.
- Three-year annual-average PM_{2.5} not to exceed 15 µg/m³ concentrations from a single community-representative site or the spatial average of eligible community-representative sites in a monitoring area.
- Twenty-four-hour average PM₁₀ not to exceed 150 µg/m³ for a three-year average of annual 99th percentiles at any site in a monitoring area.
- Three-year average PM₁₀ not to exceed 50 µg/m³ for three annual-average concentrations at any site in a monitoring area.

The statistical form of these standards and the CORE monitoring sites used for PM_{2.5} and PM₁₀ compliance give less emphasis to rare occurrences of high concentrations. The three-year averaging of 98th and 99th percentile concentrations attenuates the influence of an unusual event during a year. The form of these standards requires long-term monitoring to determine compliance. PM_{2.5} and PM₁₀ mass concentrations are considered to be indicators of adverse health, but are not necessarily the direct causes of adverse effects. It remains to be established how good these indicators are, and whether or not other practical indicators might better represent human exposure and reaction to harmful substances.

EPA's Supersites program (U.S. EPA, 1998) intends to operate research-grade air monitoring stations in several urban areas within the United States to improve understanding of measurement technologies, source contributions and control strategies, and effects of

suspended particles on health. Guiding principles (U.S. EPA, 1998) for Supersites are that they: (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 five to seven Supersites established nationwide; (3) are integrated into larger monitoring networks and research studies; and (4) leverage EPA investments with contributions from other agencies.

Albritton and Greenbaum (1998) summarize the types of studies and observables that are feasible and desirable for application at Supersites. They specify observables, monitoring periods, sample durations, measurement frequencies, and site types that are related to source apportionment, control strategy evaluation, and health. These are consistent with several, but not all, of the measurement, data analysis, and modeling activities planned for the California Regional PM_{2.5}/PM₁₀ Air Quality Study (CRPAQS, Watson et al., 1998a, <http://sparc2.baaqmd.gov/centralca/publications.htm>), an \$11.5M field study from December 1999 through January 2001. CRPAQS is intended to support the development of State Implementation Plans (SIPs). CRPAQS offers synergistic opportunities to accomplish control strategy development as well as methods evaluation and health objectives with the initiation of an EPA Supersite at Fresno.

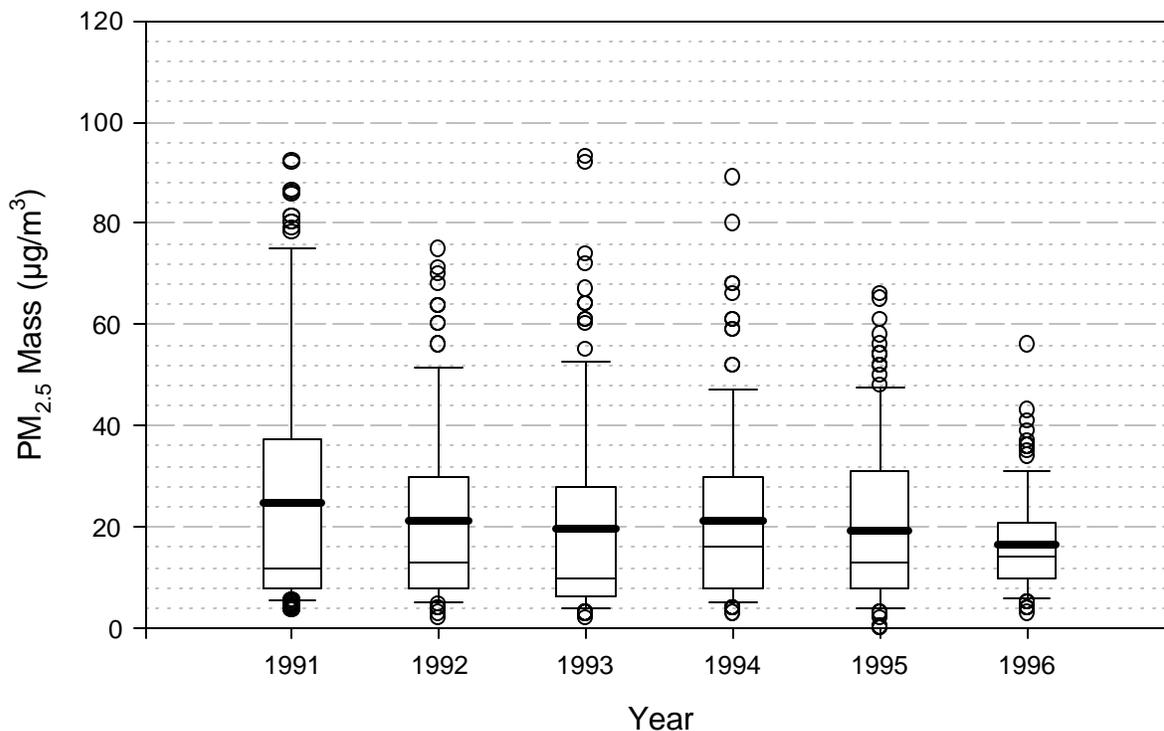
1.2 Fresno First Street Site

The California Air Resources Board's (ARB) Fresno First Street site is located at 3425 First St., approximately 1 km north of the downtown commercial district. First Street is a four-lane artery with moderate traffic levels. Commercial establishments, office buildings, churches, and schools are located north and south of the monitor. Medium-density single-family homes and some apartments are located in the blocks to the east and west of First Street.

Limited PM_{2.5} measurements from central California indicate that the annual 15 µg/m³ standard will probably be exceeded in several populated areas, especially in the San Joaquin Valley. Figure 1-1 shows the PM_{2.5} levels measured at the First Street site for a six-year period, indicating that this site may achieve annual average PM_{2.5} levels in excess of 15 µg/m³ annual average over a multi-year period. Figure 1-1 also shows substantial variability in mass concentrations over a year-long period. The highest PM_{2.5} concentrations are typically found during winter and fall, with the lowest concentrations occurring during spring and summer (Watson et al., 1998a).

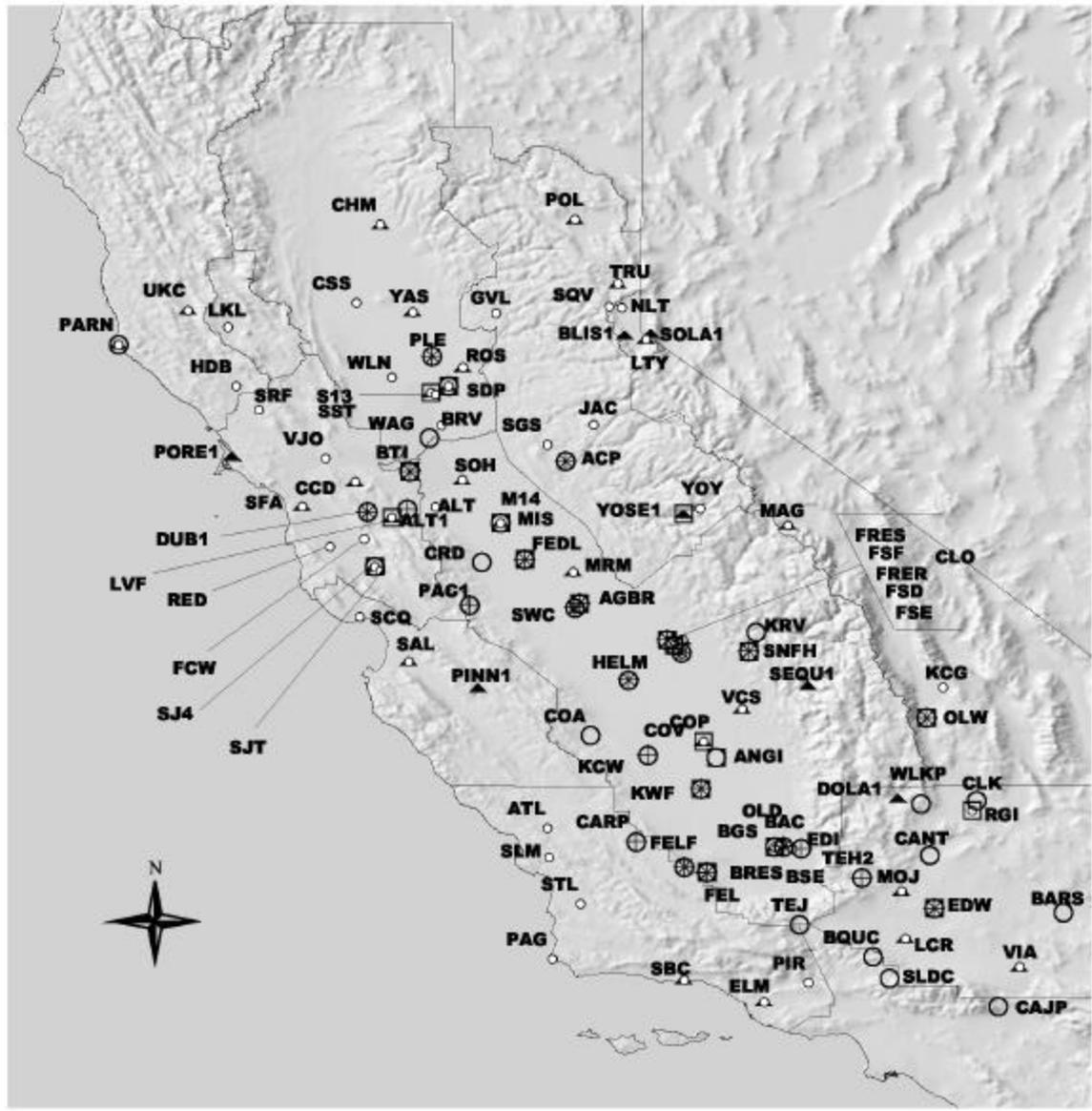
While a few PM_{2.5} concentrations have exceeded 65 µg/m³ during winter, the frequency of these events is not sufficient, nor are the exceedances so consistent from year to year, that the 24-hour standard is likely to be exceeded. The existing record is based on sixth-day sampling, however, and a higher sampling frequency may reveal a larger number of these high concentrations. PM_{2.5} constitutes ~80% of PM₁₀ during winter and ~50% of PM₁₀ during the rest of the year. The annual PM_{2.5} standard is most likely to be exceeded in several parts of central California, and emissions reductions that lower PM_{2.5} concentrations will also lower many excessive PM₁₀ levels.

Figure 1-1. Annual average and maximum PM_{2.5} from 1991 to 1996 at the Fresno First Street site for sixth-day dichotomous sampling. (Circle=extreme value, dark bar=arithmetic average, light bar=median, ends of box=25th &75th percentiles, whiskers=5th and 95th percentiles.)

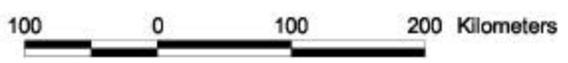


The Fresno Metropolitan Planning Area (MPA) contains more than 500,000 people, and two nearby PM_{2.5} sites will be operated within the urbanized area at 4706 E Drummond St. and 908 N. Villa Ave. as part of the national network. In addition to these sites, other PM_{2.5} monitors will be operated within and around the Fresno metropolitan area as part of the CRPAQS. Figure 1-2 shows the locations of these sites and their intended measurements that will be used to evaluate spatial and temporal similarities and differences with respect to the Fresno First Street CORE site. The locations in Figure 1-2 provide measurements that represent urban, agricultural, industrial, and background PM_{2.5} concentrations and composition. This larger data base will allow ample opportunity to evaluate measurements at Fresno First Street within the context of PM_{2.5} sources with continental, regional, urban, and neighborhood scale zones of influence. CRPAQS (Watson et al., 1998a) will also operate an extensive network of gas, PM₁₀, and surface- and upper-air meteorological monitors. These data will be further supplemented by measurements from ARB and air quality district monitoring sites as well as more than 400 meteorological stations from various networks in central California. These data will be unified by the ARB, and relevant portions will be combined with those from the Fresno Supersite to test hypotheses.

Figure 1-2. PM_{2.5} mass, chemical, and light scattering measurements at CRPAQS monitoring locations (from Watson et al., 1998a).



- × PM_{2.5} minivol with quartz-NaCl & IC, AC, AA & TOR
- + PM_{2.5} minivol with Teflon/citric acid & grav, XRF, AC
- Light Scattering/PM_{2.5} mass (nephelometer)
- PM_{2.5} minivol-Teflon coated glass fiber & GC/MS
- PM_{2.5} FRM single with Teflon & grav, XRF on 10 days
- ▲ PM_{2.5} EPA or IMPROVE speciation sampler
- Air Basins



1.3 Objectives and Hypotheses

General objectives of the Supersite program are:

- Test and evaluate non-routine monitoring methods, with the intent to establish their comparability with existing methods and determine their applicability to SIP development, exposure assessment, and health impact determination.
- Acquire data bases that can be used to evaluate relationships between aerosol properties, co-factors, and observed health end-points.
- Support regulatory agencies in the development of emissions reduction implementation plans that cost-effectively reduce particle concentrations.

Specific hypotheses are presented under each objective that will be tested using data acquired specifically from Fresno Supersite measurements and other studies.

1.3.1 Method Testing and Evaluation

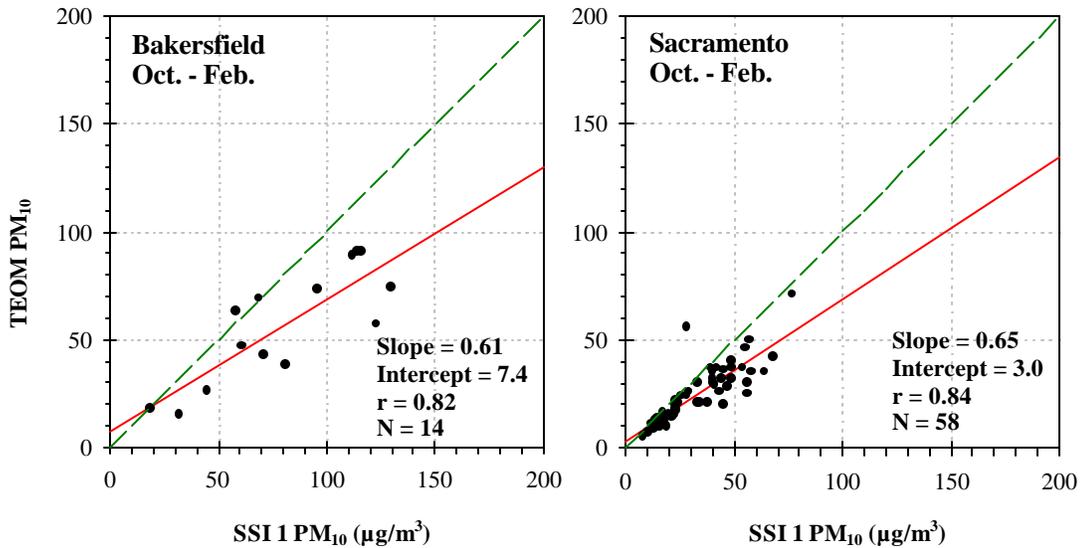
Methods testing and evaluation at the Fresno Supersite is based on evidence that there is a climatology for the validity and comparability of measurements acquired by the same instrument. Meteorological conditions, source contributions, and aerosol chemical composition in central California are known to change substantially over a year and even between different parts of the day (Chow et al., 1992, 1993a, 1994a, 1994b, 1996, 1998, 1999). Long-term measurements for a year or more are needed to evaluate the feasibility, practicality, and equivalence of measurements. 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. For example, Figure 1-3 compares PM_{10} mass from a TEOM and a filter sampler at two central California sites during fall/winter and spring/summer months. During spring/summer, the measurements are comparable and one can be substituted for another. During fall/winter, however, the heated (50 °C) TEOM evaporates volatile ammonium nitrate and some carbon from woodburning contributions, resulting in a much lower measured PM_{10} concentration than actual atmospheric concentrations.

Specific hypotheses about measurement methods to be tested by Supersite measurements are:

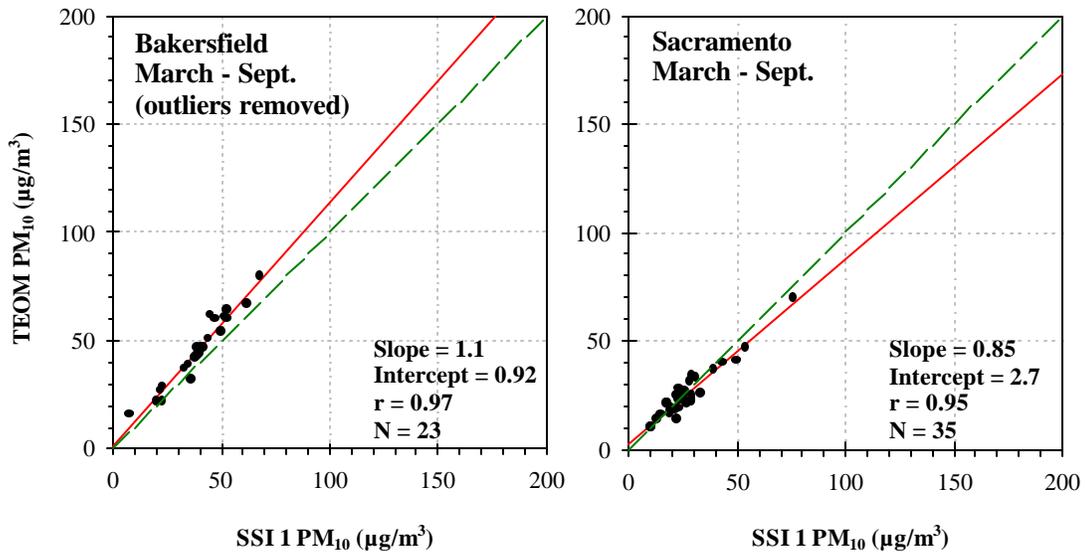
1. **Mass and chemical (elements, ions, and carbon) measurements from routine filter samplers with a Teflon filter (from FRM or saturation samplers) represent actual $PM_{2.5}$ mass within the spatial zone of representation of a CORE site.** CORE sites, such as Fresno First Street, that meet $PM_{2.5}$ siting criteria (Watson et al., 1997a), 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.

Figure 1-3. Collocated comparison of 24-hour-averaged TEOM and high-volume, size-selective-inlet (SSI) PM₁₀ during winter and summer at the Bakersfield and Sacramento sites in central California between 1988 and 1993.

**Collocated Comparison
SSI 1 and TEOM (Winter/Fall)**



**Collocated Comparison
SSI 1 and TEOM (Summer/Spring)**



2. **Elemental analysis of Teflon filters under a helium atmosphere 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. The potential advantage of this modification is that volatile species, such as ammonium nitrate, may experience less evaporation than under vacuum. 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 volatiles regardless of the surrounding atmosphere.
3. **Carbon gases 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 backup filter absorption was smaller when a quartz fiber denuder preceded the filter pack (Chow et al., 1993b). 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.
4. **Volatilized particulate nitrate is a minor (<10%) part of particle nitrate during winter, but a major (>50%) fraction of particle nitrate during other seasons.** Substantial savings in monitoring costs can be attained if it can be shown that nitrate is accurately sampled with a single filter during cool winter and fall months when nitrate levels are high.
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 mass under certain conditions.
6. **Most non-winter particulate nitrate is lost during warm afternoons, including that which is sampled as particles during night and morning when temperatures are lower.** While equilibrium theory indicates that this should be true, time resolution in particle nitrate and gaseous precursor measurements has been insufficient to evaluate it.
7. **PM_{2.5} 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 PM_{2.5} surrogate measurements taken at other sites and lessen the need for extensive collocated measurements.

While not explicitly stated nor analyzed as hypotheses, method testing and evaluation will also include the development and refinement of procedures for making research measurements over long time periods with minimal operator intervention. These operational findings will directly serve the needs of California regulatory agencies in the conduct of CRPAQS measurements. They will also serve the broader needs of national PM_{2.5} networks that may incorporate some of these methods as Special Purpose Monitors for source assessment in other areas.

1.3.2 Emissions Reduction Plans

Emissions reduction plans need to determine source contributions to primary particles and the limiting precursors for secondary particles. Specific hypotheses to be tested are:

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.
2. **Nearby emitters represent a small (<15%) fraction of PM_{2.5} measured at a CORE sampling site.** If a CORE site is properly sited, the spikes caused by nearby emitters should be a small proportion of the PM_{2.5} contributed by sources with urban and regional zones of influence.
3. **The majority of ultrafine particles are from nearby (<500 m), fresh emissions 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.
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 indicates that this is the case. Existing measurements do not represent short enough sample durations or all seasons of the year to determine the need for ammonia or oxide of nitrogen emission reductions.
5. **Advanced gas and particle organic speciation measurements, coupled with elements, ions, and organic and elemental carbon fractions, consistently and accurately distinguish contributions from: (a) different types of suspended dust; (b) secondary sulfate and nitrate; (c) wood combustion; (d) field burning; (e) meat cooking; (f) gasoline engine exhaust from cold starts, high emitters, and hot stabilized operations; (g) diesel exhaust; and (h) primary industrial emissions.** Watson et al. (1998b), Schauer et al. (1996), and Schauer and Cass (1998) show the possibility that this may be the case in Denver, Los Angeles, and

in wintertime Fresno. A more extensive evaluation of these approaches, combining gas and particle organic and inorganic speciation, is needed.

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 combustion 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 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.
7. **Gasoline-engine cold starts and high emitters are the major sources of gasoline-fueled vehicle contributions to PM_{2.5}, and they cause gasoline exhaust contributions to exceed diesel exhaust contributions.** Current emissions 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.

1.3.3 Health Relationships

Mauderly et al. (1998) identify the following potential indicators for adverse health effects: (1) PM mass; (2) PM surface area; (3) PM number (i.e., ultrafine concentration); (4) transition metals (especially soluble fraction); (5) acids (especially sulfuric acid); (6) organic compounds; (7) biogenic particles; (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.

Practical measurements at the Fresno Supersite can be acquired for more than one year to support health studies related to categories 1, 2, 3, 4, 7, 8, 10, and 11. Although sulfuric and other acids (category 5) could be quantified, there is sufficient evidence from previous studies to demonstrate that available anions are completely neutralized by ammonia and alkaline species in central California. Organic composition (category 6) will be quantified by CRPAQS during summer and winter, but these measurements are not of sufficient duration for direct relation to health end-points. Peroxides and free radicals (category 9) will also be quantified for a brief period as part of CRPAQS at a nearby non-urban location, but these will not be of sufficient duration for epidemiological or exposure studies. Biogenics can be practically quantified in terms of scanning electron

microscopic analysis to identify and quantify pollens and spores that coexist with other particles of vegetative origin.

Specific health-related hypotheses that can be tested with Supersite measurements are:

- 1. PM_{2.5} 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.
- 2. Soluble transition metals are a small fraction (<15%) of total metal concentrations in PM_{2.5}.** The soluble fraction of transition metals, especially with specific valence states, is believed to be the portion that causes health. This fraction may not be accurately quantified by total elemental analysis methods that are usually applied to aerosol samples.
- 3. Measurements at a CORE sampling site represent the minimum to which people are exposed in their neighborhoods within an urban area.** Nearby emitters, such as wood stoves and fireplaces, may add to outdoor exposure levels. These contributions have high spatial gradients that add to the urban-scale concentrations intended for quantification at CORE sites.
- 4. The ammonium nitrate portion of PM_{2.5} shows the same epidemiological relationships to health end-points as PM_{2.5} mass.** Long-time records of chemical-specific components in suspended particles have not been available to correlate with health end-points. The Fresno site experiences high and variable nitrate levels as a major component of PM_{2.5}.
- 5. Ultrafine particle concentration, PM₁₀ mass, and coarse particle mass relationships to health indicators are more significant than PM_{2.5} relationships.** Long time series of different size fractions have not been available for establishing epidemiological relationships. While ultrafine particles may show toxicological effects in laboratory studies, their presumed short lifetime and contributions from nearby sources may make them a poor indicator of population exposure. Similarly, coarse particle concentrations may show larger spatial gradients that cause measurements at a single CORE site to be a less effective indicator of population exposure.

1.4 Fresno Supersite Measurements

Table 1-1 summarizes measurements to be made at the Fresno Supersite as part of EPA Supersite program, as part of CRPAQS, and as part of ARB's statewide air quality monitoring network. While Table 1-1 specifies only those measurements acquired at the Fresno First Street location, data analysis to test hypotheses will require air quality,

Table 1-1. Fresno Supersite measurement specifications.^a

Observable and Method	Operator	Period	Avg Time	Frequency
Gases				
NO/NO _x (TEI 42 Chemiluminescence)	ARB	_____ onward	1-hr	daily
Ozone (API 400 UV Absorption)	ARB	_____ onward	1-hr	daily
Carbon Monoxide (Dasibi 3008 Infrared Absorption)	ARB	_____ onward	1-hr	daily
Non-Methane Hydrocarbons	ARB	_____ onward	1-hr	daily
NO _y /HNO ₃ (High sensitivity TEI 42 or Ecophysics chemiluminescent monitor with external converters, denuders & sequencers)	DRI/ARB	10/1/99-3/31/01	5-min	daily
Ammonia (TEI 17C or API 200D high sensitivity with NO _x scrubbers and oxidizers)	DRI/ARB	10/1/99-3/31/01	5-min	daily
Filter Mass and Chemistry				
TSP Mass (Hivol w/ quartz filter) and Lead	ARB	_____ onward	24-hr	12th day
PM ₁₀ Mass, Sulfate, Nitrate, Chloride, Ammonium Carbon (Hivol SSI w/ quartz filter)	ARB	_____ onward	24-hr	6th day
PM ₁₀ and PM _{2.5} Mass, Elements (collocated dichotomous sampler with Teflon filter)	ARB	_____ onward	24-hr	6th day
PM _{2.5} mass (collocated Andersen sequential FRM w/ Teflon filter)	ARB	1/1/99-present	24-hr	daily for primary sampler and 3rd day for collocated sampler
Toxic (metals, chromium VI, aldehydes) (Xontec 920)	ARB	_____ onward	24-hr	12th day
PM _{2.5} mass, light absorption, elements, and ions (additional sequential FRM w/ Teflon filters)	DRI/ARB	6/1/99-5/31/00	24-hr	6th day
PM _{2.5} mass, elements, ions, carbon, nitric acid, ammonia (Five channel Met One SASS speciation sampler w/ denuders and backup filters)	DRI/ARB	6/1/99-5/31/00	24-hr	6th day
PM _{2.5} mass, elements, ions, carbon (Two channel Met One SASS speciation sampler)	DRI/ARB	6/1/00 onward	24-hr	6th day
PM ₁₀ single particles Elements (Airmetrics MiniVol w/ Nuclepore filter for microscopic analysis)	DRI/ARB	6/1/99-5/31/00	24-hr	6th day
PM _{2.5} mass, elements, ions, carbon (Two channel sequential filter sampler w/ denuders and backup filters; mass on all, chemistry on 100 samples)	CRPAQS	12/1/99-1/31/01	24-hr	daily

Table 1-1. (continued)

Observable and Method	Operator	Period	Avg Time	Frequency
Filter Mass and Chemistry (continued)				
PM _{2.5} mass, elements, ions, carbon (Two channel sequential filter sampler w/ denuders and backup filters; on 15 episode days)	CRPAQS	forecasted 15 episode days between 12/1/00 and 1/31/01	3-hr, 5-hr, and 8-hr samples	daily, 5 times/day during 15 pollution episode days
PM ₁₀ mass, elements, ions, carbon, and fugitive dust markers (Methods to be specified by CRPAQS Fugitive Dust Characterization Study)	CRPAQS	9/15/00-11/15/00	24-hr	daily sampling with selected characterization
Continuous Particle Mass and Chemistry				
PM _{2.5} mass (heated TEOM)	DRI/ARB	6/1/99-3/31/01	1-hr	daily
PM ₁₀ mass (heated TEOM)	DRI/ARB	6/1/99-3/31/01	1-hr	daily
PM _{2.5} mass (ambient BAM)	DRI/ARB	4/1/99-3/31/01	1-hr	daily
PM ₁₀ mass (ambient BAM)	DRI/ARB	4/1/99-3/31/01	1-hr	daily
PM _{2.5} nitrate, sulfate, and carbon (ADI Flash Volatilization with TEI NO _x , SO ₂ , and NDIR Detectors)	ADI/DRI/ARB	10/1/99-3/31/01	10-min	daily
PM _{2.5} organic and elemental carbon (R&P or Met One In Situ Analyzer)	ADI/DRI/ARB	4/1/99-3/31/01	30-min	daily
Individual particle size and chemistry (UC Riverside Time of Flight spectrometer)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	5-min	daily for Episodes
Organic Gases and Particles				
Toxic hydrocarbons (Xontec 910 canister sampler)	ARB	_____ onward	24-hr	12th day
Carbonyls (Xontec 925 DNPH sampler)	ARB	_____ onward	24-hr summer 4 per day	12th day 3rd day
Light hydrocarbons (canister & GC/FID)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	4 of 5 to 8-hr	daily for Episodes
Heavy hydrocarbons (TENAX & GC/TSD/FID)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	4 of 5 to 8-hr	daily for Episodes
Aldehydes (DNPH & HPLC)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	4 of 5 to 8-hr	daily for Episodes
PM _{2.5} organic compounds (Teflon-coated glass fiber/PUF/XAD & GCMS)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	4 of 5 to 8-hr	daily for Episodes

Table 1-1. (continued)

Observable and Method	Operator	Period	Avg Time	Frequency
Organic Gases and Particles (continued)				
PM _{2.5} organic compounds (Teflon-coated glass fiber/PUF/XAD & GCMS)	CRPAQS	6/1/00-8/31/00	24-hr	6th day
PM _{2.5} organic compounds (Minivol w/ Teflon-coated glass fiber & GCMS)	CRPAQS	1/1/00-12/31/00	24-hr, aggregated for 1 year	6th day
Continuous Light Scattering				
Light scattering (OPTEC NGN3 heated nephelometer)	DRI/ARB	4/1/99-3/31/01	5-min	daily
Light scattering (OPTEC NGN2 ambient temperature nephelometer)	DRI/ARB	4/1/99-3/31/01	5-min	daily
Light scattering (Greentek or DUSTTRACK photometer)	DRI/ARB	4/1/99-3/31/01	5-min	daily
Light scattering (Radiance M903 heated nephelometer)	DRI/ARB	6/1/99-3/31/01	5-min	daily
Light Absorption				
Coefficient of Haze (AIS1 paper tape sampler)	ARB	_____ onward	2-hr	daily
Light absorption/elemental carbon (aethalometer)	DRI/ARB	6/1/99-3/31/01	5-min	daily
Light absorption/elemental carbon (7-wavelength aethalometer)	DRI/ARB	12/1/99-3/31/00	30-min	daily
Particle Sizes				
0.003-0.2 µm size distribution (TSI 3025A Ultrafine Condensation Particle Counter) ^b	ADI/DRI/ARB	10/1/99-3/31/01	5-min	daily
0.3-30 µm size distribution (Grimm Technologies Optical Particle Counter)	ADI/DRI/ARB	10/1/99-3/31/01	5-min	daily
Mass and ion size distribution (MOUDI 0.054 to 15 µm in 9 size fractions with Teflon & IC, AC)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	5-hr to 8-hr	daily for Episodes
Carbon size distribution (MOUDI 0.054 to 15 µm in 9 size fractions with aluminum & TOR)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	5-hr to 8-hr	daily for Episodes
Meteorology				
Wind Speed/Direction (High sensitivity wind vane and anemometer)	ARB	4/1/99-3/31/01	5-min	daily
Temperature (High accuracy sensor)	DRI/ARB	4/1/99-3/31/01	5-min	daily

Table 1-1. (continued)

Observable and Method	Operator	Period	Avg Time	Frequency
Meteorology (continued)				
Relative Humidity (High accuracy sensor)	DRI/ARB	4/1/99-3/31/01	5-min	daily
Solar Radiation	DRI/ARB	4/1/99-3/31/01	5-min	daily
Data Acquisition and Processing				
On-site instrument polling computer accessible by dial-up modem	DRI	4/1/99-3/31/01	as specified	daily

^a This table includes measurements to be acquired at the Fresno First Street location. Gas, particle, and meteorological measurements from nearby sites that will be used for hypothesis testing are described by Watson et al. (1998a). Health end-point data will be acquired by existing and planned studies described in Section 3.

^b May be integrated with scanning mobility particle sizer (0.005 to 1.0 μm).

meteorological, and emissions measurements from other sites within and around the Fresno metropolitan area. Watson et al. (1998a) describes the additional measurements that will be available during the Fresno Supersite monitoring period. These measurements will be obtained and integrated into the Supersite data base where needed.

Table 1-1 shows a phase-in period for more complex measurements that is consistent with the schedule for planned health studies and for CRPAQS monitoring. Readily available and tested instruments are installed and operation begins immediately. More complex measurements are phased in after the results of pilot studies conducted during January 1999 at the ARB Bakersfield site have been analyzed. This phase-in will also provide for evaluation of information obtained from measurement comparisons made at the Atlanta Supersite.

Hypotheses relating to health effects and personal exposure will also require measurement and analysis of health end-points concurrent with Supersite operations. Fortunately, such studies are being conducted or are being planned. The measurements specified in Table 1-1 may be modified to accommodate the needs of these health studies as part of a planning task that will be completed early in the project.

2. SCOPE OF WORK

Supersite planning, operations, and data analysis will be accomplished by the following seven tasks.

2.1 Task 1: Fresno Supersite Program Plan

Prepare program plans for the study. The program plan will include: (1) review of prior information on emissions, meteorology, ambient measurements, and modeling efforts; (2) sampling site locations, descriptions, and justification; (3) rationale for sampling periods and methods; (4) descriptions of field and laboratory operations; (5) data processing, validation, and management; (6) quality assurance methods, (7) data analysis, interpretation, and modeling approaches; and (8) responsibilities, schedules, and reporting procedures. An initial plan will be prepared and modified with annual updates during the three-year project duration. Each draft will be available on the CRPAQS web site.

Conduct a one-day workshop in Sacramento with representatives from the California Air Resources Board, the U.S. EPA, and the California health effects community along with researchers from the California Regional PM_{2.5}/PM₁₀ Air Quality Study (CRPAQS) and the Central California Ozone Study (CCOS). Describe the plan and coordinate measurements with those to be taken in and needed by other studies. Modify the plan with respect to observables, sampling frequencies, sample durations, and satellite locations to maximize the benefit of Supersite measurements to other, simultaneous air quality and health studies.

Coordinate with ARB and CRPAQS site operators to optimize and amortize resources required to modify the Fresno First Street site for Supersite and CRPAQS measurements. Define an appropriate phase-in and technical support needed by ARB monitoring staff to maintain the First Street monitors during Supersite and CRPAQS operations.

2.2 Task 2: Procurement, Installation and Procedures Development

Specify and verify the availability of equipment designated in Table 2-1. Order new equipment and arrange for long-term loan of existing equipment as needed. Summarize data logging capabilities and outputs of each instrument and adapt a Windows-NT based personal computer to poll each instrument on a periodic basis and provide an in-station unified data base that can be remotely polled by telephone modem. Configure and bench test instruments in the laboratory prior to field deployment.

Create engineering drawings for instrument placement, sample presentation tubing, and wiring. Cooperate with ARB staff for installation of adequate circuits, phone lines, equipment racks, sample manifolds, and working surfaces at the Fresno First Street site. Install equipment at the site, calibrate it, and commence operations.

Assemble and modify standard operating procedures (SOPs) for each field and laboratory measurement. SOPs include: (1) summary of the measurement method, principles of operation, expected accuracy and precision, and assumptions for it to be valid; (2) materials, equipment, reagents, and suppliers; (3) traceability path, the designation of

Table 2-1. Proposed measurements at the Fresno Supersite.

	Manufacturer/Model	Provided by ^a
I. Gases		
NO/NO _x (chemiluminescence)	TEI 42	ARB
O ₃ (UV absorption)	API 400	ARB
CO (infrared absorption)	Dasibi 3008	ARB
NO _y / HNO ₃	TEI 42CY or Ecophysics 770	DRI
NH ₃	TEI 17C or API 200A	DRI
NMHC	TEI 55	ARB
II. Filter Mass and Chemistry		
TSP High-Volume Sampler	General Metal Works	ARB
PM ₁₀ Hivol SSI	Graseby Andersen	ARB
Dichotomous	Graseby Andersen	ARB
Air toxic monitor (trace metals, chromium VI, aldehydes)	Xontec 920	ARB
Sequential FRM (2 units)	Graseby Andersen	ARB
Sequential FRM	Graseby Andersen	EPA/ORD
SASS and SASS cassettes	Met One	Met One/DRI
PM _{2.5} MiniVol Portable Sampler w/ filter holders and impactors	Airmetrics	DRI
PM _{2.5} Sequential Speciation Sampler	CRPAQS	CRPAQS
PM ₁₀ Fugitive Dust Characterization Sampler	CRPAQS	CRPAQS
III. Continuous Particle Mass and Chemistry		
PM _{2.5} TEOM ^a	R&P 1400A	EPA/ORD
PM ₁₀ TEOM ^a	R&P 1400A	EPA/ORD
PM _{2.5} BAM	Met One 1020	DRI
PM ₁₀ BAM	Met One 1020	DRI
Ambient Particulate Nitrate Monitor (flash volatilization w/ TEI NO _x detector)	ADI/R&P	ADI/R&P
Ambient Particulate Sulfate Monitor (flash volatilization w/ TEI SO ₂ detector)	ADI/R&P	ADI/R&P
Ambient Particulate Carbon Monitor (flash volatilization w/ NDIR CO ₂ detector) ^b	ADI	ADI
Ambient Carbon Particulate Monitor (combustion for organic and elemental carbon)	R&P 5400	R&P
Time-of-Flight Mass Spectrometer (individual particle size and chemistry)	U.C. Riverside	CRPAQS
IV. Organics		
Hydrocarbons	Xontec 910	ARB
Carbonyls	Xontec 925	ARB
Light Hydrocarbons (Canister and GC/FID)	CRPAQS	CRPAQS
Heavy Hydrocarbons (Tenax and GC/TSD/FID)	CRPAQS	CRPAQS
Aldehydes (DNPH and HPLC)	CRPAQS	CRPAQS
PM _{2.5} Organic Compounds (Teflon-coated glass fiber/PUF/XAD and GCMS)	CRPAQS	CRPAQS
PM _{2.5} Organic Components	Airmetrics	CRPAQS
V. Light Scattering		
PM _{2.5} Nephelometer	Optec NGN-3	DRI/ARS
Open-Air Nephelometer	Optec NGN-2	DRI
Ambient Particulate Monitor (photometer)	Greentek GT-640A or DUSTRAK	CRPAQS
Nephelometer	Radianc M903	EPA/ORD
VI. Light Absorption		
Coefficient of Haze	Research Appliance AISI	ARB
Aethalometer	Magee Scientific AE14U	DRI
Multiwavelength Aethalometer ^c	Magee Scientific AE30S	Magee Scientific

Table 2-1. (continued)

	Manufacturer/Model	Provided by ^a
VII. Particle Sizes		
Ultrafine Condensation Particle Counter w/ Fast-Scanning EPROM ^d	TSI 3025A	DRI
Optical Particle Counter	Grimm	DRI
Rotating MOUDI w/ accessories (4 units) for mass, ions, and carbon size distributions	MSP 100	CRPAQS
VIII. Meteorology		
High-Sensitivity Anemometer (wind speed) ^e	Met One	ARB
High-Sensitivity Windvane (wind direction) ^e	Met One	ARB
High-Accuracy Temperature Sensor ^e	Met One	ARB
High-Accuracy Relative Humidity Sensor ^e	Met One	ARB
TOTAL		

^a Prototype TEOM with temperature and relative humidity control features may be available during Phase II (12/1/99 to 3/31/01).

^b Under development.

^c Available during Phase II (12/1/99 to 3/31/01).

^d Currently investigating using a scanning mobility particle sizer (0.005 to 1.0 µm) in addition to TSI 3025A condensation particle counter.

^e Upgrade of high-sensitivity sensors may be required.

primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification; (4) start-up, routine, and shut-down operating procedures and an abbreviated checklist; (5) copies of data forms with examples of filled out forms; (6) routine maintenance schedules, maintenance procedures, and troubleshooting tips; (7) internal calibration and performance testing procedures and schedules; (8) external performance auditing schedules; (9) references to relevant literature and related standard operating procedures; and (10) designation of the personnel responsible for each part of the procedure.

Each of the monitors specified in Table 2-1 has its own data acquisition system, and these will be interfaced to a station computer that polls them on a regular basis and places the acquired data into a Microsoft Access[®] data base with units and variable naming conventions defined by CRPAQS. This unified data set will be accessible by modem, as well as in the shelter, to remotely evaluate instrument performance.

The PM_{2.5} speciation monitor will be configured as in Figure 2-1 for the first year until it is transferred to ARB to be integrated into part of the statewide PM_{2.5} monitoring network (U.S. EPA, 1999). The channels, denuders, filter substrates, and analyses shown in Figure 2-1 are needed to test the different hypotheses specified in Section 1.3. The PM_{2.5} FRM monitor will be operated on the same schedule with analyses comparable to those specified for the Teflon filter channel on the speciation monitor. The FRM monitor will be configured as in Figure 2-2. The FRM filter will be analyzed by x-ray fluorescence under

Figure 2-1. Sample configuration and analyses for the Met One PM_{2.5} SASS (Spiral Aerosol Speciation Sampler). Flow rate through each channel is 6.7 L/min. In each box, *AAS*=Atomic absorption spectrometry, *AC*=Automated colorimetry, *IC*=Ion chromatography, *ICP/MS*=Inductively coupled plasma/mass spectrometry, *TOR*=Thermal/optical reflectance, *Transmission*=Light transmission, and *XRF/He*=X-ray fluorescence with helium atmosphere.

2-4

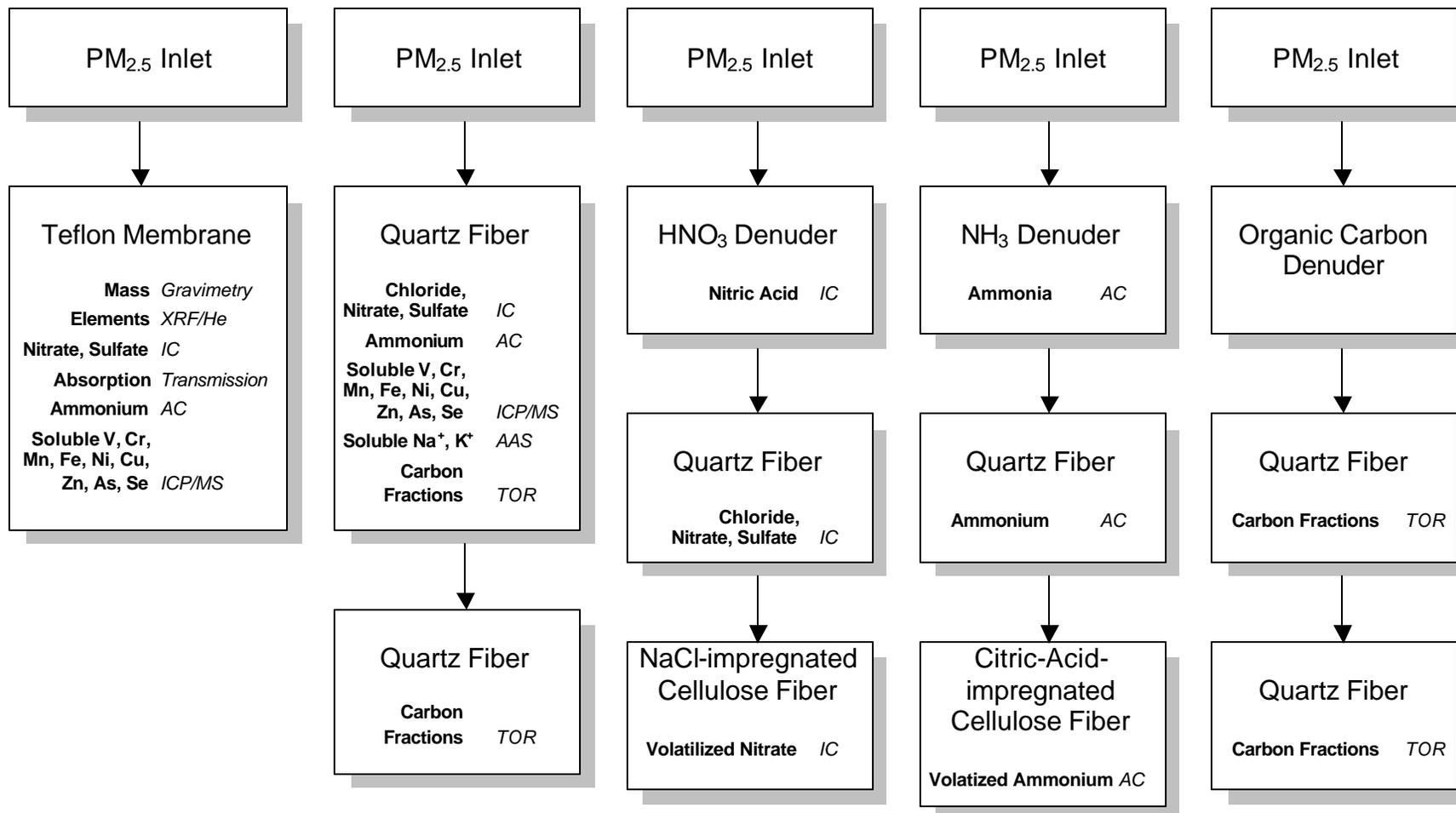
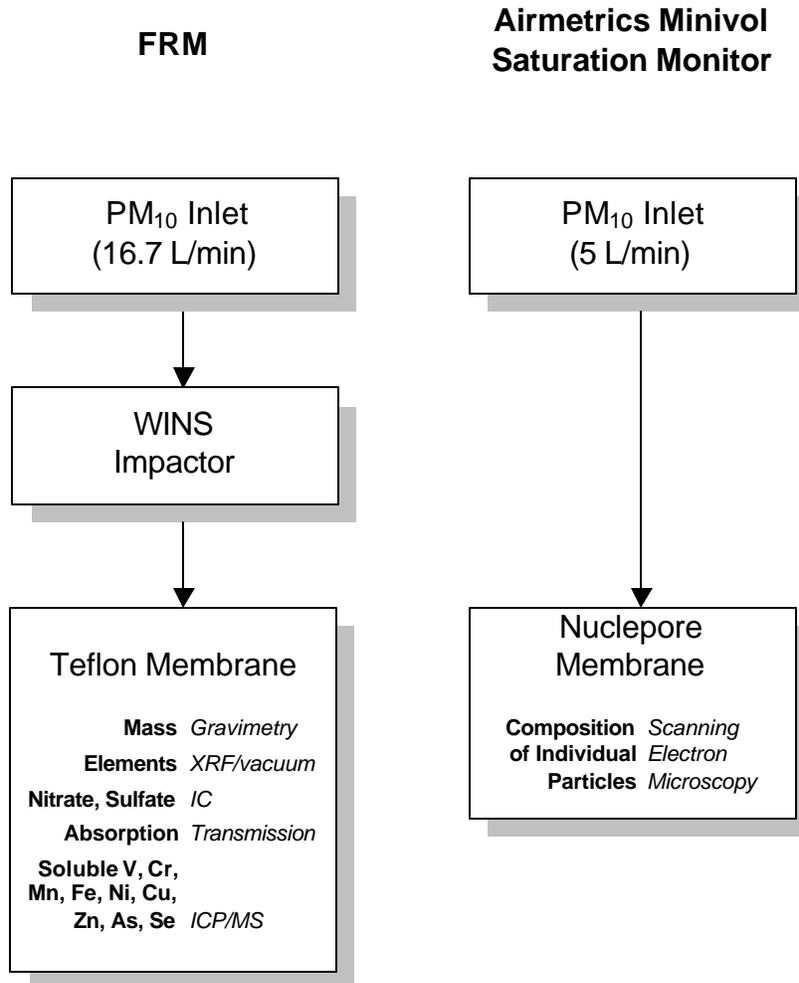


Figure 2-2. Configurations of the PM_{2.5} FRM and saturation monitors.



vacuum (instead of under helium as specified in Figure 2-1) to evaluate the extent to which volatile substances are stabilized in a helium atmosphere. Nuclepore-membrane filters from a MiniVol PM₁₀ saturation monitor will be analyzed by scanning electron microscopy analysis.

2.3 Task 3: Network Operations and Data Processing

Conduct long-term field operations in collaboration with an ARB on-site station operator. These operations include: (1) inspection of instruments by remote dial-up and on-site visit for acceptable operation; (2) performance tests defined in the SOPs; (3) instrument re-calibration; (4) sample receipt and changing; (5) documentation of instrument, station, and meteorological conditions; (6) preventive maintenance; (7) corrective maintenance; (8) transmission of data, samples, and documentation; (9) replenishment of consumable supplies; and (10) participation in external quality audits.

Plan and conduct quality audits in collaboration with ARB and CRPAQS auditing. Conduct audits soon after transfer of instrument operations to ARB staff. Coordinate ARB annual audits of gaseous monitors, meteorological sensors, and aerosol sampler flow rates. With CRPAQS auditors, specify methods, standards, and comparison methods for size- and chemical-specific continuous monitors and laboratory measurements. Participate in interlaboratory comparisons with the ARB aerosol analysis laboratory. Consolidate and evaluate audit results and take remedial action where needed.

Supervise and support field operations from the DRI central laboratory, including: (1) resupply of field site expendables; (2) coordination and verification of substrate shipments to and from field; (3) review of field data and log sheets; (4) regular contact with field technicians; (5) review of performance test data and correction of deficiencies; (6) continuous data review and reporting; and (7) coordination of field audits and corrections of deficiencies revealed by audit.

For data acquired from laboratory analysis of substrates, calculate the averages and standard deviations of field blank measurements and subtract these from measurements of gaseous and particulate chemical species. Calculate sample volumes from flow rates and sample durations for each sample. Calculate ambient concentrations of particulate species and the precision as a function of analysis and blank variability. Remove invalid values and flag or correct suspect values as determined from field and laboratory documentation.

Obtain additional air quality, visibility, and meteorological data that correspond to the measurement periods. Examine time series plots and invalidate outliers. Evaluate and rate the quality of data from each source and integrate it into the Supersite data base. Unify data from measurements into formats and units compatible with the CRPAQS data system described by Watson et al. (1998a). Perform Level 1 (defined by Watson et al., 1998a) validation by removing invalid values during instrument maintenance periods, power outages, and calibrations. Perform calibration adjustments, if needed, after examination of performance test data. Perform Level 2 validation by applying maximum/minimum, runs, and jump tests. Adjust acceptable ranges for these tests to reflect realistic values for central California levels. To the extent possible, automate these tests in data management software.

Provide via internet a Level 2 validated data base of Supersite measurements to data analysts within one calendar quarter of the previous calendar quarter. Upon completion of Supersite and CRPAQS monitoring, provide an integrated Level 3 validated data base on CD-ROM. Included on this CD-ROM the available historical data base of gas, particle, and meteorological measurements for the Fresno First Street site. Submit Fresno Supersite data to EPA's Supersite data base and to applicable NARSTO data archives.

2.4 Task 4: Sample Preparation and Laboratory Analysis

Acceptance test Teflon-membrane, quartz-fiber, and cellulose-fiber filters and denuders. Acceptance testing includes chemical analysis of 2% of all substrates received and visual inspection of every substrate. Pre-fire quartz-fiber filters, impregnate cellulose-fiber filters with gas-absorbing solutions, and maintain all substrates under refrigeration during non-active periods (Chow and Watson, 1998).

Prepare and label sample filter packs for the FRM, speciation, and saturation monitors. These filter packs include 10% dynamic field blanks, 3% spares, and 2% laboratory control blanks. Ship pre-loaded filter packs and accompanying field data sheet in cooler with ice packs to field and receive exposed filter packs from the field in cooler with ice packs on a biweekly basis. Document the chain-of-custody of samples.

Perform pre- and post-sampling gravimetric analysis on Teflon-membrane filters for PM_{2.5} mass concentrations from FRM and speciation monitors. Perform pre- and post-sampling light transmission analysis on Teflon-membrane filters from FRM and speciation monitors.

Perform x-ray fluorescence (XRF) analysis on Teflon-membrane filter samples for 40 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U). Use normal chamber evacuation for the FRM filters and a helium atmosphere for the speciation monitor filters (Watson et al., 1999).

Section quartz-fiber filters and gas-absorbing filters (i.e., cellulose-fiber filters impregnated with sodium chloride or citric acid). Extract filter halves and denuders in deionized-distilled water (DDW) for water-soluble ion and metals analysis. Analyze Teflon and quartz-fiber filter extracts for chloride, nitrate, and sulfate by ion chromatography. Analyze denuder and sodium-chloride-impregnated backup filter extracts for nitrate by ion chromatography (IC) to estimate nitric acid and volatilized nitrate concentrations, respectively (Chow and Watson, 1999).

Analyze quartz-fiber filter, citric-acid-impregnated backup filter, and denuder extracts for ammonium ion by automated colorimetry (AC). Analyze extracts of Teflon-membrane filters from FRM and speciation monitors and extracts of quartz-fiber filters from speciation monitors for vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, and selenium by inductively coupled plasma mass spectrometry (ICP/MS). Analyze quartz-fiber filter extracts for soluble sodium and potassium ion by atomic absorption spectrophotometry (AAS).

Analyze 0.5 cm² sections of quartz-fiber front and backup filters for total organic, high-temperature organic, low-temperature organic, total elemental, high-temperature elemental, and low-temperature elemental carbon by thermal/optical reflectance carbon analysis (Chow et al., 1993b). Report carbon concentrations as total carbon, as organic carbon, as elemental carbon, and as seven carbon fractions differentiated by combustion temperature and combustion atmosphere. Analyze half of Nuclepore filters taken every 6th day for single particles by computer-controlled scanning electron microscopy, with particle identification optimized for pollen and spores.

Each analysis includes daily calibration, 10% replicates, standards, and blanks, and re-analyses when performance tolerances or data validation criteria are not met. Remaining sample sections will be archived under refrigeration for the duration of the project for potential re-analysis or analysis for other species.

2.5 Task 5: Technology Transfer

Work with ARB site operators and data base specialists to perfect procedures and transfer station operations to ARB. Conduct three technology sharing workshops in Sacramento on the topics of: (1) instrument operation, calibration, and maintenance; (2) data validation and management; and (3) data analysis to test hypotheses.

2.6 Task 6: Data Validation and Interpretation

Using data from the integrated data base, perform data analyses that proves, disproves, or qualifies the hypotheses stated in Section 1.3. These tasks will be performed as part of this project, CRPAQS, and existing and planned health studies in central California. Potential sponsors and data analysis responsibilities are designated in parentheses after each hypothesis statement. Specific data analysis tasks for each hypothesis include:

- **Mass and chemical (elements, ions, and carbon) measurements from routine filter samplers with a Teflon-membrane filter (from FRM or saturation monitors) represent actual PM_{2.5} mass within the spatial zone of representation of a CORE site (EPA/CIASTA, DRI).** Compare mass and elemental concentrations measured on the 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 temperatures during sampling, and high and low relative humidities. 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 different Fresno PM_{2.5} sites.
- **Elemental analysis of Teflon-membrane filters under a helium atmosphere does not result in a significant (>10%) loss of volatile nitrate (EPA/CIASTA,**

DRI). Compare elemental and nitrate measurements from the FRM filter analyzed by XRF under vacuum with those from the speciation sample analyzed under helium, and quantify losses of potentially volatile species. Compare nitrate levels from both of these with the nitrate measured by a speciation monitor on a quartz-fiber filter, non-volatilized nitrate from a denuded quartz-fiber filter, and volatilized nitrate from a backup quartz-fiber filter. Quantify any advantages to be gained from the extra expense and lower sensitivity afforded by XRF analysis under a helium atmosphere.

- **Carbon gases absorbed on quartz-fiber filters are a small (<15%) fraction of organic carbon measured on these filters (EPA/CIASTA, DRI).** 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.
- **Volatilized particulate nitrate is a minor (<10%) part of particle nitrate during winter, but a major fraction of particle nitrate during other seasons (EPA/CIASTA, DRI).** 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 and 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.
- **Volatilized particulate nitrate is a minor (<10%) part of actual PM_{2.5} during all seasons (EPA/CIASTA, DRI).** Plot volatilized nitrate and ammonium concentrations as a function of PM_{2.5} and PM₁₀ from different monitors, including the heated 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} and PM₁₀ to determine the extent to which TEOM volatilization is specific to ammonium nitrate.
- **PM_{2.5} 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 (EPA/CIASTA, DRI).** 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, spatial variability, and filter-based sampler differences.

- **Short duration (~5 min) spikes in particle measurements represent contributions from nearby (<500 m) emitters (CRPAQS, Data Analyst).** 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 portable nephelometers (e.g., Greentek Ambient Particulate Monitor or DUSTRAK), used at CRPAQS satellite sites, show short-duration peaks that correspond to these variables at the CORE site. 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 sampling and for 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 portable nephelometer measurements from satellite sites surrounding the CORE site. Calculate spatial correlations of 5-min spikes over longer-term averages to evaluate zone of influence of nearby sources.
- **Nearby emitters represent a small (<15%) fraction of $PM_{2.5}$ measured at a CORE sampling site (CRPAQS, Data Analyst).** 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 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. 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 1-hr, 3-hr, 5-hr, and 8-hr 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.

- **The majority of ultrafine particles are from nearby (<500 m), fresh emissions sources (EPA/CIASTA, DRI, ADI).** From 5-min spikes over longer-term averages of ultrafine particles as small as $0.003 \mu m$ 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.
- **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 (CRPAQS, Equilibrium Modeler).** Using continuous measurements for particle sulfate, particle nitrate, ammonia, 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 ammonia levels, and when they are limited by nitrate levels, 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.
- **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, wood combustion, field burning, meat cooking, gasoline engine exhaust from cold starts, high emitters, and hot stabilized operations, diesel exhaust, and primary industrial emissions (CRPAQS, Receptor Modeler).** 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 (e.g., Watson et al., 1997b, 1998b; Schauer et al., 1996; Schauer and Cass, 1998). 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 super-position of sources.

- **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 combustion and meat cooking), gasoline engine exhaust (cold starts, high emitters, and hot stabilized), diesel exhaust, and primary industry contributions (CRPAQS, Receptor Modeler).** 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 collinearity. 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.
- **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 (CRPAQS, Receptor Modeler, Emissions Modeler).** Compare the proportional contributions from different source categories with similar proportions in emissions 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.
- **PM_{2.5} 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 (EPA/CIASTA, DRI, ADI).** 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.

- **Soluble transition metals are a small fraction (<15%) of total metal concentrations in PM_{2.5} (EPA/CIASTA,DRI).** Plot the concentrations of soluble transition metals and total transition metals. 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.
- **Measurements at a CORE sampling site represent the minimum to which people are exposed in their neighborhoods within an urban area (CRPAQS, Spatial Data Analyst).** 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 (see Figure 1-2) with those at the Fresno CORE site. 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 (such as 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: (a) new sites, and (b) site classification changes for long-term measurement sites.
- **The ammonium nitrate portion of PM_{2.5} shows the same epidemiological relationships to health end-points as PM_{2.5} mass (ARB, Epidemiologist).** Calculate multivariate Poisson regressions and perform other statistical analyses between health end-points (derived from concurrent studies described in Section 3) and PM number, surface area, and mass in different size fractions, chemical components, and co-factors (including meteorology). Substitute PM_{2.5} nitrate for PM_{2.5} mass in these different models and determine the significance and differences between correlations with different health end-points.
- **Ultrafine and coarse particle mass concentrations show weaker epidemiological relationships to health end-points than does PM_{2.5} mass (ARB, Epidemiologist).** Calculate multivariate Poisson regressions and perform other statistical analyses between health end-points (derived from concurrent studies described in Section 3) and PM number, surface area, and mass in different size fractions, chemical components, and co-factors (including meteorology). Substitute coarse and ultrafine mass for PM_{2.5} mass in these different models and determine the significance and differences between correlations with different health end-points.

2.7 Task 7: Management, Reporting, and Integration with Other Studies

Set task goals and schedules and monitor adherence to those schedules. Facilitate communications among project team members and technical committees. Track costs against budgets, and pay invoices to subcontractors. Conduct up to three one-day data analysis workshops in Sacramento, CA to share and summarize progress on data analysis related to this project, CRPAQS, CCOS, and health studies.

Maintain standard operating procedures, quality assurance methods and results, interim finding, interim data deliveries, and preliminary reports and publications on a web site available to other Supersite investigators and to CIASTA, CRPAQS, and ARB data analysts. Prepare research publications describing the measurement program, standard operating procedures, and results of data analysis applied to hypothesis testing.

3. PROJECT PARTICIPANTS

The Fresno Supersite measurements will be coordinated by the Desert Research Institute of the University and Community College System of Nevada. Dr. John G. Watson will be principal investigator. He will be assisted by Dr. Judith C. Chow. DRI staff specializing in instrument design and operation, chemical speciation, data management, and data analysis, and air quality modeling will be incorporated into the project as needed to accomplish the specified tasks.

Continuous particle measurements will be supervised by Dr. Susanne Hering of Aerosol Dynamics, Inc., of Berkeley, CA. Dr. Hering will assist in equipment selection/procurement, bench testing and calibration, procedures development, and data reduction for measurements from the condensation particle counter, the optical particle counter, and continuous sulfate, nitrate, and carbon analyzers.

The Fresno First Street site is leased and operated by the California Air Resources Board (ARB). The ARB will provide for on-site assistance in day-to-day operation and will phase in complete site operation, including data validation and management, by the end of the two-year monitoring period. It is intended that several of the instruments will continue operation as part of the ARB's statewide PM_{2.5} network after the Supersite monitoring is completed. The ARB also operates long-term air quality and meteorological networks and is phasing in a statewide PM_{2.5} compliance network. The ARB also unifies statewide data from more than a dozen long-term meteorological networks throughout the state, including more than 400 surface stations and more than ten upper air monitors.

The CRPAQS is currently recruiting investigators for anchor and satellite site operation, organic sampling and analysis, and additional surface and upper air meteorological monitoring that are relevant to the Fresno urban area for the period of December 1, 1999, through January 31, 2001. These will be further enhanced during the summer of 2000 by CCOS measurements related to ozone.

An epidemiological health study of particulate air pollution and morbidity in California's central valley has been initiated by the ARB and EPA. This study will relate Kaiser Permanente Medical Care Program data bases on doctor office visits, hospitalization, and emergency room incidences of respiratory and cardiac distress to particulate pollution in the San Joaquin Valley. Fresno Supersite measurements will enhance this study by providing a wider range of air quality indicators that can be related to these medical records.

An exposure study is being planned by Lawrence Berkeley Laboratory, with Department of Energy sponsorship, to evaluate indoor particle concentrations and human exposure relative to outdoor concentrations in the Fresno area. Fresno Supersite measurements will enhance this study by adding a larger variety of indicators that might be better related to human exposure than PM_{2.5} mass. The exposure data from this study will enhance hypothesis testing about the zone of representation for a CORE site used to determine compliance.

Two clinical health studies are under consideration for sponsorship by the ARB to take advantage of CRPAQS measurements. These studies would benefit from the larger set of observables and longer-term monitoring records provided by the Fresno Supersite. These studies would gather and analyze health information on 200 to 400 young asthmatics and individuals with cardiovascular ailments in the region obtained concurrently with ambient monitoring. The Fresno Metropolitan Statistical Area reports among the highest rate of asthma in the U.S. The timing and intensity of effects would be related to indicators of particle pollution at the Fresno Supersite and other sites. Crucial to these experiments are Supersite objectives that determine the zone of representation for a CORE compliance site and the relationships between complex measurements taken at a single site and less costly but less detailed measurements taken at many sites to represent population exposure.

ARB is also considering sponsorship of a long-term time series epidemiological study that would relate hospital admission/discharge data from the Statewide Health Planning Hospital Discharge Database to particulate pollution. Fresno Supersite measurements, especially those that are incorporated into ARB's long-term PM_{2.5} network after the first two years of operation, will provide more definitive information on epidemiological effects of specific PM components than has been possible in the past.

As investigators are identified for these projects, they will be invited to participate in Fresno Supersite planning and data analysis to optimize the utility of its data for testing additional health-related projects.

4. GUIDING PRINCIPLES

This section evaluates this proposal against the guiding principles for Supersite operation.

- **Test specific scientific hypotheses appropriate for the monitored airshed and suite of measurements.** Hypotheses have been advanced with respect to measurement evaluation, source apportionment and control strategy development, and health effects. These hypotheses will be refined and augmented as part of program planning. Analyses of measurements are described that show how these hypotheses can be tested with the proposed measurements. It is not anticipated that the hypotheses stated here will be proven or disproven. It is anticipated that when they are examined using a detailed, long-term data base of the proposed measurements that qualifications will be identified, and that these qualifications can be related to a climatology of meteorology, emissions, and atmospheric variations that recur year after year in central California.
- **Obtain measurements that can be compared and contrasted among Supersites established nationwide.** Measurements at the Fresno Supersite include most of those proposed for the Atlanta Supersite, including detailed aerosol chemistry, continuous sulfate, nitrate, carbon, precursor gases, and criteria pollutant gases, and continuous particle size from ultrafine through coarse particle modes, and high resolution winds, temperature, and humidity at the surface and aloft. Special studies for organic speciation, single particle chemical characterization, and chemical-specific particle size will also be taken at the Fresno Supersite as part of CRPAQS. CRPAQS will also operate several anchor sites acquiring much of the same information as the Fresno Supersite. The anchor sites provide a basis for establishing similarities and differences among pollutant concentrations within central California. Specifically, the non-urban Angiola site located ~100 km south of Fresno will have nearly identical measurements that will allow differentiation of regional from urban contributions to the variables measured within the Fresno urban area. The Fresno Supersite intends to establish relationships between complex Supersite measurements and less comprehensive measurements such as speciation monitors, FRMs, and saturation monitors. These data will be available over a wider spatial scale, both in central California and throughout the United States. A better understanding of where and when these more widely available measurements are adequate surrogates for more complex measurements will provide opportunities for comparisons and contrasts.
- **Integration into larger monitoring networks and research studies.** Fresno Supersite measurements are fully integrated into the ARB's 48-station PM_{2.5} compliance network in central California, the \$11.5M California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) that will acquire measurements from December 1, 1999, through January 31, 2001, the \$5.5M Central California Oxidant Study (CCOS) that will acquire measurements from June 15, 2000, through September 30, 2000, and ongoing or planned clinical, epidemiological, and exposure studies. The Fresno Supersite will supply data to, and obtain

relevant data from these studies to test the hypotheses advanced in this proposal and the specific hypotheses proposed for those studies.

- **Leverage EPA investments with contributions from other agencies.** In addition to the supplemental measurements available from existing air quality and meteorological networks, and from the concurrent PM, ozone, and health studies, the ARB will make a substantial contribution by supplying the measurement facility, utilities, and security for the two-year monitoring period. ARB will also supply on-site field support for the operation and maintenance of continuous field monitors and filter samplers. As procedures are perfected for data acquisition and validation, ARB will take on these tasks such that many of the measurements will be continued at this site after the first two-year monitoring period. The Desert Research Institute, the U.S. Environmental Protection Agency, Aerosol Dynamics Inc., Rupprecht and Patachnick Inc., Met One Instruments, and Air Resource Specialists will provide several continuous monitors and aerosol samplers to the site without cost to the project for its duration. Feedback to these instrument suppliers about operating methods and procedures will assist them in perfecting their products for application elsewhere. EPA sponsorship through the Cooperative Institute for Atmospheric Sciences and Terrestrial Applications (CIASTA) provides a lower indirect cost recovery rate than DRI projects that are directly sponsored by EPA. Each of these efforts enhances the other by providing a set of measurements that would be beyond the resources of an individual program. It is estimated that EPA/CIASTA obtains a minimum of four-to-one leveraging of its investment for the Fresno Supersite.

5. SCHEDULE AND BUDGET

Figure 5-1 shows the milestones for completion of the seven tasks specified in Section 2. Deliverables will consist of: (1) a program plan, (2) field and laboratory standard operating procedures, (3) up to three technology transfer workshops, (4) a data report, and (5) draft manuscripts for submission to peer-reviewed journals.

An initial draft program plan will be prepared in 1999. This program plan will be an evolving document and will remain in draft form until the majority of activities and responsibilities have been executed. It will be revised annually and finalized at the end of the project to reflect actual conduct of the program and to identify improvements that should be incorporated into future plans.

It is anticipated that monitors will be deployed between April 1, 1999, and November 15, 2000. Table 5-1 shows milestones for commencing various measurements. Additional instruments such as a scanning mobility particle sizer (capable of measuring particles in the 0.005 to 1.0 μm size fraction) are currently under investigation and may be added to acquire higher-resolution size distributions of ultrafine ($dp < 0.01 \mu\text{m}$) and fine ($dp < 1.0 \mu\text{m}$) particles. $\text{PM}_{2.5}$ speciation monitoring will commence on June 1, 1999, for a period of one year to test non-routine monitoring methods and determine their compatibility with respect to $\text{PM}_{2.5}$ FRM monitors. New equipment will be identified and procured at the beginning of the project. This equipment will be configured and bench tested in a laboratory prior to field deployment on October 1, 1999.

CRPAQS annual measurements that are concurrent with collocated Supersite measurements will begin December 1, 1999, for a period of 14 months. This will also include a summer intensive study (June 1, 2000, to August 31, 2000), a fall fugitive dust characterization study (September 15, 2000, to November 15, 2000), and a winter intensive study (November 15, 2000, to January 31, 2001).

Technology transfer workshops will be conducted in Sacramento, CA, on an annual basis or as needed in coordination with U.S. EPA, ARB, and other study participants. The information exchange will include, but shall not be limited to: (1) instrument operation, calibration, and maintenance; (2) data validation and management; and (3) data analysis to test hypotheses.

Level 2 validated data with specified formats for each calendar quarter will be assembled within three months of the end of the quarter, and all data will be compiled by June 30, 2001 (three months after the completion of two years of monitoring). The final data base will document the measurement locations, sampling and analysis methods, standard operating procedures, audit results, precision and accuracy estimates of each measurement, as well as the validated final data base. Data analysis tasks will continue until December 31, 2001. Data reporting formats, variable names, and file names will be established as part of the program plan. Internet connections between ARB and DRI are already established and will be used to make interim results available for early examination. The project final report, including data analysis reconciled with the available resources, will be completed by

Table 5-1. Project milestones to phase in Supersite measurements.

Projected Commencement Date	Instrument	Measurement	Projected Measurement Period
April 1, 1999	Met One PM _{2.5} Beta Attenuation Monitor Met One PM ₁₀ Beta Attenuation Monitor R&P 5400 Ambient Carbon Particulate Monitor Optec NGN-2 Ambient Temperature Nephelometer Optec NGN-3 Heated PM _{2.5} Nephelometer Magee Scientific AE14U Aethalometer Greentek GT640A or DUSTRAK Ambient Particulate Monitor Upgrade Meteorological Sensors (High-Sensitivity Wind Vane, Anemometer, Temperature Sensor, and/or Relative Humidity Sensor) Data Acquisition System	PM _{2.5} mass PM ₁₀ mass Organic and elemental carbon Ambient temperature light scattering Dry particle light scattering Particle light absorption at 880 nm Particle light scattering Wind direction, wind speed, temperature, and relative humidity Continuous 5-min to 1-hr data	
June 1, 1999	Rupprecht & Patashnick 1400A PM _{2.5} Monitor Rupprecht & Patashnick 1400A PM ₁₀ Monitor Radiance M903 Heated Nephelometer Met One Speciation Monitor (SASS) (one year only) Airmetrics MiniVol Saturation Monitor (one year only – samples for computer-controlled scanning electron microscopy analysis) Additional Graseby Andersen Sequential FRM Monitors (one year only)	PM _{2.5} mass PM ₁₀ mass Dry particle light scattering PM _{2.5} mass, light transmission, elements, ions, and carbon Individual particle composition PM _{2.5} mass, elements, and ions	

Table 5-1. (continued)

Projected Commencement Date	Instrument	Measurement	Projected Measurement Period
October 1, 1999	TEI 42CY or Ecophysics 770 Continuous NO _y /HNO ₃ Monitor TEI 17C or API 200 NH ₃ Monitor Aerosol Dynamics/Rupprecht & Patashnick Ambient Particulate Nitrate Monitor Aerosol Dynamics/Rupprecht & Patashnick Ambient Particulate Sulfate Monitor Aerosol Dynamics Ambient Particulate Carbon Monitor TSI 3025A Ultrafine Condensation Particle Counter Grimm Technologies Optical Particle Counter	NO _y , HNO ₃ NH ₃ Nitrate Sulfate Carbon Particle number distribution for particles between 0.003 and 0.2 μm diameter Particle size distribution for particles between 0.3 and 30 μm diameter	
December 1, 1999	CRPAQS Two-Channel Sequential Filter Sampler (for 14 months only) Magee Scientific AE30S Multiwavelength Aethalometer	PM _{2.5} mass, elements, ions, and carbon Light absorption at seven wavelengths (450, 570, 590, 615, 660, 880, and 950 nm)	
January 1, 2000	CRPAQS MiniVol Sampler (for one year only)	PM _{2.5} organic compounds (Teflon-coated glass-fiber for GC/MS)	
June 1, 2000	CRPAQS Organic Sampler (for three months only)	PM _{2.5} organic compounds (Teflon-coated glass-fiber/PUF/XAD for GC/MS)	
September 15, 2000	CRPAQS Fugitive Dust Characterization Study Sampler (to be determined) (for two months only)	PM ₁₀ mass, elements, ions, carbon, and fugitive dust markers	

Table 5-1. (continued)

Projected Commencement Date	Instrument	Measurement	Projected Measurement Period
November 15, 2000	CRPAQS Two-Channel Sequential Filter Sampler (for 15 episode days between 11/15/00 and 1/31/01) MSP100 MOUDI Cascade Impactors (for 15 episode days between 11/15/00 and 1/31/01) U.C. Riverside Time-of-Flight Spectrometer (for 15 episode days between 11/15/00 and 1/31/01) CRPAQS Canister Sampler CRPAQS Tenax Sampler CRPAQS Aldehyde Sampler (for 15 episode days between 11/15/00 and 1/31/01) CRPAQS Organic Sampler (for 15 episode days between 11/15/00 and 1/31/01)	Diurnal (3- to 8-hr, 5 times/day) mass, elements, ions, and carbon Diurnal (5- to 8-hr, 4 times/day) mass, ions, and carbon size distributions in nine size fractions between 0.054 and 15 μm Individual particle size and chemistry Light hydrocarbons (C ₂ to C ₁₁) Light hydrocarbons (C ₁₀ to C ₂₀) Aldehydes Particle organic compounds	

February 28, 2002. Informal progress reports will be provided as needed. Research publications describing Supersite measurements and documenting the results of methods evaluations will be prepared as data become available.

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