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RECOMMENDATIONS OF THE EXPERT PANEL ON THE EPA SPECIATION NETWORK

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INTRODUCTION

The expert panel met on May 18-19 in Las Vegas, NV, to review the EPA's revised guidance document on the speciation network. Members of the panel are: Drs. Tom Cahill, Phil Hopke, Lara Gundel, John Ondov, and Petros Koutrakis. Mr. Robert Stevens, who is also a panel member, did not attend the meeting, but he submitted his comments in writing. Members of the speciation group, which consists of EPA staff and representatives from several states, also participated in this meeting. Below is a summary of the expert panel recommendations.

Overall, the panel was impressed with the progress made since the last review held in Seattle a year ago. Most of the panel and working group recommendations were considered and have been incorporated into the Guidance Document. The panel strongly believes that the goals, objectives, and monitoring strategy of the Speciation Network are sound and have been communicated to a great extent to the states and the scientific community. The revised Guidance Document will help to further inform the stakeholders about the different aspects of this program.

We feel that significant progress was made in many areas, including:

Particle Measurements: A list of particle measurement methods has already been developed and is included in the Guidance Document. This list is final and there is consensus about the particulate constituents to be measured.

Sampling Frequency: Increasing the sampling frequency from every sixth day to every third day will provide sufficient statistical power to detect trends, as discussed in the Guidance Document. Furthermore, increasing the sampling frequency to every day for several sites will make it possible to carry out longitudinal air pollution health effects studies. This new generation of observational investigations will allow the examination of associations between morbidity and mortality outcomes, and a large spectrum of fine particle components. The panel realizes that augmenting the sampling frequency will result in increasing the cost of the network and will be burdensome to the states; however, the panel strongly believes that collecting more samples per site will be crucial to the EPA's efforts to detect trends. Therefore, if needed, the number of sites could be less than 55 to reduce costs.

Sampler Development: EPA staff have been working very intensively over the last year to evaluate and improve several candidate sampling devices. To date, many design and operational problems have been solved and a comprehensive field intercomparison study has been completed. The findings of this study will enable EPA scientists to determine the accuracy and precision of these methods, as well as to recommend further improvements, if needed. Trends networks require data of great quality; thus, it is of paramount importance that the proposed sampling devices be tested fully prior to their implementation. In spite of all this progress, the panel believes that there remain a number of issues regarding the sampling strategy which should be addressed by the EPA, as discussed below.

Laboratory Contracts: The EPA is in the process of selecting several laboratories to support the states in the preparation of the sampling media and the chemical analysis of the samples. Also, a couple of EPA laboratories which will participate in the quality assurance activities have been identified.

As discussed above, tremendous progress has been made since the inception of the speciation program. The panel recognizes that the development and implementation of a such a large network is very challenging and will require a great deal of effort in the future. A large number of issues have been successfully addressed; however, these efforts primarily have preoccupied the EPA staff, so there was little time to focus on implementation of the network, quality assurance, and data analysis. Considering the limited number of EPA staff available to support the speciation network, the panel feels that the focus should be different for each of the first four years:

First Year: During the first year, the EPA staff focused its efforts on the design of the speciation network. Last year at the Seattle meeting, the expert panel had the opportunity to review the objectives of the network and the list of measurement parameters.

Second Year: Since the Seattle meeting, a series of field studies have been conducted to evaluate the performance of the candidate sampling devices. In addition, the EPA staff has initiated the process of contracting the laboratories designated to perform the sampler preparation and chemical analysis.

Third Year: The focus should be on the completion of the sampler tests, completion of the sampling and analysis protocols, and start-up of the first ten sampling sites. An effort should be made to develop an implementation plan for the speciation network and to set up a managerial structure. It is important to present a structured plan outlining the responsibilities and duties of the participating groups.

Fourth Year: State scientists have a tremendous experience in particle sampling and to, some extent, in chemical analysis methods; however, the state scientists have little experience in analyzing particulate data. Therefore, before the end of the fourth year, a plan should be presented to provide training to state scientists in source apportionment methodologies and their interpretation.

GUIDANCE DOCUMENT

The revised draft Speciation Network Guidance Document represents a significant improvement over the previous versions and has incorporated many of the suggestions of the various advisory groups who have commented upon the earlier versions. In general, the panel was very pleased with the progress made since last year. Overall, the network goals and objectives, as well as the network design, were well presented. Moreover, the discussion on the sampling and analysis methods, quality assurance, and data analysis were very comprehensive. The panel members had a number of minor comments on the document, which have been submitted directly to the EPA staff.

The panel recommends that the Guidance Document remain a living document to be updated periodically. For instance, the document can be used to: (i) discuss changes in the sampling and analysis technologies; (ii) provide reports on the laboratory and field audits; (iii) discuss changes in the list of species to be measured; (iv) inform about the selection and initiation of the sites; (v) present summary results from the different sites; (vi) present lists of publications relevant to the network; etc.

Instead of continuously revising the document, it may be preferable to establish successive editions of the document (e.g., edition 1, 2, 3 . . .). This will make it possible to maintain a record of the evolution of the network, and thereby enable us to understand why, how, and when the different changes were made.

In order to sustain the production of the different editions in a cost-effective way, the panel offers the following suggestion: reduce the volume of the document to approximately fifty pages and use web link sites to provide the support information for the document. For example, the discussion on sampling methodology could be reduced from twenty pages to five if, at the end of this chapter, a link site was provided describing in detail the different methods. The link site-appended documents should be updated to reflect any changes which occur. If substantial revisions are necessary, then it would be desirable to have new editions for the appendices as well. Another example is the data analysis section. Here it is possible to present publications or data summaries by the link sites.

Furthermore, the order of the chapters should be changed. For example, the network design should be placed after the introduction or even be incorporated into the introductory section. The data analysis section should be placed after the sampling and data processing chapters. After reducing the text, the authors should ensure that there are no redundancies. Also, a couple of important components are missing from the document, such as the overall managerial structure of the network and the implementation strategy of the network. These two important issues are discussed in the following section.

IMPLEMENTATION

The panel recognizes the challenge of sustaining the focus and the quality of the network as it evolves. Therefore, the panel feels that the continuous involvement of the EPA and the working group will be imperative for the success of this large program. It was not clear, either from the presentations of the EPA staff or from the Guidance Document, what management team will be in charge of this network. To date, this program has been conceived and launched because of the creativity and commitment of several EPA staff members; yet, the panel feels that this is insufficient to fully develop and operate the speciation network. The panel proposes that a steering committee be formed as soon as possible. This committee should include scientists from OAQPS, ORD, and the states. As the speciation program makes a transition from the development stage to the implementation stage, the committee will be crucial in the effort to oversee and promote the network. The panel has been informed that an EPA Group on Standard Air Monitoring exists. Perhaps the speciation network committee, which will be accountable for the implementation of the speciation network, could report to this group.

It will be necessary for a number of scientists with well-defined responsibilities to be assigned permanently to the speciation network. The panel is concerned that if new EPA projects appear on the horizon, which frequently occurs, the staff currently involved with the speciation network may be reassigned to them. This would be detrimental to the network's continuity and success.

As mentioned above, implementation issues should be addressed during the third year of the program. Therefore, the next edition of the Guidance Document should include a section that will provide a formal structure and an organizational chart of the program. This section should address who is responsible for the day-to-day operations and who will monitor the overall success of the program. It also should address who will carry out the validation of the field data, how the data sets will flow from one group to another, and who will be responsible for their overall management.

ANALYTES

Fortunately, over the last few decades we have experienced substantial decreases of particle concentrations. It is likely that concentrations of particulate constituents will continue to decrease. An exception is nitrate concentrations which may increase due to the anticipated sulfur dioxide emission reductions. Ion chromatography, which is the preferred analytical technique for sulfate, nitrate, and ammonium, is sensitive enough and therefore will continue to be adequate even if concentrations of ionic species decrease by a factor of 10 to 20 times. This may not be the case for elements and carbon. Although XRF analysis is sensitive enough for crustal elements, it is not sensitive enough for trace elements. ICP/MS is a promising analytical technique that is more sensitive than XRF; however, it needs further validation. In addition, its performance on crustal elements is not as good as the XRF. Therefore, if concentrations continue to decrease we may have a serious problem. Similarly, for the carbon analysis of quartz filters, speciation samplers collecting at flow rates less than 16.7LPM may have sensitivity problems for a large number of sites.

Indeed, there are important analytical issues that need to be addressed by the EPA and the panel during the next year after the validation of the sampling techniques is completed. If changes in the chemical analysis scheme are to take place, then it will be necessary to establish rules to decide if and when change is necessary. For instance: When is it necessary to replace an analytical method? What happens to the data obtained from the previous methods? Do they become obsolete or can they be corrected? In an initial response to these questions, the panel suggested that changes be made only if they will help to meet the primary objectives of the network. For example, ICP/MS is more sensitive than XRF for heavy toxic metals, which is very important for health effects studies; however, if it is not suitable for crustal elements (future studies should examine this further), it cannot be used for the speciation network. This is because mass closure, which is one of the primary objectives of the network, requires the accurate determination of Si, Al, and other crustal elements.

In general the speciation network is more challenging than other trend networks because it comprises a large number of analytes. As a result, a great deal of effort will be necessary to balance network continuity and new technology. By developing guidelines based on which decisions can be made, it will be possible to overcome the large number of problems that will rise.

SAMPLING

The panel suggests that the selection of the sampling devices for the speciation network should be based on performance criteria. The panel agrees, therefore, that more than one sampler type could be adopted for the trends network. If the precision and accuracy of the recommended speciation samplers are less than 10%, then different methods could be used for trends sites; however, the panel recommends that once a sampler is selected for a given trend site, it should be used permanently at that site, in order to detect yearly trends on the order of 1-3%. If a decision is subsequently made to replace the sampler or one or more of its components, the difference between the previous and the improved method must be documented. To do this, it will be necessary to collocate the two sampling techniques (or versions) for at least one year at that site to document their difference. This process will make it possible to incorporate the data from the two methods into the same trends data set.

Considering the current state of knowledge and technology, the panel anticipates that the sampling strategy of the speciation network will change, as discussed later in this report. Although being flexible and adaptive is one of the philosophies of the network, improving and modifying the sampling and analysis techniques in a trends network can be a difficult task. The panel has given some serious consideration to this issue. Although we provide some suggestions in this report, we plan to address this issue in a more comprehensive manner in a future report, after the results from the sampler intercomparison study and the proposed laboratory tests become available.

The decision to use performance criteria for the speciation network was based on the following reasons:

- Having the flexibility to employ more than one sampling technique in the speciation network will encourage researchers and manufacturers to continue the development of continuous and integrated technologies. The development of continuous measurement techniques for sulfate, nitrate, carbon, and other species will be critical in reducing both labor and analysis costs. These new continuous samplers could be used to replace one or more channels of the speciation samplers. For instance, if an accurate carbon monitor for both organic and elemental carbon becomes available, the quartz filters and the associated sampler components can be eliminated. Thus, as new technologies will emerge, it is conceivable that speciation platforms will consist of both integrated and continuous sampling techniques.

- The panel believes that the candidate samplers present more or less similar features and that, with some additional minor improvements, most of them will be suitable for the speciation network. This will provide the states an opportunity to select the samplers of their choice, which will in turn enhance competition and help decrease the cost for sampling devices.

- A large investment already has been made in the IMPROVE network. It is anticipated that data sets from previous and future measurements of this network will be used by the speciation network. For this reason, some of the states had suggested that the IMPROVE sampler also be used for the speciation network. This is a sound proposal which has its obvious merits and still remains a possibility. By allowing the use of more than one sampling device, the states will have the option to use the IMPROVE sampler, with which they already are familiar.

One of the drawbacks of selecting more than one sampler for the speciation network is that it will be necessary to develop and implement separate field and sampler handling protocols for each method. Although this will not have an impact on the states, it definitely will be an extra burden to the laboratories and the QA/QC staff.

Below we present a series of performance criteria that can be used by the EPA for both the trends and SIP assistance sites. Since the speciation network is not a compliance one, we suggest the use of the term “recommended sampler” instead of “equivalent sampler.” The process for sampler endorsement from the EPA should be less complicated than for equivalency. If the performance criteria, which are specified below, are met by a sampling device, that sampler should automatically be designated as recommended. Continuous monitors, which measure one or more species, also can be recommended methods if they meet the performance criteria for the species they measure.

To date, the panel believes that the candidate samplers are not fully tested; however, the panel realizes that there is an urgency to start the implementation of the speciation network. Therefore, the panel proposes that two sets of performance criteria be applied to candidate samplers:

The first set of performance criteria should focus on the ability of the sampling devices to collect fine particle mass, sulfate, and elements. These evaluations will be based on a series of field studies which already have been conducted, and laboratory tests which can be completed before the end of summer 1999. The panel believes that collecting fine particles for elemental analysis should be easier than collecting ions and carbon.

The second set of performance criteria focuses on the ability of the sampling devices to collect carbonaceous aerosols and nitrate. For these evaluations it will be necessary to conduct a number of laboratory and field studies which will evaluate the performance of the nitric acid and organic carbon denuders. While the criteria for the nitric acid denuder are well understood and are presented below, this is not the case for the organic carbon denuder. As discussed below, there are still many unresolved technological and conceptual issues regarding the use of organic carbon denuders. For this reason, the proposed criteria could be modified as our scientific understanding evolves.

Therefore, as we review the results of future tests, these criteria may change and the samplers may have to be modified, for example, to include a carbon denuder. The manufacturers of sampling devices should be informed about the potential changes so that their current designs allow for future changes.

Elements/Mass:

The channel for the elemental analysis is the simplest because it does not require the use of a denuder, since most of the elements are not volatile; however, the Teflon filter of this channel should collect the same fine mass as the FRM. The same requirement applies for all three channels (elements, ions, and carbon). As recommenced by the first panel report last year, the size cut-off characteristics of the different inlets of the speciation samplers should be similar to those of the FRM. Therefore, it is important that the manufacturers of the different speciation samplers provide results from laboratory tests that report the collection efficiency and losses as a function of the particle size for each of the speciation channels of the sampler. Some of the inlets that have been used by the speciation samplers may already have been tested; however, considering the complexity of some of the samplers (e.g., too many lines, split flows which may not be isokinetic, etc.), the panel believes that the system performance needs to be tested for particle cut-off characteristics and losses.

Performance Criteria for Elements/Mass:

The performance criteria for these laboratory tests are:

First: The inlet cut-point and separation profile for the candidate method must be comparable to the WINS inlet. A number of laboratory and field tests should be conducted to demonstrate that the fine particle mass samples collected by the speciation monitor and the FRM are in good agreement. The following two criteria must be met for the candidate method to be acceptable: 1) based on linear regression, the R^2 value must be ≥ 0.9 and; 2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be 1.0 ± 0.1. At least twenty 24-hour duration samples should be used for the regression analysis.

Second: The particle size cut-off should be 2.5 ± 0.5 µm; the sharpness of the collection efficiency curve should be at least as good as the FRM; particle losses should be less than 10% for particle sizes between 0.1 and 2.5 microns. These tests should be done for the entire channel and not just for the particle selective inlet (impactor or cyclone). If channels are not identical, each channel should be tested separately.

Third: If cyclones or impactors are used for the collection of multiple samples, the capacity of these particle separators should be tested. Although there are many ways to determine the capacity of these samplers, we propose the following test. Use a nebulizer to aerosolize and aqueous suspension of polydisperse glass beads (these commercially available particles have a nominal size range of 3-10 µm, but the number distribution of smaller sizes is adequate for these tests, with density about 2.5g/cc). The generated particles should be diluted in a clean air stream of 20-30% RH. Measure the particle size distribution and number upstream and downstream the channel as a function of time. Particle concentrations should be three to four hundred times higher than the ambient ones, so that experiments can be completed in a day. By examining the sampler particle size cut-off as a function of time, it is possible to estimate the particle capacity. When the sampler size cut-off gradually starts to increase, this is an indication of particle bounce. This point will correspond to a certain total amount of particle mass removed by the cyclone or impactor. To be conservative the capacity of the sampler can be designated as half of this mass value. The use of glass particles at low RHs make this experiment a realistic simulation of the real atmosphere. A different approach is to measure the sampler partible cut-off characteristics every two months in order to determine capacity. According to Dr. Cahill, former Principal Investigator of IMPROVE, the capacity of cyclones has been tested and determined to be adequate for a year of sampling, but these data were never published.

Fourth: Although it is not required, it is desirable that the sampler collect particles at a face velocity and flow similar to that of the FRM-$PM_{2.5}$.

Sulfate Sampling:

Sulfate is one of the most robust particle species because it remains stable during and after sampling. For this reason, no sampling problems are anticipated.

Performance Criteria for Sulfates:

A number of laboratory and field tests should be conducted to demonstrate that the sulfate collected by the candidate speciation monitor and the FRM are in good agreement. For sulfate the following two criteria must be met for the candidate method to be acceptable: (1) based on linear regression, the R^2 value must be ≥ 0.95; and (2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be 1.00 ± 0.05. At least twenty 24-hour duration samples should be used for the regression analysis.

Nitrate Sampling:

In contrast to sulfate, nitrate sampling is quite challenging. Although nitrate concentrations currently are high only in the Western U.S., it is anticipated that in the future they will increase substantially in the Northeastern U.S., due the projected sulfur dioxide emission reductions. Accurate measurements of nitrate require the removal of gas phase nitric acid prior to particle collection. They also require the collection of nitrate on a filter medium, such as a nylon filter or sodium carbonate coated filter, which bind nitric acid molecules produced during the volatilization of the collected particulate ammonium nitrate. Removal of the gaseous nitric acid can be achieved by diffusion denuders coated with alkaline substances (e.g., sodium carbonate) or (unanodized) aluminum inlets. Previous methods which have used Teflon or glass fiber filters are negatively biased due to the ammonium nitrate loss during and after sampling. The equilibrium between particle ammonium nitrate, gaseous ammonia, and nitric acid can be perturbed by changes in relative humidity and temperature. Loss of ammonium nitrate also can be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media. Nitrate, as well as other semi-volatile compounds, can be lost after sampling during shipping and storage. To date, there is no agreement among the different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling methods. Therefore, the nitrate sampler should include a nitric acid denuder and a nylon filter. If the speciation sampler relies upon metallic denuders that will be used for long periods of time (e.g., more than a couple of weeks, as with the IMPROVE network), the capacity of these denuders should be determined through laboratory and field studies.

Performance Criteria for the Nitric Acid Denuder:

The collection efficiency of the nitric acid denuder can be tested easily in the laboratory. Nitric acid permeation tubes are commercially available and can be used to expose the test denuders. Also, it is possible to nebulize solutions of nitric acid (Koutrakis, et al., 1998). This method presents several advantages, such as: (i) generation of a high dynamic range of nitric acid concentrations; (ii) easy control of concentration levels; and (iii) production of a relatively constant output and low cost. Since the collection performance of a nitric acid denuder is superior at high RHs, it is suggested that laboratory experiments be conducted at low RHs, 20-30%. Because the concentration of gas phase nitrate is usually higher than that of particulate nitrate, it is necessary for the denuder to have a collection efficiency higher than 99%. [The collection efficiency is equal to 1 - C_{out}/C_{in}, where C_{out} and C_{in} are the nitric acid concentrations at the exit and entrance of the denuder.] Even a penetration of 1% of nitric acid can affect the nitrate measurement. For example, if we assume a nitric acid concentration of 25ppb, 1% will correspond to 0.65 $\mu g/m^3$ of nitrate. Considering that nitrate concentrations are typically in the range of a few $\mu g/m^3$, the collection of a small fraction of gas phase nitric acid on the nylon filter may result in significant overestimation of the particulate nitrate concentrations.

The denuder capacity is defined as the amount of nitric acid collected on the denuder before its collection efficiency starts to decrease. A conservative calculation of the nitric acid denuder must be done for the following two reasons: first, the denuder capacity is not always the same and depends upon the history of the denuder; and, second, nitric acid denuders may collect other acidic gases, such as sulfur dioxide, nitrous acid, and low molecular weight organic acids (e.g., formic and acetic acid). For this reason, the experimentally determined capacity should be divided at least by a factor of five. Assuming a nitric acid concentration of 25ppb and a use of 2,880 hours (24 hrs x 120 days/per one year), the capacity of the nitric acid should be 72 ppm/hr. Using a safety factor of 5, the capacity should be 360 ppm·hr. For a flow of 16.7 LPM, this corresponds to a collection of approximately 915 mg of nitric acid per year. Assuming that the only about 10% of the denuder coating material can be used before the collection efficiency deteriorates significantly, one would expect that about 15 grams (equivalent of sodium carbonate) of the coating substance will be necessary to coat the denuder.

There are two types of denuders: (a) the first type includes the denuders that have a relatively low capacity, such as sodium carbonate coated denuders, and therefore can only be used for a few days; and (b) the other denuders, such as (unanodized) aluminum denuders and magnesium oxide coated denuders, can have much higher capacity, and thus can be used for periods of up to a year. The high capacity denuders are more desirable, since they do not require frequent cleaning and coating; however, they must be fully validated prior to their implementation into the network. Laboratory tests can be conducted to examine the efficiency and capacity of the denuders. For low capacity denuders, laboratory tests are easy to perform. For nitric acid, the best way is to use a continuous chemiluminescent NO_x instrument to measure the nitric acid concentration upstream and downstream of the denuder. For these low capacity denuders (which have over 99% collection efficiency in the 200ppb nitric acid range) using upstream concentrations of about 200ppb nitric acid, the capacity of the annular denuder could be determined in a few hours. For high capacity denuders, longer exposure periods (several days or longer) and higher concentrations levels will be necessary; however, any denuder will maintain its given collection efficiency only for upstream concentrations below some upper limit. For concentrations above this value, the efficiency will decrease with increasing concentration, regardless of exposure duration, because the coating cannot stabilize the collected gas rapidly enough. Before testing the high capacity denuders, this upper limit must be determined (it is likely to be on the order of a few ppm). If we assume that the highest upstream nitric acid concentration that can be used is 2 ppm, then for the 360 ppm/hr estimated above (for use for 120 sampling days in a year), it would take 180 hr before the collection efficiency of the high capacity denuder would start to decrease. In general, the candidate denuder should not be used for field sampling until it has been characterized adequately using such laboratory tests. If complete laboratory testing validation is not feasible, then validation can be accomplished in conjunction with field tests. These tests need to be conducted at a site with relatively high nitric acid concentrations. One simple method would be to have simultaneous sampling with twelve denuders. Every month (up to a year) one of the denuders should be returned to the laboratory for testing, using the same technique (i.e., 200ppb nitric acid) as is used for low capacity denuders, measuring with the continuous monitor upstream and downstream of the denuder. If, after a certain number of months, the denuder efficiency drops significantly, this result determines the useful lifetime of the denuder (with a safety factor of at least 2 months).

Reference Method for Nitrate Measurement:

The reference method for nitrate measurement should include a WINS sampler, a sodium carbonate/glycerol-coated glass denuder, and a filter pack containing a sodium carbonate coated glass fiber filter or a nylon filter. The Teflon/Nylon or Teflon/sodium carbonate configuration is not appropriate because a large fraction of nitrate (20-40%) can be lost on the screen that separates the first and the second filter. Therefore, the use of a denuder with a single alkaline filter is an adequate reference method.

Performance Criteria for the Nitrate Measurement:

For nitrate, the following two criteria must be met for the candidate method to be acceptable: (1) based on linear regression, the R^2 value must be ≥ 0.9; and (2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be 1.0 ± 0.1. At least 24-hour duration samples should be used for the regression analysis.

Ammonium Sampling:

Ammonium sulfate salts are very stable, so ammonium losses from these salts during sample collection and storage are negligible; however, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage. The extent of dissociation of ammonium nitrate depends on many parameters, including temperature, relative humidity, and face velocity for the collecting filter. Thus, one would expect that current sampling techniques underestimate ammonium concentrations due to the volatilization of ammonium nitrate. Fine particle mass typically contains many acidic compounds. Consequently, a fraction of volatilized ammonium (in the form of ammonia) can be retained on the Teflon filter by reacting with the acid compounds. Therefore, it is reasonable to assume that ammonium loss is less than the nitrate loss.

Preliminary results suggest that placing an alkaline filter (nylon or sodium carbonate coated filter) directly below the Teflon filter, without using a separation screen, enhances the volatilization of ammonium nitrate from the Teflon filter (preliminary results from the Bakersfield CARB intercomparison study). Under these conditions, the majority of ammonium nitrate leaves the Teflon filter, and only a small fraction of ambient ammonium is measured. Even though volatilization losses are less with the use of a separation screen, the losses are still very significant.

Reference Method for Ammonium Measurement:

The reference method for ammonium measurement should include a WINS sampler, a citric acid/glycerol-coated denuder, and a filter pack containing a single citric acid/glycerol-coated glass fiber filter.

Performance Criteria for the Ammonium Measurement:

The candidate speciation samplers do not measure ammonium directly. Rather, the ammonium will be estimated; however, if future techniques make it possible to measure ammonium directly, the performance criteria are the following: A number of laboratory and field tests should be conducted to demonstrate that the ammonium collected by the speciation monitor and the ammonium reference method (described above) are in good agreement. For ammonium the following two criteria must be met for the candidate method to be acceptable: (1) based on linear regression, the R^2 value must be ≥ 0.9; and (2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be 1.0 ± 0.1. At least 24-hour duration samples should be used for the regression analysis.

Carbon Sampling:

Accurate mass balance and quality assurance require determination of particulate (total) carbon, C_t, because of its abundance. Differentiation of organic, C_o, elemental, C_e, and carbonate carbon, C_c, provides more useful characterization for trends analysis and source apportionment. Semi-volatile species (C_{sv}) compose a fraction of the organic carbon which exists in the atmosphere with a partition between particle and gas phases. This partition is extremely complex, and depends on temperature, vapor pressures of individual species, the absolute and relative concentrations of all of the different species, and the amounts and types of adsorbing particle surfaces. The amount of the particulate phase of these species collected on the (first) filter depends on sampling conditions (e.g., filter face velocity). C_{sv} is defined as the carbon that is collected on sorbent traps downstream of the filters on conventional samplers.

Carbonaceous particles are commonly collected on a series of two quartz filters. Presumably, the first collects all of the particle phase carbon (elemental and organic) and a very small fraction of gas phase organic carbon. Likewise, the second quartz filter is supposed to collect only the same small fraction of gas phase organic carbon as collected by the first filter. Therefore, the concentration or particle phase organic carbon is calculated by subtracting the amount of organic carbon on the second from that of the first stage; however, this assumption does not take into account particle phase organic carbon that can volatilize from the first filter and gets collected by the second quartz filter. To the extent that this volatilization occurs, it results in underestimation of particle phase organic carbon.

The use of two quartz filters for organic carbon measurements is questionable. Eatough, et al. (1989) and Tang, et al. (1994) concluded that desorption of organic gases from particles on the first quartz filter was the dominant sampling artifact (negative artifact), while Turpin, et al. (1994) suggested that organic gases can be collected by the quartz filter (positive artifact). Turpin, et al. found that adsorbed organic gases represent up to 50% of the organic carbon measured on quartz filters in southern California. This study suggested that: (1) organic gas absorption (positive bias) was much larger than organic particle volatilization (negative bias); (2) as sample durations increase, the fraction of the adsorption bias decreases because the filter becomes saturated; and (3) the magnitude of the bias depends on the composition of the organic gases and particles present in the air sample. We currently do not know to what extent the use of the second quartz filter improves the accuracy of the organic carbon measurements. For this reason, the expert panel last year recommended to analyze only one of the first quartz filters in order to reduce analytical costs.

The diffusion denuder approach may be a sound approach to overcome the problems mentioned above. According to this sampling technique, gaseous organic compounds are removed using an activated carbon or XAD coated diffusion denuder. Subsequently, the particle-phase organic carbon can be collected downstream of the denuder using a series of two quartz filters. The first filter collects particle phase organic carbon, while the second collects the organic carbon volatilized from the first quartz filter. The total particle carbon concentration is determined by adding the concentrations of the first and second filter, respectively.

During the meeting Dr. Charles Lewis, of the EPA, presented some very interesting comparisons between the different candidate carbon samplers and a sampler which was equipped with an XAD-coated organic carbon denuder. Although these results were preliminary, it was clear that organic carbon concentrations obtained from the denuder/sampler were lower, on the order of 30-50%, than those from the candidate samplers. Organic carbon concentrations obtained from the candidate samplers were not in a very good agreement, with differences of more than 20-30%. It is possible that these discrepancies could have resulted from use of different face velocities across the sample filter(s). In last year's report, the panel had underlined the need for the samplers to employ filter face velocities similar to the FRM. In contrast to organic carbon measurements, elemental carbon concentrations obtained from the denuder/sampler and the candidate samplers were in a good agreement. It is worth mentioning that the collection efficiency and capacity of the XAD-coated organic carbon denuder is not yet well-characterized. Also, it is not known whether removing gas phase organics prior to particle collection enhances the volatilization of organic carbon from the quartz filter. Such an effect also would have resulted in lower organic carbon concentrations.

While these conclusions are drawn from the presentation of preliminary results, there is good indication that further development is required to have an adequately characterized, accurate sampler for carbonaceous aerosols; however, even such a technology were available, it is not certain that it would be appropriate. This is because it is not known whether the same amount of organic carbon is lost from the Teflon filter used as the collection medium for the FRM. Until we have a better understanding of organic carbon artifacts for the FRM and the speciation sampler (one quartz filter with no denuder) it will be unwise to recommend the use of the denuder for the speciation sampler. If negligible amounts of organic carbon are lost from the Teflon filter, then it will desirable to use an accurate speciation sampler. This will make it possible to achieve a better mass closure (the sum of particle constituents collected by the speciation sampler should be equal to the mass measured by the FRM); however, if substantial amounts of organic carbon are lost from the Teflon filter of the FRM, then it will be very difficult to achieve closure. Indeed, the majority of the data that exist suggests that it is difficult to achieve closure and that the discrepancies can go both ways (Andrews, et al., in press). This suggests that artifacts for the Teflon and quartz filters are not the same. This can be a problem for the speciation sampler because the FRM is by definition the "gold standard." For example, let us assume that a state finds out that organic carbon constitutes a large fraction of the fine mass. If the speciation sampler is accurate but a large fraction of the organic carbon is lost from the Teflon filter, then a sound source reduction strategy may not be successful in terms of enabling that state to comply with the standard. The same result will occur if the speciation sampler overestimates organic carbon but the FRM is accurate. These two extreme situations illustrate the complexity of the problem. One can imagine that the situation would be even more complicated if each method has a different bias. In such a case we would be faced with both scientific and legal problems.

The intent of this discussion is not to challenge the validity of the FRM. The gravimetric method was rightfully selected because the results of the epidemiological studies on which the standard was based used mass measurements obtained from gravimetric analysis. Our intent is to stress the need for developing accurate organic carbon sampling methods and to anticipate some of the challenges we will face as we proceed with the implementation of the speciation network.

Performance Criteria for the Organic Carbon Sampler (Including Organic Carbon Denuder):

Field and laboratory studies currently are being conducted in Seattle, WA, to evaluate novel sampling and analysis techniques for organic carbon. A number of speciation and research samplers have been selected for these tests. These investigations will test the capacity and efficiency of XAD and carbon-impregnated filter denuders. These studies are also designed to determine the contribution of semi-volatile organic carbon to the total organic carbon concentrations and its partition coefficient between the gaseous and particulate phases. The results of these studies should make it possible to develop performance criteria for organic carbon samplers, including criteria for evaluating the capacity and efficiency of the organic carbon denuders. Developing performance criteria for denuder performance evaluation is a challenging task for the following reasons: first, the denuder must perform for a large number of organic compounds (currently we have limited knowledge about the identity and concentrations of these compounds); second, the collected compounds on the denuder surface may be de-adsorbed (the rate of de-adsorption depends on organic compound, denuder capacity, total gas phase organic concentration, temperature, and relative humidity).

Sampling Strategy:

Recognizing that sampling must be initiated in the near future, the panel supports the use of the current state-of-the-art technology. Although it is necessary to start out using this current methodology, the speciation network should be open to new, validated, more accurate technologies as they become available. In contrast to compliance networks, the speciation network is not bound to use Federal Reference Methods which cannot easily be changed. The speciation network needs to have the flexibility to be updated as the technology and our understanding evolve. To carry this out we must first develop a set of performance criteria to evaluate current and future sampling technologies and second, we have to enhance our understanding of the biases of the different methods. This will make it possible to upgrade the network, when appropriate, without affecting the consistency of data.

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PARTICULATE MATTER ($PM_{2.5}$) SPECIATION GUIDANCE DOCUMENT

Third DRAFT

January 21, 1999

US Environmental Protection Agency
Monitoring and Quality Assurance Group
Emissions, Monitoring, and Analysis Division
Office of Air Quality Planning and Standards
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FOREWORD

This document contains information regarding program goals and objectives, and sampling equipment; guidance for sample collection, network design, selection of target analytes, quality assurance, and network operations for the $PM_{2.5}$ speciation program. The guidance provides managers, site operators, laboratory services support personnel, and regulatory compliance data analysts the information needed to implement their $PM_{2.5}$ chemical speciation program. Comments on this, the third draft version, are welcome. Please address comments to:

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1.0 INTRODUCTION

1.1 Purpose

The EPA anticipates that approximately 300[1] monitoring sites will be included in the full chemical speciation network. About 50 NAMS (National Ambient Monitoring Stations) sites will be used for determining long-term trends of selected $PM_{2.5}$ constituents and an additional 250 sites will be used to enhance the trends network and provide State and local agencies information for developing effective State Implementation Plans (SIPs). Approximately 50 of the 250 chemical speciation sites will be integrated with the related Supersites monitoring program which is discussed in Section 1.5.4 of this document. When States and local agencies implement their individual speciation networks, they will be given flexibility by the EPA in terms of selecting sites and sampling technology, sample collection period, site mobility, and identifying additional or alternative target analytes. As States consider integrating a portion of their speciation network with the designated Supersites, they are encouraged to develop partnerships with the academic community and related agencies responsible for specific Supersites studies.

The principal focus of this speciation monitoring guidance document is to provide an overview of the principles and procedures necessary for developing and implementing the chemical speciation network. The guidance is specific and prescriptive for the routine NAMS trends portion of the program, and more conceptual where addressing the additional 250 "State/local" NAMS sites. Much of the material contained in this document dealing with siting and sampling systems, sample and data analysis methodologies, and quality assurance for the NAMS trend sites can be adapted for use in State and local speciation monitoring networks. The intended target audience for this document includes managers, site operators, laboratory services support personnel, and regulatory compliance data analysts involved in $PM_{2.5}$ chemical speciation program implementation. The guidance is organized as follows:

- ***Section 1*** gives an overview of the program requirements, goals, objectives, related program efforts and highlights relevant documents and references;

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[1] 300 sites are used as an estimate of operational units for planning purposes. The actual number of sites and samplers will be influenced by network design plans submitted by State and Local agencies in relationship to the total resources budgeted for $PM_{2.5}$ chemical speciation.

- ***Section 2*** provides a description of data uses - NAAQS support and implementation plan development (trends, control strategies, model validation, source apportionment, and visibility);

- ***Section 3*** provides a discussion of particle size distribution, major constituents of $PM_{2.5}$ and potential emission source contributions;

- ***Section 4*** provides technical guidance for network design and gives a list of the 54 core NAMS chemical speciation trends sites;

- ***Section 5*** discusses sampling artifacts, interferences, limitations and some general difficulties in making ambient aerosol measurements;

- ***Sections 6 and 7*** provide a description of the principles, procedures, and equipment used to sample and analyze air sample filter deposits for particle species; and

- ***Sections 8 and 9*** provide a discussion of the quality system requirements, data validation, and records management.

1.1.1 Summary of Changes and Revisions

A summary of changes and additions made as part of this revision to the guidance include:

- A cross-link of $PM_{2.5}$ network elements and program monitoring objectives table is added as Table 1-1.
- A discussion of the State and local non-routine NAMS (approximately 200 sites) requirements is added as Section 1.2.2.
- A brief discussion of the Supersite satellite speciation sites (approximately 50 sites) and linkage to the $PM_{2.5}$ speciation program is added in Section 1.5.3.
- A discussion of the $PM_{2.5}$ speciation Data Quality Objectives developed for the routine NAMS trend network is included in Section 1.7.
- A significant revision and expansion of the Data Analysis Section 2.0 is incorporated.
- Changes to the proposed sites for the NAMS trends network as recommended by States, and indication of the proposed co-located sampling sites are made in Table 4-1. A revised map of the proposed sites is also included as Figure 4-1.
- A section on filter media artifacts is added as Section 5.8.
- The addition of Table 6-2 has been added, which provides a comparison of the candidate speciation sampling system designs and target analytes analyzed from each filter medium.

- Schematic diagrams for each candidate sampling system have been included as Figures 6-1 through 6-4.
- Revision of Figure 7-1, which is a flow diagram of the sample analysis Delivery Order.
- Significant revision of Section 8.0 on Quality System Requirements for Sampling and Analysis and Section 9.0 on Data Validation and Records Management.

1.2 Background

$PM_{2.5}$ chemical speciation is included in the monitoring requirements and principles set forth by the ***Federal Register*** (62 FR 38763), promulgated as part of the $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) review completed in 1997. As a requirement of this rule, a chemical speciation network of trends sites to provide a basic, long-term record of the characterization of the metals, ions, and carbon constituents of $PM_{2.5}$ is. About 50 sites will be used for determination of trends. These sites will be part of the National Air Monitoring Stations (NAMS) network and will provide nationally consistent data for assessment of trends. This network will serve as a model for other chemical speciation efforts and represents a small fraction of the chemical speciation effort that EPA expects to support with Federal funds.

EPA anticipates that approximately 300 sites will comprise the full chemical speciation network. In addition to the 50 NAMS sites for the trends network, another 250 sites will be implemented to enhance the required network and provide information for developing effective State Implementation Plans (SIPs). These sites will be allowed flexibility in terms of sampling frequency, site selection, site mobility, and addition of target species. For example, some areas may choose to focus on specific episodes or seasons, such as a winter time wood smoke problem. Retaining a minimum of 50 core sites with spatial and temporal consistency for long-term trends allows States to use the other 250 sites to address regional and local issues as needed .

At a minimum, the chemical speciation network will quantify mass concentrations and significant $PM_{2.5}$ constituents which include trace elements, sulfate, nitrate, ammonium, and carbon. This series of analytes is very similar to those measured within the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. Technical and practical rationale exist for merging monitoring efforts with IMPROVE. The technical connections between visibility and $PM_{2.5}$ aerosols are given in Section 1.5.5.

The ***Federal Register*** (62 FR 38763) describes the initiation of a $PM_{2.5}$ chemical speciation network of approximately 50 core NAMS for routine speciation monitoring. About twenty-five of the monitors are to be collocated at the Photochemical Assessment Monitoring Stations (PAMS) component of NAMS, with the remaining sites to be selected in coordination among EPA, Regional Office Administrators, and the States. EPA recognizes that some PAMS locations may not be prime sites for locating the monitors and will accept alternative monitoring plans with technical justification for alternate locations. Speciation samples will be collected every 3 days at the NAMS sites.

EPA does not believe that a single nationwide approach to speciation sampling and analysis is the best approach for all 300 locations. The EPA expects that most sites will follow a sampling and analysis program similar to the core NAMS sites; however, alternative speciation approaches for non-routine NAMS will be considered on a case-by-case basis through negotiation by State agencies with EPA Regional Offices and Headquarters. EPA encourages State and local agencies to consider additional chemical analyses beyond the constituents specified for NAMS. For example, detailed analysis for compounds comprising the organic carbon fraction could provide valuable insight into development of more refined source-receptor relations, particularly in areas with significant carbon based aerosols. EPA also encourages the use of continuous monitoring techniques to the extent possible. Recent advances in measurement technologies have provided reliable and practical instruments for particle quantification over averaging times of minutes to hours. Commonly used continuous particle monitors measure inertial mass, mobility, electron attenuation, light absorption, and light scattering properties. The EPA has prepared ***Guidance for Using Continuous Monitors in PM2.5 Monitoring Networks***, (U.S. EPA 1998b) to describe available continuous monitoring methods for suspended particles.

On July 18, 1997, the U.S. EPA promulgated a new NAAQS for particulate matter (PM) in 40 CFR Parts 50, 53, and 58, ***Federal Register*** (62 FR 38761, 62 FR 38763). The NAAQS applies to the mass concentration of particles with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$) and 10μm (PM_{10}). The suite of PM standards is revised to include an annual (long-term) primary $PM_{2.5}$ and a 24-hour (short-term) $PM_{2.5}$ standard. The NAAQS for $PM_{2.5}$ specifies the following:

- The three-year average of the annual mean of $PM_{2.5}$ concentrations is not to exceed 15$\mu g/m^3$. The average may be based on a single community-oriented monitoring site or the spatial average of community-oriented monitoring sites in a community monitoring zone (CMZ).

- The 3-year average of the annual 98th percentiles of twenty-four-hour $PM_{2.5}$ concentrations is not to exceed 65$\mu g/m^3$ at any population-oriented monitoring site in a Metropolitan Planning Area (MPA).

The deployment of the national $PM_{2.5}$ monitoring network is a critical component in the implementation of the new NAAQS. Substantial resources are being provided to support the national monitoring network of gravimetric $PM_{2.5}$ sites. This network will comply with the information provided in President Clinton's Directive of July 16, 1997 (62 FR 38421) and regulations provided in the ***Federal Register*** (62 FR 38761, 62 FR 38763). The data from this network will drive an array of regulatory decisions, ranging from designating areas as attainment or nonattainment, to developing and tracking cost-effective control programs.

Data derived from the $PM_{2.5}$ monitoring network include both aerosol mass measurements and chemically-resolved or speciated data. Mass measurements are used principally for identifying areas of attainment or nonattainment. Chemical speciation data serve the needs associated with assessing trends and developing mitigation approaches to reduce ambient aerosol emissions in relation to SIPs. These needs include emission inventory and air quality model evaluation, source attribution analysis, and tracking the success of emission control programs. These chemical measurements will also provide data to support regional haze assessments, which is also a primary objective of IMPROVE.

The overall data gathering needs for the $PM_{2.5}$ program are being addressed by the following objectives and schedules:

- Designation of Federal Reference or Equivalent Method (FRM/FEM) samplers to collect data for $PM_{2.5}$ NAAQS comparison purposes.

- Establishment of a $PM_{2.5}$ gravimetric and continuous monitoring network by December 31, 1999.

- Collection, measurement, and storage of quality-assured mass data beginning on January 1, 1999, to support NAAQS comparisons and regional haze assessments.

- Development of a national chemical speciation sampling and analysis program by October 1999.

1.3 Programmatic Requirements

The full chemical speciation program incorporates a balance of prescribed requirements, particularly for the routine NAMS, and the allowance for alternative sampling and analysis protocols for other sites within the program. It is not possible to anticipate the full range of sampling and analysis approaches State and local agencies may consider, especially in light of emerging technologies and forthcoming aerosol characterizations across different locations. In addition to providing specific guidance for routine NAMS, this document largely provides support or background information that can be utilized in formulating sampling and analysis plans for non-routine NAMS. A description of required sampling and analysis plan elements and procedures for submitting monitoring network descriptions for EPA approval is provided in Section 1.5.2.1.

State and local agencies should submit preliminary speciation sampling and analysis plans as part of all network description submissions to the appropriate Regional Offices. The due date for final network descriptions was July 1, 1998. Recognizing that little lead time exists between availability of guidance and the implementation dates, EPA expects final submission of the speciation network design plans by July 1, 1999. Furthermore, subsequent annual updates are required to be submitted by States as part of their annual State monitoring report due July 1, or an alternative date negotiated by the State and the EPA Regional Administrator, per the ***Federal Register*** (62 FR 38763).

1.4 Program Goals and Objectives

The overall goal of the $PM_{2.5}$ monitoring program is to provide ambient data that support the Nation's air quality program objectives. The entire $PM_{2.5}$ monitoring program includes a substantial mass network in addition to the subject speciation program. While the elements of this large program may be administered through individual mechanisms as shown in Table 1-1, all elements must complement one another in meeting multiple objectives as an overall integrated program. These overarching objectives are presented as context to a more detailed discussion of specific objectives addressed through the speciation program.

In prioritized order, the major programmatic objectives for the routine NAMS $PM_{2.5}$ chemical speciation include:

- annual and seasonal spatial characterizations of aerosols;
- air quality trends analysis and tracking progress of control programs; and
- development of emission control strategies.

Objective 1. Annual and Seasonal Spatial Characterizations of Aerosols

The analytes chosen, specific sampling periods and frequency, spatial resolution, and data accuracy affect the overall data use. The primary use of these data will be to develop general characterizations of aerosols across the major urban areas of the country, depicting seasonal and annual patterns. To the extent that networks include sites located in "transport" and/or "background" locations, similar characterizations of rural/regional environments, especially in combination with the IMPROVE program, are expected outputs. This objective serves an important need to gain understanding of the characterization of the aerosol nationwide. The following objectives all require this initial characterization step, which in practice translates into developing common spatial and seasonal/annual displays of aerosol components. Accordingly, this objective is the highest priority. An analysis of the speciation data may lead to the classification of air sheds into groups with similar particulate composition and concentration.

Table 1-1. Cross-link of Network Elements and Monitoring Objectives

Network Element	**$PM_{2.5}$ Monitoring Objectives**						
	NAAQS Comparisons	**Public Information /PSI**	**SIP Development (AQSM,EI,S-R)**	**Assess SIPs Trends**	**Health/ Exposure**	**Visibility Assess**	**Methods Testing**
FRM Mass (110 sites)	✔			✓	✓		
Continuous Mass (125 sites)		✔	✓		✓		
Speciation (50 NAMS Trends sites)			✓	✔	✓	✓	
Speciation (250 State sites)			✔		✓		✓
Speciation (100 IMPROVE sites)			✓	✓		✔	
Supersites (5-8 sites)			✓		✓		✓

This would allow the results of intensive studies to be more broadly applied to appropriate locations and reduce excessive redundancy of efforts on a national level.

Objective 2. Air Quality Trends Analysis and Tracking Progress of Control Programs

The use of observational data to play a central role in ongoing SIP improvement has been encouraged by the scientific community through the 1991 National Academy of Sciences Report on Tropospheric Ozone (NRC, 1991) and the forthcoming North American Research Strategy for Tropospheric Ozone (NARSTO) Assessment (Planned for release in 1999). The ability to detect trends in ambient concentrations that are associated with planned air quality control efforts must be incorporated in SIP assessments.

Objective 3. Developing Emission Control Strategies

A combination of prospective air quality modeling and semi- quantitative source attribution analyses will generate objective information for decision makers with underlying emission control decisions. Speciated data will be used in evaluating air quality model performance and fulfilling the requisite emission fields. A variety of source attribution techniques will be exercised. Recognizing the uncertainties and limitations in models, inventories, and sampling/analysis methods, this objective is of lower priority.

There exists a constant need to develop information that may lead to more definitive associations between adverse health impacts and specific aerosol properties. The speciation program provides greater chemical resolution than standard mass measurements and therefore, should provide data of value to health studies. Nevertheless, this routine speciation program must enlist input from health scientists to optimize overall value. For example, emissions from combustion processes include fine particles containing trace elements of varying toxicity. Information is needed which relate emissions characteristics from processes such as fossil fuel combustion, prescribed burning, and wild land fires, to urban and nonurban $PM_{2.5}$ concentrations and the magnitude of toxicity relative to the exposure of populations to such particles. In contrast, some $PM_{2.5}$ may not be harmful, such as the $PM_{2.5}$ transported from North Africa, which is thought to primarily be very finely ground limestone or calcium carbonate.

1.5 Program Components

The speciation program includes multiple elements with different, yet overlapping objectives. The major program components include:

- The 50 or so NAMS dedicated to characterizing major aerosol mass components in major urban areas of the United States for discerning long-term trends and providing an accountability mechanism to assess the effectiveness of emission mitigation programs;

- Approximately 200 dedicated State/local sites for evaluating source-receptor relationships in support SIPs; including more detailed characterizations, data for source attribution tools and evaluation of air quality simulation models and emissions inventories;

- Approximately 50 sites to be integrated as “satellites” to the Supersites program (see below);

- Between 5 to 8 Supersites areas identified to serve as scientific research platforms for addressing advanced monitoring technology assessments, investigating atmospheric processes and their impacts on public health and epidemiological issues; and

- Approximately 100 IMPROVE sites dedicated to assessing regional haze progress.

1.5.1 National Air Monitoring Stations (NAMS) Trend Sites

The Code of Federal Regulations (CFR), Part 58 contains the EPA ambient air quality surveillance regulations. Section 58.20 of 40 CFR, Part 58 requires States to provide for establishment of air quality surveillance systems as part of their State Implementation Plans (SIPs). The air quality surveillance system consists of a network of monitoring stations designated as State and local Air Monitoring Stations (SLAMS), which measure ambient concentrations of those pollutants for which standards have been established in 40 CFR Part 50. NAMS, which are a subset of SLAMS, and PAMS (Photochemical Assessment Monitoring Stations) must also meet the requirements of 40 CFR Part 58, Appendices A (Quality Assurance Requirements), C (Ambient Air Quality Monitoring Methodology), D (Network Design Criteria) and E (Probe and Path Siting Criteria).

The NAMS sites are dedicated to providing air quality trends over time and therefore, require consistent sampling and analysis protocols. The EPA expects that sites not designated as NAMS may conform to similar protocols. Recognizing that a national protocol for trends does not meet the specific needs for every location, the EPA will allow deviations from NAMS protocols at non-routine NAMS sites when adequate network descriptions and justification are provided in the plans described below (Section 1.5.2.1). The major requirements for each NAMS network description include:

- **Sampler type** - To ensure consistency, the EPA, through consultation with the speciation workgroup, will determine the sampler type(s) utilized at NAMS. The sampler will be a multiple filter device capable of collecting the target analytes listed below.

- **Sampling Frequency** - One 24-hour sample will be collected at each site every 3 days. As a result of feedback obtained from the NAS, EPA is planning to increase the sampling frequency to once per day at 10 core NAMS sites in year 2000.

- **Target Analytes** - Elements will be determined using X-ray fluorescence spectroscopy (XRF); major ions [sodium, potassium, sulfate, nitrate, ammonium] will be determined using ion chromatography (IC); and total, elemental, organic and carbonate carbon will be determined by thermal optical analysis (TOA).

1.5.2 State/Local sites

A substantial portion of the program lacks the prescriptive natural design elements associated with the NAMS to accommodate area specific tailoring of measurement programs, recognizing both the diverse character of aerosols across the United States and the benefit of regional and local knowledge and expertise. This element of the speciation program is the most flexible component of the entire $PM_{2.5}$ monitoring program. In broad terms, the principal objective of this program is to support the development of emission control strategies. Tasks associated with strategy development that require speciated data include airshed characterization (i.e., resolving aerosols into its spatial, temporal, chemical and size properties), operation of source attribution tools (e.g., CMB8, UNMIX), an array of observational analyses that help to understand transport phenomena and precursor limiting identification (e.g., ammonia versus nitrogen oxides), and evaluation of air quality stimulation models and its associated emissions input fields. This emphasis on SIP development is not intended to preclude other important objectives such as long term trends or ongoing assessment of strategy effectiveness. Indeed, in many cases State and local agencies may determine that available NAMS need very similar complementary sites given the spatial complexity posed by aerosols combined with a relatively limited 50 site national network. Nevertheless, the State and local sites need to address the near term development of control strategies when viewed more broadly across a matrix of principal objectives by program elements.

A measurement approach at the State/local sites that deviates from the NAMS is reasonable, given that the objectives for these sites are not identical to NAMS objectives. Therefore the overriding guidance for State and local agencies is to establish network-specific objectives which will drive the design of their sampling and analysis program. Any program proposed is required to meet the requirements described below in Section 1.5.2.1. Examples of measurement approaches that might be pursued by State and local agencies include:

- ***Increased temporal resolution of major components*** to support tools and studies that benefit from resolution greater than that typically provided by 24 hour filter-based samples in the NAMS; example needs include: elucidation of diurnal emissions profiles, evaluation of air quality simulation models, drive source attribution methods and support health effects and exposure studies. This increased time resolution could be accomplished through some combination of filter based methods which provide sample material for detailed laboratory analysis and emerging continuous techniques that provide high time resolution capability (e.g., 4 hour sampling period) with potentially limited labor requirements.

- ***Organic chemistry speciation*** to provide detailed information of the major fractions of total carbon particulate content. Detailed organic chemistry speciation is extremely useful for source apportionment techniques that relate emission source "markers" to ambient data, and by extension might provide important accountability markers for emissions control programs, and potentially provide support for a range of health effects and exposure studies.

- ***Exploratory "movable" sites*** to provide analyses for emissions strategy development. The NAMS are designed as fixed site platforms to provide consistent measurements over time. This approach is not necessarily optimized for objectives that attempt to characterize a spatially heterogeneous airshed as an initial basis for emissions strategy development. Therefore, consideration could be given to moving speciation samplers (filter based or continuous) across different platforms at sampling intervals that enable a collection of characterizations at several locations. Examples might include rotation across sites on a biweekly basis up to an annual basis depending on the specific objectives set forth. Flexibility to accommodate movable sampling schemes would open up collaborative possibilities with research organizations investigating health effects and exposure relationships among ambient concentrations and specific communities.

1.5.2.1 State and Local agency monitoring network descriptions and plan elements

The monitoring network descriptions should provide the speciation monitoring strategy and document any deviations from approaches used in the NAMS. Additional guidance is provided in the ***Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10}*** (U.S.EPA, 1997c). At a minimum, the following elements must be included and be reviewed each year as part of the annual network review.

- **Program Objectives -** A description of the basic technical objectives to be addressed. These objectives should go beyond very generic categories such as "develop control strategies" and address the specific technical needs/issues relevant to a particular area.

- **Sampling Network Design -** Location and description of sampling platforms, including additional collocated instrumentation as applicable.

- **Sampler Type** - Plans should provide the vendor name and instrument model selected. Preliminary plans may have to reflect generic descriptions of sampler types.

- **Sampling Frequency** - In many cases, sampling will be conducted with 24-hour sampling periods on an every 3-day or 6-day basis with exceptions for episodic coverage. These sampling schedules may be analyte or instrument dependent (e.g., use of continuous analyzers).

- **Target Analytes** - A description of the components to be analyzed, including associated sampling frequencies if analyte specific.

- **Sample Handling** - A description of the sample collection, transport, laboratory identification and archive procedures. Provide a detailed description (life history) of the sequence of filter collection, transport to analysis laboratory, and subsequent storage for future analysis.

- **Data Analysis** - This description should include initial data assessments at the sample level; spatial and temporal aggregation techniques; and more refined and exploratory analyses addressing stated program objectives.

- **Supersites Communications** - A description of mechanisms for interaction with Supersites activities, where applicable.

- **Program accountability** - A description of the program organizational structure which defines the persons responsible for management, implementation, and quality assurance of the network. Describe the management plan and accountability measures used.

1.5.3 Supersites

In addition to the “routine” chemical speciation network of NAMS trends sites and additional 250 sites for SIP development, the EPA anticipates that special study activities will enhance the information base for control strategy development (emission inventory and air quality model evaluation) and health related studies. As part of this initiative, EPA anticipates establishment and operation of the “Super Sites” network to provide resolved characterizations (time, space, composition) of aerosols as well as related precursor, intermediate, and sink species that lead to greater understanding of $PM_{2.5}$ (and ozone) formation and loss processes. These studies should not be confused with the $PM_{2.5}$ chemical speciation network and are intended to foster collaborative relationships among State/local agencies, academia and industry. The mechanisms for conducting these projects may include any combination of public/private partnerships, State/local partnerships with EPA, or partnerships with universities. Certain projects may consist of a series of special field studies aimed at supporting ongoing epidemiological studies, and others may be specific to a single area. Depending upon the study location, the EPA may be able to expand upon existing contractual and grant agreements as vehicles for this work. More information on this program is available in the document entitled: ***Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related to Airborne Particulate Matter***, (Albritton and Greenbaum, 1998).

1.5.4 Supersite Satellite Sites

The Supersites program and the speciation program operated by State and local agencies must be integrated as each provide valuable complements to one another. Among other objectives, the Supersites provide a means for testing new sampling technologies that eventually may be incorporated into the speciation network. The speciation network provides a needed spatial complement to Supersite areas that may focus on intensive measurement at a very limited number of locations. The EPA believes that the entire speciation program conceptually should be fully integrated with the Supersites program. Practical considerations and area specific needs of State and local agencies logically suggest various levels of coordination, ranging from a less resource demanding information and status communications approach for the 200 sites discussed in Section 1.5.2 to more explicit coordination for 50[2] satellite sites. The EPA is requesting that State and local agencies join in collaborative partnerships with the appropriate local oversight group responsible for Supersites activities. As of November, 1998, EPA has identified Atlanta, Georgia and Fresno/Bakersfield, California as the initial Supersite locations[3]. The level of interaction between State/local agencies and Supersite activities is subject to arrangements made by the relevant organizations. Chemical speciation plans submitted by State and local agencies that include a Supersite must address the communication and coordination mechanisms for liaisons across regulatory and Supersites groups. EPA expects that the ***minimum*** level of interaction would involve the sharing, review of and comment on relevant sampling and analysis

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[2] Counted within the 50 satellite sites are the 10 daily sampling trends sites that are earmarked for long term health panel studies.

[3] Supersite contacts for Fresno/Bakersfield include Dr. Marc Pitchford, U.S EPA (702-895-0432) and Karen Magliano (916-322-5350), California Air Resources Board; Atlanta (Dr. Ellis Cowling, North Carolina State University, 919-515-7564 and Dr. Paul Solomon, U.S. EPA, 919-541-2698).

plans with agreement reached between State/local agencies and relevant Supersites organization on the utilization of resources explicitly dedicated[4] to Supersites integration.

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[4] EPA grant guidance to Sates on the use of section 103 federal Grants will explain resource allocations set aside for integration with Supersites.

1.5.5 IMPROVE

The 40 CFR 51 Regional Haze Regulation, proposed in the ***Federal Register*** (62 FR 41137), includes visibility monitoring requirements. The technical connections between visibility and fine aerosols are solid and logically point to a comprehensive monitoring program that services both $PM_{2.5}$ and visibility assessments. The technical connections between the chemical speciation program and visibility monitoring are given below:

- Fine particles are responsible for nearly all visibility degradation.
- Visibility extinction budgets are calculated through speciated aerosol measurements; the measurement and analysis approaches are virtually the same for the $PM_{2.5}$ speciation program and IMPROVE.
- Spatial scales associated with visibility measurements (regional) are frequently the same as spatial scales associated with background and transport $PM_{2.5}$ measurements (regional, urban). It is important to consider including data collected under the Regional Haze program as part of the $PM_{2.5}$ data analysis activities.
- Sources that affect visibility are the same sources that affect $PM_{2.5}$, and control programs that influence visibility also influence $PM_{2.5}$ levels.

Clearly, the technical justification exists for merging these monitoring efforts. Similarly, there is value to combining resource planning and network deployment efforts simultaneously as combined planning is far less burdensome than separate efforts. The IMPROVE chemically speciated data will also be useful to the overall $PM_{2.5}$ program. In fact, the nation is currently in the unusual position where aerosols are better characterized in rural/remote environments relative to urban and populated areas due to the effectiveness of the IMPROVE program.

1.6 Data Use and Analysis

The expectations for data emerging from the routine NAMS program should be put in context. In communicating the need for gaining a gross understanding of aerosol concentration, composition, and distribution across the United States, the inherent limitations of such a program are not obvious. As one proceeds down the list of priorities, important limitations arise. For example, the lack of time resolved measurements constrains the ability to interpret air monitoring data with air quality models and emission estimates, both of which incorporate strong diurnal trends. Clearly, the effectiveness of assessment tools increases with more resolved information (space, time, composition, size, phase, etc.). The aggregate approach (24-hour sampling, 1 size fraction, 1 vertical plane) across all aerosol properties is an acknowledged current shortcoming. This program must reflect a reasonable balance that considers available resources, technological limitations, and other efforts. The EPA recognizes that, in future years, there may be a need to adjust the objectives and requirements for speciation sampling and analysis. Just as control programs need to be assessed periodically, a major data acquisition program should undergo periodic assessments as well. However, there must be careful balance between having a flexible monitoring network which is able to adjust to new technologies as they arise, and the problematic issue of wide scale implementation of innovative technologies with little cohesion between data gathering activities.

Guidance on how to organize and analyze the data is given in Section 2.0. Software applications are needed to easily organize and display the data in meaningful ways which might be of great use in identifying and understanding significant $PM_{2.5}$ characteristics and trends. Personnel resources will need to be identified in order to properly analyze the data.

Within the current network design framework, data collected every third day within the NAMS sites will have limited use for epidemiological studies. A majority of the sites would have to be located in highly populated areas with greater than 500,000 inhabitants, which are more appropriate for health assessment studies. For the longer term, when continuous methods that provide equivalent data become available, the network can be upgraded. As these methods are implemented, they will also provide valuable diurnal information while reducing sampling and analysis costs.

1.7 $PM_{2.5}$ Speciation Data Quality Objectives

An important concern in the collection and evaluation of ambient air monitoring data is the level of uncertainty. Uncertainty arises due to temporal and spatial variability in the ambient air, variability in the samplers, and variability in the laboratory analyses. The data quality objective (DQO) process, a strategic planning approach, is used to structure the $PM_{2.5}$ speciation data collection activity. The DQO process provides a systematic procedure for defining the criteria that the $PM_{2.5}$ speciation data collection design should satisfy, including when to collect samples, where to collect samples, how many samples to collect, and the tolerable level of decision errors. By using the DQO process, EPA assures that the type, quantity, and quality of the data are appropriate for the intended application, while guarding against committing resources to data collection efforts that do not support the program objectives.

For the $PM_{2.5}$ speciation monitoring network, the DQO process will proceed down two tracks due to differing primary objectives. For the NAMS sites, the primary objective is to determine trends on the national level. For the remaining 250 sites, objectives may vary, depending on the regional and/or local data needs. For example, a State with high concentrations of $PM_{2.5}$ might consider the primary objective to be the characterization of the fine particulate aerosol to assist with the development of control strategies, whereas a State with Class I areas might consider the primary objective to be measuring trends in visibility. For each objective, the DQO process might result in different optimal monitoring designs and tolerable errors; therefore, DQOs will be developed with both objectives in mind.

The Monitoring and Quality Assurance Group (MQAG) within the Emissions, Monitoring, and Analysis Division (EMAD) of the OAQPS has initiated an effort to ensure that the data collected by the ambient $PM_{2.5}$ speciation network is of a sufficient quantity and quality to support the intended uses of the data. This effort includes development of DQOs for the NAMS sites dedicated to measuring national trends in the $PM_{2.5}$ species (U.S. EPA, 1998c) and a blueprint of the DQO process for the remaining 250 sites (expected to be available May 1999). A speciation DQO Work Group was developed, and a discussion of the DQOs developed for the trends sites is presented below.

Generally, the DQO process is used to determine the sampling frequency, location of the samples, and tolerable measurement errors needed to achieve desired levels of errors associated with decisions that will be based on data collected by the $PM_{2.5}$ speciation trends sites. Most of the monitoring characteristics have already been established for the trends network as the result of regulations or recommendations from the $PM_{2.5}$ Speciation Expert Panel (Koutrakis, 1998) and $PM_{2.5}$ Speciation Workgroup. Thus, the issues to be addressed with this DQO process included (1) estimating the decision errors resulting from the characteristics of the network, (2) recommending changes to the sampling plan if the resultant decision errors were unacceptably large, and (3) prescribing required measurement precision.

The following items summarize the monitoring characteristics that had been established for the trends network prior to the beginning of the DQO process.

Number of sites: The $PM_{2.5}$ speciation trends network is to consist of approximately 54 sites as proposed by the EPA.

Location of sites: Approximately 25 of the sites are to be located in PAMS areas. The remaining sites are to be selected in coordination among the EPA, Regional Offices, and the States and local agencies. Twenty-four of the 54 proposed sites are in PAMS areas.

The rationale for the selection and the resulting locations of all the sites are documented in Section 4.0.

Sampling frequency: The $PM_{2.5}$ Speciation Expert Panel and EPA have determined that the sampling frequency for the trends sites should be once every 3 days which is documented in ***Summary of the Recommendations of the Expert Panel on the EPA $PM_{2.5}$ Speciation Guidance Document*** (Koutrakis, 1998).

Sampler type: The sampler will be a multiple filter device that collects 24-hour integrated samples.

Analytes to be measured and the method of measurement: The species to be measured include:

- elements Al through Pb using X-ray fluorescence spectroscopy (XRF),
- major ions (sulfate, nitrate, ammonium, sodium and potassium) using ion chromatography (IC), and
- total, elemental, organic and carbonate carbon using thermal optical analysis (TOA).

The DQO process incorporates input from a planning team consisting of program staff, technical experts, managers, a quality assurance/quality control advisor, and a statistician. This enables data users and relevant technical experts to specify their particular needs prior to data collection. These decision makers decided that the primary objective of the trends component of the $PM_{2.5}$ speciation network is to detect trends in individual component species on a site-by-site basis. Specifically, the decision makers wanted to be able to detect a 3-5% annual trend (increasing or decreasing) with 3-5 years of data.

Although the data collected by the $PM_{2.5}$ speciation network will be invaluable for a multitude of data analyses, the detection of trends is the primary objective of the NAMS portion of the $PM_{2.5}$ speciation network. The decision makers and the $PM_{2.5}$ Speciation Expert Panel concurred with this primary objective and therefore is the one on which the DQOs were based. This means that the tolerable decision errors will be based exclusively on trends analyses, even though other data uses might have larger resultant decision errors. The need for accurate trends at the site level is due to the manner in which the trends will be used. The decision makers decided that trends are needed to evaluate the long-term effectiveness of control strategies. Incorrect estimation of trends may lead to incorrect assessments about the effectiveness of implemented control strategies. Since control strategies likely will be developed, applied, and/or evaluated at the Metropolitan Statistical Area (MSA) level and given that at most one trend site will be within an MSA, the trends need to be accurate on a site by site basis. Additionally, the decision makers thought that regional or national trends would be difficult, if not impossible, to interpret because of the geographical variability in meteorology, species composition, and control strategies.

Variation in meteorology can mask or attenuate trends that are due to changes in emissions. Given the intended use of the trends data, the decision makers decided that meteorological variation needs to be removed before the trend analysis is performed. That is, the trends in which the decision makers wanted to have the specified decision errors are ones for which the impact due to variation in meteorology has been removed. The details for how this adjustment was accomplished are included in the appendix. Basically, a seasonal component based on the number of days into a year was added to the statistical model of the data.

Lastly, the development of the DQOs was done for four analytes, those being sulfate, nitrate, total carbon, and calcium. The target analytes of interest for the speciation trends sites were selected to include those which have been historically measured within the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. To ensure that data from the speciation trends sites could be compared with IMPROVE data sets, the trends DQO development considered an analysis of the ability to sample and measure selected analytes which are thought to be major components of aerosols collected in both networks (sulfate, nitrate, and total carbon) and whose concentrations could be expected to vary with the implementation and effectiveness of emissions controls. Sulfate is a direct indicator of anthropogenic emissions, primarily from fossil-fuel fired combustion sources and can be effectively measured by most fine particulate sampling systems. Sulfate levels are usually the highest in the eastern United States. In contrast, nitrate is an indicator of secondary atmospheric aerosol formation resulting from nitrogen oxides emissions and is somewhat difficult to quantitatively sample because of volatilization artifacts which can occur in many sampling systems. Nitrate levels are usually the highest in the western United States. Total carbon in fine aerosol particles is associated with wood combustion and mobile source emissions and also represents an analyte which has the potential for either positive or negative sampling artifacts. Calcium was included since it is an element which is generally associated with non-anthropogenic emissions such as windblown soils, mineral materials, and dusts. Calcium is usually assumed to occur in particles predominantly greater than 2.5 microns. Therefore, fine particulate calcium should be present at low background levels and represents an aerosol constituent which is not expected to vary significantly with source emissions controls implementation.

Data from the IMPROVE program was used to estimate the variability likely to be observed in national $PM_{2.5}$ speciation measurements. This was done because each of the analytes to be monitored at the routine NAMS sites is currently being monitored in the IMPROVE program and the analytical methods used in the IMPROVE program are similar to those to be used in the national program.

The national chemical analysis methods for calcium and total carbon differ from those used in the IMPROVE network. The IMPROVE network uses proton induced X-ray emission (PIXE) to analyze the PTFE filter for calcium and thermal optical reflectance (TOR) to analyze the quartz filter for total carbon. Due to the lack of long-term data collected using EDXRF and TOA, it is an assumption of this DQO process that EDXRF and PIXE have similar percentages of non-detects and levels of precision and similarly that TOR and TOA have similar percentages of non-detects and levels of precision. This assumption is questionable for calcium based on a recent article that indicates that the detection limit for calcium using XRF may be 5 times that for PIXE, 2.4 ng/m^3 for XRF versus 0.5 ng/m^3 for PIXE (Nejedly, 1998). The recent literature supports the assumption regarding the comparability of TOR and TOA (Birch, 1998).

An additional difficulty in using the IMPROVE data for the national trend network planning is that the IMPROVE sites, by design, are predominantly located in rural areas. This will not be true of the NAMS sites. Anticipated differences in variability of speciated $PM_{2.5}$ data between rural and urban sites was factored into estimates obtained based on the IMPROVE data. This was accomplished by analyzing the data from the urban IMPROVE site located in Washington DC, the only long-term urban IMPROVE site.

Descriptive statistics were calculated and models fitted to assess seasonal trends, time trends, auto-correlation, and variability of sulfate, nitrate, calcium, and total carbon measurements in the IMPROVE data on a site by site basis. The methods and models used to describe the IMPROVE data are documented in the ***Data Quality Objectives for Detection of National Trends in Speciated Data*** (U.S. EPA, 1998c). Table 1-2 presents statistics on the geometric mean concentrations, measurement error rates, and percentages of non-detects.
The measurement error rates and percentage of non-detects are quantities provided from the IMPROVE database. Generally, small non-detect percentages were observed for each of the species across the network. This suggests that the ability of laboratories to detect concentrations of each of the species at levels actually present in rural areas is good. Since urban concentrations are anticipated to be higher than rural concentrations, inability to detect species should not be an issue. Note that the measurement error is small compared to the variability remaining after fitting the model. This can be seen by comparing the coefficient of variation in the second part of the table (measurement error) with the coefficient of variation in the first part of the table (variability remaining after fitting the model).

The decision makers ($PM_{2.5}$ speciation DQO Work Group) agreed that the objective of a 3-5% trend per year needs to be detected with 0.8 power within 3-5 years of initiation of sampling. Table 1-3 summarizes the percent reductions (or increases) that can be detected with 0.8 power under a variety of assumptions. Based on this information it was concluded that even with 1 in 3 day sampling, five years of data will only detect 5% reductions (or increases) in some pollutants. *Daily sampling provides little advantage in trend detection over one in three day sampling relative to the increased cost.* Analyses indicated that power is relatively robust to

Table 1-2
IMPROVE Data Summary

Parameter	Concentration ($\mu g/m^3$)		Measurement Error (Average coefficient of variation)		Percentage Non-Detects (%)	
	Mean	**Range**	**Mean**	**Range**	**Mean**	**Range**
Sulfate	1.357	0.246-4.932	0.055	0.036-0.124	0.293	0.000-3.343
Nitrate	0.261	0.029-1.321	0.133	0.046-0.502	4.118	0.000-37.021
Calcium	0.026	0.008-0.083	0.089	0.062-0.129	2.078	0.000-13.566
Total Carbon	1.295	0.342-4.119	0.176	0.064-0.421	0.000	0.000-0.000

changes in measurement error up to 2 times IMPROVE's rate. This is because measurement error is small compared to variability left unexplained by the seasonal and time trend component model. Analyses depicting the effect of measurement error if a better data model were developed were evaluated. However, it is anticipated that measurement error may be more critical for uses of the speciated $PM_{2.5}$ data other than trend detection. Therefore, it is advantageous to control measurement error at levels comparable to the IMPROVE data given in Table 1-2. Thus, one in three day sampling for five years with measurement error rates similar to IMPROVE's is recommended for trend identification.

Table 1-3
Increase or Reduction in Power for Two Sampling Periods and Three Sampling Frequencies

Species	Daily Sampling		One in Three Day Sampling		One in Six Day Sampling	
	Three Years	**Five Years**	**Three Years**	**Five Years**	**Three Years**	**Five Years**
Sulfate	7.5	3.6	8.6	4.1	10.9	5.2
Nitrate	12.2	5.9	13.0	6.3	15.3	7.4
Calcium	7.4	3.5	8.5	4.1	10.9	5.2
Total Carbon	5.5	2.6	7.3	3.4	10.0	4.8

1.8 Related Documents and References

An expert panel met on May 12-13, 1998, in Seattle, WA, to review an earlier draft of the EPA guidance document for chemical speciation which was also provided for public review and comment through the Internet at the EPA Air Monitoring Technical Information Center (AMTIC) $PM_{2.5}$ bulletin board. The panel represented nationally-recognized expertise in fine particle and aerosol sampling and analysis as well as linkage to the assessment of the role of aerosol chemical components to health effects research. Other participants in this meeting included the EPA Speciation Workgroup and representatives from several States.

The panel reviewed EPA's monitoring strategy, selection of target analytes, samplers, and analysis methods. A summary of the panels findings and recommendations can be found on the AMTIC bulletin board. Specific recommendations, such conducting a speciation sampler intercomparison study, have been addressed and are discussed in this current version of the guidance document.

The ***Guideline on Speciated Particulate Monitoring*** prepared for EPA by the Desert Research Institute is forthcoming and will be included as an addendum to this guidance document when available. It includes a detailed discussion on the physics and chemistry of atmospheric particles, particulate samplers, laboratory analysis methods, and measurement artifacts and interferences. Other documents are listed below and in the references given at the end of this document.

Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10} (U.S. EPA, 1997a).

Quality Assurance Guidance Document 2.12: Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods (U.S. EPA, 1998a).

Guidance for Using Continuous Monitors in $PM_{2.5}$ Monitoring Networks (U.S. EPA, 1998b).

Visibility Monitoring Guidance Document, Draft (U.S. EPA, 1998d).

Air Quality Criteria for Particulate Matter (U.S. EPA, 1996a)

EPA Air Monitoring Technical Information Center (AMTIC) $PM_{2.5}$ bulletin board is also accessible via the Internet at: **http://www.epa.gov/ttn/amtic/amticpm.html**

2.0 DATA ANALYSIS

The $PM_{2.5}$ program objectives described in Section 1 will be supported through various data analysis and interpretation activities. In recent years, increasingly greater reliance has been placed on observational data for air quality planning needs beyond NAAQS comparisons; this is especially true of the type of data that will be produced in the $PM_{2.5}$ speciation networks. Many of the recommendations from the NAS Report on Tropospheric Ozone (NRC, 1991) reflect the need to better integrate observations into air quality planning rather than rely completely on emissions-based air quality modeling approaches. That message is being reinforced in the current ozone science assessment conducted through NARSTO; their report is scheduled to be released early in 1999. A new approach for integrating observations in air quality planning through continuous iterative assessments which revisit program objectives and adjust, where practical, the implementation strategies is described in U.S. EPA, 1995a. Observations represent our best attempt at defining truth and must be a critical component of planning. Planning must be an iterative process given the current and even more substantial future system uncertainties.

A wealth of new data on $PM_{2.5}$ constituents will be made available on a routine basis with the implementation of the speciation networks. Previously, detailed aerometric data of this type have only been collected on a national scale in rural environments (i.e., CASTNet and IMPROVE) or as part of special studies of just a few days or months duration. The availability of routinely collected speciation data will enable a range of analyses which have not been possible until now. Results of these analyses are anticipated to provide air quality managers with valuable information on:

- The important chemical constituents and associated emission sources of fine particulate and their influence on elevated $PM_{2.5}$ mass levels.
- Trends in mass component concentrations and related emissions, including from specific source categories.
- Effectiveness of implemented control strategies.
- Possible errors in emission inventories, emission factors, and speciation profiles .
- The relative impact of PM components and precursors transported into and out of an air basin from upwind or downwind sources.
- The effects of atmospheric constituents on visibility impairment and regional haze.
- Population exposures to certain toxic components of $PM_{2.5}$.

Insightful analysis of speciated PM data requires a clear understanding of the goals of the analysis (i.e., a precise statement of the questions to be answered by the investigation), familiarity with the range of possible analysis techniques and their individual advantages and limitations, and the ability to properly interpret the results. Detailed information of this type is beyond the scope of this Section. Instead this Section seeks to illustrate the intended value of the speciation measurements, to present a framework for data interpretation and use, to contrast the roles of States and EPA in analysis activities, to highlight some of the relevant tools, and to accent the link between data use and network design.

2.1 Data Analysis Guidance and Training

EPA has established a ‘virtual’ work group on the Internet to facilitate the development of practical guidance using real world examples for the overall $PM_{2.5}$ program. State and local environmental agency staff as well as consortiums and other environmental groups (such as NESCAUM, MARAMA, WESTAR, LADCO, A&WMA, and STAPPA/ALAPCO) are encouraged to participate in this web-based group; the Internet URL is

http://capita.wustl.edu/PMFine/.

In the virtual work group, analysis topics are broken into the following components: Resources, Status & Trends, Attainment Issues, Source Attribution, and Control Strategies. Subgroups have been (or will soon be) formed for each of these subjects areas. As a product of the ‘virtual’ collaborative effort, EPA intends to issue initial $PM_{2.5}$ data analyses guidance in the form of a workbook in late summer 1999. The work groups or hybrids of them will continue to function, however, and the web site and workbook will continue to evolve over time. A dynamic web-based version of the workbook also will be maintained. An initial workshop addressing the overall $PM_{2.5}$ program objectives and introducing the initial draft guidance is tentatively scheduled for September 1999; feedback and additional input will be solicited on the guidance document at that time. A series of subsequent regional based workshops are envisioned for FY 2000 and 2001. Demonstrations and training for analysis tools will be an integral part of all the workshops; more detailed videotaped broadcasts are being considered. An additional EPA web site has been initiated at

http://www.epa.gov/oar/oaqps/pm25/

to help disseminate vital program information (such as guidance and on training opportunities). This site consists of topics such as General Information; Publications, Papers and Reports; and Data Analysis Support. The site will provide direct links to PAMS data analysis, Toxics data analysis, and the Virtual Work Group web site described above.

The purpose of this "Data Analysis" section is to present a framework for data interpretation and use. Accordingly, portions of it draw strongly from the current working outline of the virtual work group workbook. The forthcoming detailed "guidance" is not intended as a prescriptive cookbook which the States are dictated to follow. Rather, EPA seeks to present a variety of ideas of how the $PM_{2.5}$ data can useful for developing and assessing emissions control strategies. Although many apparently disparate methods address similar objectives, the use of redundant techniques with resulting agreement leads to further confidence in the analytic methods and conclusions.

2.2 General Conceptual Flow of Data Analysis Activities

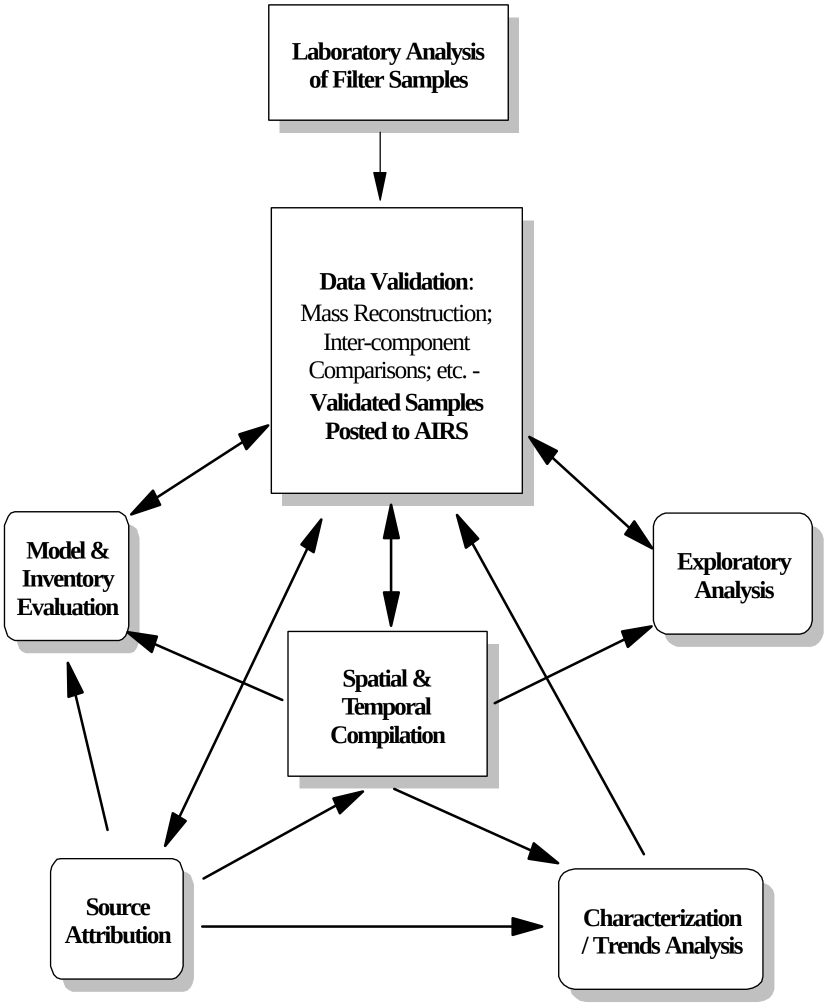

Figure 2-1. Data analysis flow diagram

Common data processing steps for speciated aerosol data are depicted in Figure 2-1. Note that this flow is conceptual and for illustrative purposes only; variations (additional paths, diverse breakouts, etc.) are possible. Following laboratory analyses of filter samples, the speciated data will be validated. A core check of data reasonableness is then developed through mass reconstruction. In this process, the total $PM_{2.5}$ mass is reconstructed by aggregating individually measured components. Typically, this initial reconstruction for a particular sample reflects an atmospheric composition for a single 24-hour period in one location. The result often is simply tabulated or presented graphically to illustrate the fractional contributions of individual components. This step incorporates some internal quality control. Reasonable comparisons (acknowledging discrepancies due to sampling and filter artifacts) to gravimetric mass should be expected, ideally resulting in greater confidence that the laboratory analyses and associated filter handling have acceptable system accuracy. Inter-component comparisons should also be performed to further affirm data validity. After validation, the data stands as an end product for exploration and policy relevant analyses (e.g. source attribution evaluations or event based emissions inventory comparisons) or can be expanded over greater spatial and temporal frames for further analysis. The time and spatial scales of interest partially dictate the degree of aggregation.

The annual $PM_{2.5}$ standard suggests that yearly aggregation of data might drive many analyses. However, the principal SIP modeling and emission inventory tools operate over highly resolved time periods (e.g., hourly intervals). Accordingly, both time aggregate and time resolved applications should be performed. Relatedly, the expansive regional domains of air quality models, and the recognition of interacting spatial scales, suggests that many analyses should consider multiple monitoring locations. Spatially, temporally, and/or spatially-and-temporally aggregated data are necessary for trends evaluations and are also valuable for inventory and model evaluations. Ambient data apportioned to sources can help quality assure emission inventories and models. Trends in source-apportioned data are beneficial for evaluating control strategy effectiveness. Exploratory analyses are performed on individual samples and aggregated data. Feedback paths to data validation are present from every analysis activity since in-depth evaluations almost always lead to further refinement of the raw data. And, refinements to raw data always should be carried back to AIRS. The specific data analyses activities are described in somewhat more detail in the next section.

2.3 Data Analysis Activities

The data collected by an ambient air network are of little use unless analyzed. Thus, data analysis activities should be an integral part of a State's $PM_{2.5}$ Implementation Plan. Although data collection precedes analysis and interpretation, an understanding of the eventual use of the data must drive the design of the data collection program. This is especially relevant to the non-routine portion of the speciation network which is more flexible. Additionally, analyses will be performed at various levels including State and local agencies, consortiums, Regional Offices, ORD, and OAQPS/EMAD.

All of these need to be coordinated to ensure the most efficient and appropriate use of the data to meet the specified program objectives. A brief description of the currently-envisioned potential uses for speciation data and related activities are discussed below. Note that there exists a significant amount of overlap among the listed topics and that different breakouts could be equally appropriate. Substantially more detail will be provided in forthcoming guidance.

2.3.1 Data Validation

Although by itself it is not a major policy-relevant data analysis activity, data validation is a requisite building block for all analyses. The quality and applicability of data analysis results are directly dependent on the inherent quality of the raw data itself. Although EPA and reporting organizations will employ rigorous quality assurance and validation measures to insure optimum data quality, errors are still bound to pass through the system. This is especially likely with the new and complex speciation monitoring and sample analysis methods being employed. Quality system requirements for $PM_{2.5}$ speciation sampling and analysis are documented in Section 8 of this document and data validation is addressed in Section 9. In that Section, a four-level data validation system is suggested for the speciated data. The full-service contract laboratories will conduct at least a Level I validation on samples they analyze. To assure national consistency, States will submit (at a minimum) samples from the trend sites to these contract labs. States will be responsible for the additional levels of validation for the samples submitted to the national laboratories. For samples not submitted to the labs, States will be responsible for all levels of validation. EPA is sponsoring development of a software data validation tool, called PMDat, to assist with data validation tasks. This software will be modeled after the VOCDat package which is currently in use by many PAMS reporting organizations to validate their volatile organic carbon (VOC) species data. PMDat will utilize time series, scatter, and ‘fingerprint plots’ to help identify suspect data points. PMDat will also derive a ‘reconstructed’ mass total for comparing to various other mass measurements (e.g. gravimetric mass total, collocated FRM, collocated PM_{10},). PMDat is not the only data validation alternative. Commercially off-the-shelf (COTS) statistical software packages (e.g. SAS, S-PLUS, Statistica, etc.) and custom-coded applications can also be used to perform similar validation tasks, as well as additional types of QA checks such as spatial mapping and pure statistical ‘outlier’ tests (e.g. standard deviations or confidence intervals). Data validation methods documented in the PAMS 1996 Data Analysis Results Report (EPA, 1996c) for PAMS data are equally relevant for the data that will be generated at the $PM_{2.5}$ speciation sites. EPA will issue periodic reports describing the quality of the data collected by the $PM_{2.5}$ network.

2.3.2 Exploratory Data Analysis

There is a fine line separating data validation and data exploration. Although there are differing goals for the two tasks (i.e., the goal of validation is to remove invalid data or qualify suspicious data; the goal of exploratory analyses is to understand the data set and problem better), the methods incorporate similar attributes. One way to explore a particular data set, is simply to plot the raw data in a variety of standard formats (temporally/seasonally, species-to-species, species-to-total, etc.) such as mentioned in 2.3.1 above. Thus, the PMDat package will be a viable tool for some types of exploration. In addition to PMDat, EPA also has developed AMDAS to facilitate exploratory analysis. AMDAS (Ambient Monitoring Data Analysis System), is an enhanced and renamed version of the existing PAMSDAS (PAMS Data Analysis System) package. Release of the AMDAS tool is anticipated in January, 1999. The AMDAS / PAMSDAS tools are add-on modules for the COTS statistical package S-Plus.

Exploratory analysis can include initial probes or tests of more refined objectives-based hypotheses. Exploratory analyses can be viewed as an activity area wherein ideas develop and evolve to inform other analysis areas such as validation or compliance-type issues. One example of a question that needs to be explored early in (if not prior to) the speciation program is, can we we reconstruct $PM_{2.5}$ mass concentrations from speciated concentration data?" Once we know the 'answer' to this exploratory question, we may be able to construct a validation test to identify questionable or invalid data points. Additional analysis of cases where reconstructed mass does not compare well with FRM or other mass measurements (using previously determined formulae) can perhaps point to unusual compliance-related conditions that exacerbate $PM_{2.5}$ loading. Other examples of exploratory questions that will need addressed through speciated data include:

- $PM_{2.5}$ chemical characterization: What are the chemical components of the fine particulate matter?

- $PM_{2.5}$ physical characterization: What is the particle size and morphology comprising the fine particulate matter?

- Pollutant interactions: What are the interactions between $PM_{2.5}$ versus ozone, wet deposition, toxics, greenhouse gases. What are the interactions between VOCs and organic aerosols?

- What are the meteorological conditions that are conducive to $PM_{2.5}$ formation, accumulation, and removal.

- What are the impacts of natural sources of $PM_{2.5}$, such as, biogenics, wildfires, dust on measured levels of $PM_{2.5}$ constituents?

- What are the origins and potential controls of organic aerosols?

- What are the fundamental differences in formation, accumulation, and removal of $PM_{2.5}$ in the Eastern U.S. versus the Western U.S?

There are several important points that should be made about the above "idea" list:

1) Exploratory analyses spans all facets of data analyses and data utilization.
2) A logical extension of exploratory analyses is data characterization. Characterization generally entails spatial and/or temporal aggregation, or even further types of binning such as by meteorological conditions. Characterization establishes data expectations. It is a fundamental and requisite first step to accomplishing subsequent data objectives such as trends evaluations and checks of control strategy effectiveness. A baseline <u>must</u> be establish before comparisons can be made against it. $PM_{2.5}$ data characterization is discussed further in Section 2.3.3
3) The EPA prescribed speciation trend network <u>will not</u> provide all the information necessary to adequately evaluate even the short (albeit ambitious) list above. Particle size distribution data, for example, will not be determined routinely. However, this information will enhance our understanding of the particle size and morphology comprising the fine particulate matter and such understanding might lead to improved source apportionment techniques which might aid in the development of attainment strategies. States will need to design complementary non-Trend networks that have an objective-based design. The EPA-stipulated number (of 250 non-trend sites) is not 'etched in stone'. EPA will consider State plans that have augmented sampling at Trends sites in leu of a separate 'non-Trends' site. Special studies, especially in the early implementation period may also be favorably viewed. Supersites can also play a role with specialized, higher resolution, and/or more intensive monitoring, however, that program will only encompass a handful of sites and only operate for a limited time frame.

2.3.3 Data Characterization and Trends

The range of this analysis activity includes the spatial, temporal, and compositional patterns of $PM_{2.5}$ concentrations and the influences that changes in meteorology or emissions may have on these patterns. As mentioned in Section 1, one of the primary objectives of the $PM_{2.5}$ chemical speciation program is to provide "Annual and Seasonal Spatial Characterizations of U.S. Aerosols". Although little is known about the chemical characterization of the $PM_{2.5}$ mass data in urban areas, there are an increasing number of literary references. The guidance will document some of these historic, recent, and ongoing studies, but unless the information presented (or other current analyses produced by or for a reporting organization) is particularly relevant to a given area, States should 'start from scratch' with the new speciation program data. The Trends sites should be given the highest priority for initial characterizations since 1) they will be on-line first, and 2) the monitoring devices will all be comparable (hence facilitating site-to-site and area-to-area comparisons). Characterizations for the speciation data will frequently concentrate on the relative contribution of species details to total mass. ‘Seasonal’ characterizations can be generated for calender quarters, traditional season definitions (fall, winter, summer, spring), or other time periods found to exhibit similar characteristics. The calender quarters (Jan-Mar; Apr-Jun; Jul-Sep; Oct-Dec) are important since the annual $PM_{2.5}$ mass NAAQS is based on a weighted quarter average. Special, approved monitoring exceptions should be reflected in the levels of aggregation.

The second ranked speciation program objective (as designated in Section 1) is “Air Quality Trends Analysis and Tracking of Control Programs”. The annual trends in $PM_{2.5}$ constituents will be analyzed to track progress in solving $PM_{2.5}$ air quality problems. Various statistics and indicators (such as component to mass ratios) may be appropriate and will be described in initial guidance. To ascertain true $PM_{2.5}$ and component trends, it may be necessary to adjust the data for meteorological conditions as is often done for ozone. EPA is currently exploring this issue.

It will be several years before there is a sufficient amount of data to construct trends from the speciation data; since a minimum of 3 years is needed to establish a 'trend', these type of evaluations will probably not be possible until 2002 or later. The first few years of data, however, can be used for comparative purposes such as inter-season, episode versus non-episode (high mass percentile vs low mass percentile), divergent meteorological condition, and geographic area comparisons. National scope analyses such as more robust East versus West comparisons (and the culling of associated policy ramifications) will be performed by EPA. Also, since most speciated particulate data available now is from rural environments, comparing the urban-based trends network data to this existing rural centered information will be another early EPA endeavor. The EPA will describe these characterizations, as well as national scope trends (once a sufficient bank exists in various reports such as the annual ***National Ambient Air Quality and Emissions Trends Report*** (U.S. EPA, 1998e).

As mentioned, the first set of sites put in operation will be the National Trends network of approximately 54 sites. Because of

Table 2-1. Status and Trends Working Outline from the Virtual $PM_{2.5}$ Workbook
(http://capita.wustl.edu/PMFine/Workgroup/Status&Trends/Outline/S&TOutline.html)

I. Resources
    A. Data
    B. Tools
    C. Historical Literature
    D. Web Links
II. Data Processing
    A. QA Review
    B. Data Screening & Aggregation
    C. Data Updates
III. Temporal Patterns
    A. Diurnal
    B. Day-of-Week
    C. Episodic
    D. Seasonal
    E. Long-Term
IV. Spatial Patterns
    A. Urban
    B. Urban/Rural
    C. Elevational
    D. Regional
    E. National/International
V. Compositional Patterns
    A. Fine Mass
    B. General Species
    C. Detailed Species
VI. Discerning Influences
    A. Meteorology
    B. Emissions
    C. InterPollutant Relationships
    D. Natural Events
VII. Feedback Loops
    A. Data Processing
    B. Network Design
    C. Attainment Issues
    D. Source Attribution
    E. Control Strategies

their placement (in high emissions areas), their similar instrumentation, and their timing (first implemented, thus they will always have the longest data record), these sites will be the best suited for trends and comparison purposes. Data from these sites can eventually be complemented by data from the non-Trends sites; however, the effect of differences in sampling and analysis equipment and techniques on the data must be considered. A variety of statistical techniques are available for comparative and/or trend detection purposes. Examples include t-tests, F-tests, linear regression, analysis of variance, Spearman's rho, Kendall's tau, Theil/Sen slope estimator, etc. Many of these techniques were discussed in a PAMS related document, ***Recommendations for Analysis of PAMS***, (U.S. EPA 1994) and are equally appropriate for the $PM_{2.5}$ speciated data. These techniques will be addressed in future EPA guidance but are well beyond the scope of this Section. The AMDAS module mentioned earlier will include several valuable options for characterizing and summarizing speciated data. A trend detection and display facility will also be available.

Table 2-1 shows the current Status and Trends working outline from the virtual $PM_{2.5}$ workbook work group. The outline and corresponding sub-work group are concerned with all $PM_{2.5}$ program data, not just the speciation data. Accordingly, some aspects of the outline may pertain exclusively or chiefly to mass data. Also, the outline structure is admittedly not extremely detailed nor intuitive; the work group is itself trying to define each of outline items.

2.3.4 Tracking Progress of Control Programs

Once control measures are implemented, either nationwide or in certain nonattainment areas, the speciation network will provide the information necessary for verifying the efficacy of those strategies. This analysis activity has Status & Trends, Source Attribution, and Emission Inventory Evaluation facets to it. Individual specific strategies or an entire suite of activities (such as stipulated in a SIP) can be evaluated to ascertain progress. Control strategy effectiveness checks can encompass simple before-after comparisons (i.e. significance tests of difference) of a parameter’s annual mean (or a species to mass ratio); similar comparisons of annual relative contributions of a particular species from a particular source category; or in-depth trends analyses for a particular indicator. $PM_{2.5}$ SIPS may eventually contain emission reduction targets for key $PM_{2.5}$ components and precursors similar to the previous VOC 15% (RFP) plans. The speciated $PM_{2.5}$ ambient data are needed to corroborate the realized emissions reductions. Although “Tracking Progress of Control Programs” sounds like a far-off distant activity which might not start until 2003 or so, such opportunities might be available much sooner. Because many environmental programs and control strategies have multiple goals, serendipitous side effects, and sometimes unforseen negative consequences, the effect of such programs may be evaluated far before any specific $PM_{2.5}$ controls are even enacted. States need to be cognizant of all implemented ambient controls and their possible outcomes.

2.3.5 Source Attribution

The $PM_{2.5}$ mass monitors will identify the regions of the country with high $PM_{2.5}$ concentrations. The speciation network will be used to determine which constituents contribute to the high mass concentrations. Source attribution not only helps identify 'what' is causing the ($PM_{2.5}$) problem, but also addresses the question: 'Who' or 'what' is causing my problem? The scope of this question ranges from general identification of PM-Fine mass fractions which result from local and regional source influence, to the quantitative identification of PM-Fine concentration and composition resulting from specific local and regional sources. As seen in the latter task (quantitative identification), speciation data can also provide information on 'how much' a particular source or source area is responsible for a specific $PM_{2.5}$ episode, its components, or its precursors. Source apportionment information will critically aid the development of strategies for controlling $PM_{2.5}$. Although the PM fine components collected at the Trends sites are useful for source attribution, finer time resolution measurements are preferred. States will need to address the time interval limitation and opportunity with their non-Trend network designs. Speciation monitoring equipment are perfectly capable of collecting samples of less than 24 hours (e.g. 3-,4-, or 12-hour). However, if too short of interval is monitored, the concentration of components may be too small (i.e. less than the detection limit) to be of value. With shorter intervals some tradeoffs can be made by increasing the flow rate or using smaller filters. Without these adjustments, a good compromise (for the non-Trend sampling, of course) may be to collect two 12-hour samples, one during the daylight hours (e.g. 6am-6pm) and one at night (e.g. 6pm-6am). Real-time speciation monitoring is also possible and should be considered for non-routine NAMS.

A variety of tools and techniques are available for source attribution / source apportionment. These methods range from simple pollution-rose plots to complex meteorological trajectory models; multivariate and mass balance receptor models; optical microscopy; and combinations thereof. Pollution roses use concentration data (e.g. a $PM_{2.5}$ speciated component) with co-located or nearby-monitored wind direction data, to produce a graphical plot that shows (theoretically) the source direction and associated relative strength for that parameter. There are at least two versions of EPA-supported pollution rose plots that will be available to $PM_{2.5}$ State analysts. An AIRS-Graphics version has been in production for several years on the IBM mainframe but has inflexible input limitations. This plot (and so the entire system) will soon be ported to a UNIX / Internet platform and some enhancements (such as input flexibility) are being requested. The new AIRS-Graphics pollution rose is expected to be in production around July

1999. The S-Plus based tool AMDAS will also contain a pollution rose plot. Because a 10 meter meteorological tower is required at each of the Trends sites, these sites will provide the necessary wind data for these inputs. Meteorological trajectory models are also useful aids in determining an air parcel's source region. These tools, however, require extensively more meteorological data than will be monitored at the speciation sites. External data can be utilized with these analysis tools, and thus their application is recommended for corroborating other aerosol-based methods. An example of a publically available trajectory model is NOAA's HYSPLYT, which is available from NOAA's Real-time Environmental Applications and Display sYstem (READY); a link to this tool is provided on the virtual workgroup web site.

Receptor models are perhaps the most valuable of all source attribution tools. Receptor models use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. Receptor models are generally contrasted with dispersion models that use pollutant emissions rate estimates, meteorological transport, and chemical transformation mechanisms to estimate the contribution of each source to receptor concentrations. The two types of models are complementary, with each type having strengths that compensate for the weakness of the others; see next section on Air Quality Model Evaluation. One class of receptor models include principal components and factor analysis, cluster analysis or other multivariate statistical techniques. Factor analysis is a method of decomposing a correlation or covariance matrix. Cluster analysis procedures are also used to detect natural groupings in data. In general, a grouping can be either exclusive (i.e., does not allow the same object to appear in more than one cluster) or hierarchical (consists of clusters that completely contain other clusters). Although numerous air pollution analysis experts have devised useful custom-coded receptor models (using SAS, S-Plus, MATLAB, Fortran, etc.), only a limited number of these are ever 'packaged' for public use. An upcoming multivariate receptor modeling tool that shows significant potential and may soon be available for public use, is the UNMIX package created by Dr. Ron Henry of the University of Southern California. UNMIX interprets a time series of ambient data (PM components, VOC species, etc.) to estimate the number of emission source types impacting a site, the source compositions, and the source contributions to each sample. UNMIX is a new rendition of SAFER (Source Apportionment by Factors with Explicit Restrictions). Unlike the Chemical Mass Balance package (CMB8, discussed below), UNMIX does not require prior knowledge (and profiles) of the sources that impact the receptor; it can, therefore, be used to identify sources missing from the inventory. The EPA Office of Research and Development (ORD) is presently evaluating UNMIX with PM-fine data sets from Phoenix, Baltimore, Fresno, and Seattle; initial feedback is positive. Dr. Phil Hopke of Clarkson University is also developing several promising source attribution applications, and one in particular, Positive Matrix Factorization (PMF) - an allegedly better factor analysis method, has kindled some EPA interest (Hopke, 1998).

OAQPS/EMAD intends to intercompare various source apportionment techniques (UNMIX, Hopke methodology, CMB8 mentioned below, and whatever else looks promising) over the next year. Conclusions and recommendations will be reflected in future $PM_{2.5}$ data analysis guidance and EPA support.

CMB is another type of receptor model and is perhaps the most widely used receptor modeling applications due to its proven history and user-friendly ‘packaging’. The CMB utilizes a sophisticated least squares statistical method for identifying the most likely source categories to a given ambient sample, based on the relative amounts of each species present in the sample, and the relative amounts of those same species present in the emissions of source categories. The newest version of CMB (CMB8, a Windows application) and User’s Manual will soon be posted on EPA’s Support Center for Regulatory Air Models (SCRAM) web site; once there, a link will be set on the Fine Particulate Analysis Workbook site. A draft of a key CMB8 guidance document, ***CMB8 Application and Validation Protocol for $PM_{2.5}$ and VOC*** (U.S. EPA, 1998f), is already posted on the virtual workbook web site; $PM_{2.5}$ application examples contained in that document (or along those lines) will be highlighted in the August guidance.

Optical microscopy, or polarized light microscopy (PLM), is another method for distinguishing atmospheric aerosols and their source. The source of individual particles is determined by characterization of the following properties: morphological, optical, physical, and crystallographic. PLM does not require particle removal for analyses and source sampling is not a prerequisite. PLM can distinguish flyash from soils/pavement; biologicals; and raw coal, coke, and partially pyrolyzed coal. PLM will be addressed in more detail in future guidance.

Scanning Electron Microscopy (SEM) is a related method, whose superior size resolution allows examination of submicron particles. When combined with energy dispersive x-ray fluorescence (SEM/EDX) the method can determine the elemental composition of individual particles, as well as their size and shape. PLM and SEM will be addressed in more detail in future guidance.

Table 2-2. Source Attribution Working Outline from the Virtual $PM_{2.5}$ Workbook (http://capita.wustl.edu/PMFine/Workgroup/SourceAttribution/Outline/SAOutline.html)

I. Resources
- A. Data (PM-$_{2.5}$, emissions inventories & profiles, meteorology, other pollutants)
- B. Source Attribution Tools and Techniques
- C. Training and User Groups
- D. Literature References

II. Data Processing
- A. Q/A Review
- B. Data Screening, Aggregation and Fusion
- C. Treatments for MDL and Measurement Error
- D. Data Formats for Source Attribution Tools

III. Discerning Local vs. Non-local Source influence
- A. By Species (mass, sulfates, organics, nitrates, soil, etc.)
- B. Over Time (annual, seasonal, weekday, episode, diurnal, long term trend)
- C. Over Space (define "local" as function of monitoring network)

IV. Discerning among Source Categories
- A. Natural vs. Anthropogenic (by species, time and space)
- B. Anthropogenic Source Categories (wood smoke, utilities, automotive, etc. - by species, time and space)
- C. Refinement of B (proscribed burning vs woodstoves, oil vs coal utilities, Motor vehicle exhaust vs evaporative vs diesel, fugitive dust, etc.)

V. Discerning among Source Regions
- A. By Direction from receptor(s)
- B. By distance from receptor(s)
- C. By location (distance and direction)
- D. By regional "fingerprint"

VI. Discerning Specific Source Influences
- A. Within local jurisdiction(s)
- B. Beyond local jurisdiction(s)
- C. Changes over time, space or species

VII. Assessing and Reducing Uncertainties
- A. Influences of Emissions vs. Meteorology
- B. Receptor Model Performance Evaluation
- C. "Representativeness" of Short-term Results
- D. Tracers of Opportunity (in space, time, species)

VIII. Emission Profiles and Inventories
- A. Validating Emission Profiles and Inventories
- B. Improving Emission Profiles and Inventories
- C. Estimating Emission Profiles and Inventories
- D. Identification of Unusual Events

IX. Feedback to Network Design (Current and Future)
- A. Identifying and Reducing Uncertainties in Source Attribution
- B. Routine & Enhanced Measurements for Source Attribution
- C. Improving Emissions Profiles and Inventories
- D. Identifying Inefficient/Redundant Measurements

Table 2-2 shows the current Source Attribution working outline from the virtual $PM_{2.5}$ workbook work group. As noted for Status and Trends, the outline and corresponding sub-work group are concerned with all $PM_{2.5}$ program data, not just the speciation data, and thus some aspects of the outline may pertain exclusively or chiefly to mass data. Parties interested in participating in the source attribution (or any of the workbook) work group are encouraged to visit “http://capita.wustl.edu/PMFine/”.

2.3.6 Air Quality Model Evaluation

The speciation network will provide the data necessary to compare the concentrations predicted by the air quality models to the ambient concentrations at various levels. Such comparisons will be useful for identifying ways to improve the air quality models and will also aid in evaluating the emissions inventories that are integral to the modeling process. Speciated data play an especially important role as the deterministic models predict exact chemical components which can be compared to some of the specific measured analytes. However, the analysis must be tempered with the knowledge that surface point sampling systems, whether measuring exact "gases" or complex aerosols, reflect space and time frames that may not be compatible with averaging schemes used in models. The sampling complexity of aerosols adds greater complexity to model-observation comparisons.

There are at least two EPA modeling systems that will play a near term significant role with fine particulate, the Regulatory Modeling System for Aerosols and Deposition (REMSAD), and the Community Multi-scale Air Quality (CMAQ) model. The REMSAD system is built on the foundation of the UAM-V regional air quality model. An integrated photochemical module provides an active link between oxidant levels and secondary particulate formation. The REMSAD system can be applied at scales ranging from a single metropolitan area to a continent containing multiple urban areas. The model is usually run for multiday period, typically a full year. As such, model comparisons will generally be made to aggregated ambient data. In addition to comparing mass levels, comparisons can also be made for elemental and organic carbon, and a fine particulate remainder; a recent such comparison relied on data from the CASTNet and IMPROVE programs. The Trends site data may be acceptable for future comparisons. Comparisons of modeled versus ambient levels of cadmium, total sulfate, particulate nitrate, ammonium nitrate, and mercury are also plausible. Additional species concentrations from the chemistry module could be extracted from REMSAD if they proved to be important for interpretation of the model results. CMAQ is part of the Models-3 open system framework, and has integrated meteorology, emissions, and transport processors. Like REMSAD, CMAQ is a multi-pollutant model ($PM_{2.5}$, ozone, visibility, and acid deposition); CMAQ, however, utilizes a full-blown ozone photochemistry module, not a reduced-form one as incorporated in REMSAD. ORD will perform a diagnostic evaluation of the CMAQ:Models-3 $PM_{2.5}$ capabilities beginning in summer 1999. Model evaluation is inherently an EPA function, especially in the early implementation (models and monitoring) period. States, however, need to produce and appropriately caveat, the necessary (quality assured) ambient data. Once $PM_{2.5}$ models are dictated for regulatory purposes and ‘modeled attainment demonstrations’ are required, States may take a more proactive interest in model performance.

2.3.7 Evaluation of Emission Inventories, Factors, and Speciation Profiles

One of the key inputs to the aforementioned models are emission inventories. $PM_{2.5}$ speciated data will prove an invaluable aid in evaluating emission inventories and related emission factors and speciation profiles. Both mass data and its components will play an important role in the evaluation of inventories. Because mass can be ‘reconstructed’ from the speciated data, and because other mass totals will also be generated at the speciation sites (even collocated FRM), mass utilization is discussed here. Ambient-derived ratios of $PM_{2.5}$ mass to other pollutants such as VOC, NO_x, SO_x, and NH_3 (e.g. PM/NO_x) can be compared to similar emissions-derived ratios (for a specific area) to highlight possible discrepancies. Year-to-year and multi-year shifts in ambient mass levels or in ambient pollutant ratios can also be contrasted with the same from the emission inventory. For example: If the emission inventory shows a 10% decline in $PM_{2.5}$ levels over a certain time period, once could check to see if the ambient data also had a similar reduction. Because ambient concentrations are significantly influenced by chemical reactions, as well as mixing height, transport, and carryover effects, it is preferable to make these comparisons using data for morning time periods. This is just another reason that States should consider time resolved measurements in their non-Trend network designs. Also, States need to consider the availability of other pollutant measurements (such as SO_x or NH_3); siting at an existing platform may alleviate this concern.

Speciated data are critical for performing a comprehensive inventory evaluation; emission factors and speciation profiles can not be evaluated without it. Currently, inventories are not routinely maintained (at least not at EPA) for the individual mass components. Thus, to compare ambient speciated data to the inventories, the inventory must be speciated. This should be done with the same system and profiles that are used for model preparation. REMSAD uses the $EMS_{2.5}$ system; CMAQ currently uses MEPPS but will migrate to SMOKE in mid-1999. Emission-derived component and component to mass ratios can then be compared to the ambient data in manners similar to described above for mass. Component grouping (e.g. elements) comparisons may also be appropriate. Significant differences between the ambient and E.I. data can point to problems with emission factors, speciation profiles, temporal allocation factors, or even the spatial allocation method (or related surrogate data). Source attributed data can isolate the source type (point, area, mobile) or specific categories most out of line. An emission inventory evaluation can and should be complemented with a bottom-up look at those categories that don't match up well. Diurnal ambient data can help validate and improve temporal allocation factors. Enhanced spatial coverage can aid the validation and improvement of the spatial allocation method (and surrogate data). Ambient : E.I. comparisons can encompass large areas but are typically confined to a small number of emissions dominated grid cells. Upwind grid cells can be included in the comparison but are sometimes not given equal weight. Recommendations relating to these issues will be included in the August guidance. States should design their network their speciation networks with emission inventory validation in mind.

2.3.8 Development of Control Strategies

Speciated day will play a vital role in the development of control strategies. In addition to helping 'prove in' the models (F) and validate the model input inventories (G), ambient data also help in other modeling support activities. Ambient data can be used to help define or affirm the modeling domain (area); the boundary ('initial') conditions; and the selection of the modeled episode, season, or year. Analysis of observational (including speciated) data can be used in its own right to suggest strategies, or to corroborate or fine-tune modeled ones. The latest ozone attainment demonstration guidance dictates the following policy, "Provided the modeled attainment test and a supplementary screening test are passed or close to being passed, States may use a broader set of analyses to estimate if attainment is likely. This is called a 'weight of evidence' determination. A 'weight of evidence' determination includes results obtained with air quality simulation models plus conclusions drawn from analyzing monitored air quality data, emissions estimates and meteorological data. Results of each analysis are considered in concert to determine whether or not attainment is likely. At a minimum, a weight of evidence determination should consider the following 3 types of corroborative analyses: application of air quality simulation models, observed air quality trends and estimated emissions trends, and outcome of observational models. Although these statements are drawn from the 8-hour ozone attainment guidance, a similar policy is expected for the new fine particular standard.

2.3.9 Other Analysis Activities

Listed below are several additional analysis activities that should be explicitly mentioned. There is some coverage of a few of these items in the categories above, but they are highlighted again to stress their importance.

- **Correlation with FRM Mass Concentrations:** Where $PM_{2.5}$ mass and speciation monitors are collocated, it will be useful to develop an empirical relationship between the

$PM_{2.5}$ mass observations and the mass concentration obtained from the speciation monitors. Such an analysis will provide information about the comparability of the measurements from the FRM's and from the speciation monitors.

- **Health Studies:** Speciated $PM_{2.5}$ data will be important to continued epidemiological studies into the health effects of $PM_{2.5}$ and its constituents. The ‘every 3rd day’ sampling regime of the Trends Sites may not be sufficient for most of these studies, and neither may the non-Trends component; the supersites’ design, however, should reflect the health effects community’s needs. Some of the monitored target speciation parameters are HAPs or HAPs constituents (selected elements and ultimately some semi-volatile organic compounds). Speciation data can thus be used for toxics exposure assessments, including estimation of risk levels and the size of effected populations.

- **Transport Analysis:** Speciated data can be used in conjunction with collocated or other available meteorological data to characterize and quantify the flow of pollutants / $PM_{2.5}$ components into or out of a particular region.

- **Synthesis with Oxidant Data:** At the sites with both $PM_{2.5}$ speciation monitoring and monitoring for oxidant precursors and sinks, it will be possible to perform analyses to investigate the relationships between $PM_{2.5}$ constituents and other important atmospheric constituents to gain better process understanding of both $PM_{2.5}$ and ozone formation, maintenance, and removal. Ozone formation and formation of secondary particulates result from several common reactions and reactants. Often similar sources contribute precursors to both ozone and fine particulate problems. In some regions of the U.S., high regional ozone and secondary particulates have been observed under common sets of meteorological conditions. Reducing fine particulate matter is the principal controllable means for improving regional visibility. U.S. EPA policy is to encourage integration of programs to reduce ozone, fine particulates and regional haze to ensure they do not work at cross purposes and to foster maximum total benefit for lower costs.

- **Integration with Other Databases:** There are several other databases containing speciated $PM_{2.5}$ data, for example, the data collected through the IMPROVE network, Clean Air Status and Trends Network (CASTNET), and the data used in the numerous health effects studies. It will be important to integrate the data from these various databases to increase the amount of information in one of the networks using the information in these other networks. EPA will support the creation and public posting of integrated data sets.

2.3.10 Section Summary

The key points of this Section are reiterated below:

- The $PM_{2.5}$ speciation networks will generate data useful for expanded understanding of fine particulate formation and removal processes, general characterization and comparison purposes, trends analysis, source attribution, control strategy development, checks of control strategy effectiveness, emission inventory and model evaluation, and other related uses. All these intended uses are interrelated.

- The EPA will issue guidance documents detailing potential uses for the $PM_{2.5}$ mass and speciation data. The first iteration of guidance will be issued around August, 1999. These guidance documents will be based on (1) techniques described in the published literature and (2) concepts offered by the State and local agencies, the Regional Offices, and EMAD. After a panel of experts peer reviews each document, the documents will be made publicly available through the Internet.

- The EPA will sponsor development of tools to assist with some of the analyses described in the guidance documents. Many software packages have already been developed for other criteria pollutants and some may be modified to accommodate $PM_{2.5}$ mass and speciation data. Examples include VOCDat and PAMSDAS. Also, an U.S. EPA web site called PM Fine Data Analysis will be available, consisting of topics such as General Information; Publications, Papers and Reports; and Data Analysis Support. The site will provide direct links to PAMS data analysis, Toxics data analysis, and the Virtual Work Group web site.

- Training and workshops will be conducted to demonstrate proven data analyses, to present potential limitations of the conclusions from the data analyses, and to demonstrate the software tools that have been developed/modified specifically for $PM_{2.5}$ data analysis. The first national data analysis workshop is tentatively scheduled for September, 1999. Subsequent workshops (planned for FY ‘00) will be conducted in accordance with the Regional and State and local needs.

- The EPA will issue periodic reports describing the national trends and the quality of the data collected by the $PM_{2.5}$ network. Trends for mass and key constituents, for example, will be highlighted in the annual National Ambient Air Quality and Emissions Trends Reports.

- The creation and evolution of the guidance documents, tools, workshops, and reports will be aided by the virtual PM Fine Data Analysis Work Group, an interactive web site that will solicit ideas and comments from the ambient air monitoring and analysis community at large, particularly from groups such as NESCAUM, MARAMA, WESTAR, LADCO, TNRCC, CARB, A&WMA, and STAPPA/ALAPCO. In addition, more focused groups and subgroups comprised of individuals from EMAD, AQSSD, Regions, and States who have expertise in areas such as ambient air data analysis, chemistry, and meteorology will help address specific and pressing issues.

- States need to consider the goals of the data collection in their network design, especially in the non-Trends portion. These considerations include siting, monitoring schedule (more frequent than every 3rd day and/or intervals less than 24-hours), and availability (collocated or nearby monitoring) of other related pollutant and meteorological parameter data.

2.3.11 Additional References

Additional references to related readings on exploratory and interpretive data analyses are listed below.

Guthrie, Paul; Gao, Dongfen; Mansell, Gerard (1998). Evaluation of the Performance of the REMSAD Modeling System for Fine Particles and Deposition - Final Report, produced for EPA-OAQPS. Systems Applications International; SYSAPP-98/24; June, 1998.

Introduction to Receptor Modeling, APTI Course 424; U.S. Environmental Protection Agency, Air Pollution Training Institute; January, 1998.

Use of Models and Other Analyses in Attainment Demonstrations for the 8-Hour Ozone NAAQS - Draft; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards; October 1986.

3.0 PARTICLE CHARACTERISTICS AND TARGET SPECIES

The following section discusses particle size distribution, the major constituents of $PM_{2.5}$, potential source contributions relative to the chemical speciation program, and the target species and their characteristics. For clarification, a table is included in Section 3.3 that provides a matrix of filter type, the target chemical species measured on that filter type, and the analytical technique used to determine the species concentration for samples collected within the routine speciation monitoring network.

3.1 Particle Size Distributions

Atmospheric particles originate from a variety of sources and possess a range of properties. Atmospheric particles contain inorganic ions and elements, elemental carbon, organic and crustal compounds. Some particles are hygroscopic and contain particle-bound water. Particulate matter (PM) is a generic term applied to this broad class of chemically and physically diverse substances that exist as discrete particles over a wide range of sizes. Particles are liquid droplets or solids that originate from a variety of natural and anthropogenic stationary and mobile sources. Atmospheric PM occurs as fine-mode and coarse-mode particles that, in addition to falling into different size ranges, differs in formation mechanism, chemical composition, sources, and exposure relationships. Primary particles are composed of material directly emitted into the atmosphere, while secondary particles form as a result of chemical reactions involving gas-phase precursors or other processes involving chemical reactions. Examples of primary particles include wind-blown dust, seas salt, road dust, and mechanically-generated or combustion-generated particles such as fly ash and soot. An example of secondary particles include sulfate formed from the atmospheric oxidation of sulfur dioxide.

Size is one of the most important characteristics in the determination of the properties, effects and fate of atmospheric particles. Three approaches are used to classify particles by size:

- modes, based on formation mechanisms and modal structure observed in the atmosphere (e.g., nuclei and accumulation modes which comprise the fine and coarse particle mode;
- cut point, based on the 50% cut point of the specific sampling device (e.g., $PM_{2.5}$ and PM_{10}); and
- dosimetry, based on the ability of particles to enter certain regions of the respiratory tract.

Fine and coarse particles are often defined in terms of the modal structure of particle size distributions typically found in the atmosphere. An important feature of atmospheric aerosol size distributions is their multimodal nature. The $PM_{2.5}$, PM_{10}, and total suspended particulate (TSP) size fractions are ideally measured by air quality monitoring devices by range of size distribution.

The mass collected is proportional to the area under the distribution curve within each range. The TSP fraction ranges from 0 to about 40 μm in aerodynamic diameter, the PM_{10} fraction ranges from 0 to 10 μm, and the $PM_{2.5}$ fraction ranges from 0 to 2.5μm. No monitoring device passes 100 percent of the particles below a certain size and excludes 100 percent of the particles above that size. When particulate sampling occurs, each of the size ranges contain a certain number of particles above the upper size designation of each range.

Condensable species can either nucleate to form a new particle (nucleation), or condense onto the surface of an existing particle (condensation). Nucleation results in an increase in particle number and particle mass. Condensation leads only to an increase of aerosol mass and surface area, but does not affect the total number of particles. The “nucleation” range consists of particles with diameters less than ~ 0.1 μm, also termed “ultra fine particles,” that are emitted directly from combustion sources or that condense from cooled vapors soon after emission. Nucleation particle lifetimes are usually less than one hour because they rapidly coagulate with larger particles or serve as nuclei for cloud or fog droplets. The nucleation range is detected only when fresh emissions are closest to a measurement site or when new particles have been recently formed in the atmosphere (Lundgren and Burton, 1995). However, ultra-fine particles can persist in the atmosphere if removal mechanisms are weak.

The “accumulation” range consists of particles with diameters between ~ 0.1 and 2μm. These particles contains fresh accumulation aerosol emitted from combustion sources, and can also result from gas-to-particle conversion, condensation of volatile species, and finely ground dust. Nucleation and accumulation ranges primarily constitute the $PM_{2.5}$ or “fine” particle size fraction, and the majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon is found in this size range. The $PM_{2.5}$ accumulation range shows two sub-modes, the condensation mode (containing gas phase reaction products), and the droplet mode (resulting from growth by nucleation and reactions that take place in water droplets). When these modes contain water soluble particles, their peak will shift toward larger aerodynamic diameters as the humidity increases.

Particles larger than ~2 or 3 μm are called “coarse particles” that result from grinding activities and are dominated by material of selective biological, geological, and man-made origins (pollen and spores, ground up trash, leaves, and tire abrasion). There are certain conditions under which coarse particles are created from secondary reactions in the atmosphere. For example, the coarse nitrate particle fraction in Los Angeles, California, is believed to occur from a reaction of NO_x with sea salt.

Figure 3-1 shows the size distribution of suspended particles measured from common emissions sources (Ahuja et al. 1989; Houck et al. 1989). The data present here are meant to illustrate “rough” average concentrations of individual components. Windblown dust from soil, unpaved roads, construction, evaporation of sea spray, pollen, mold spores, and dusts formed from the grinding of larger particles are predominantly in the coarse particle size range, with minor or moderate quantities in the $PM_{2.5}$ fraction. Fine particulate can be secondarily formed from gases or by chemical reaction or vaporization. Sources of fine particulate include the combustion of coal, oil, gasoline, diesel fuel, and wood, and high temperature processes such as steel mills, etc. It is important for network operators and data analysts to understand that at various places and times, any one of the three or four major components can dominate the particulate mass in a 24-hour sample.

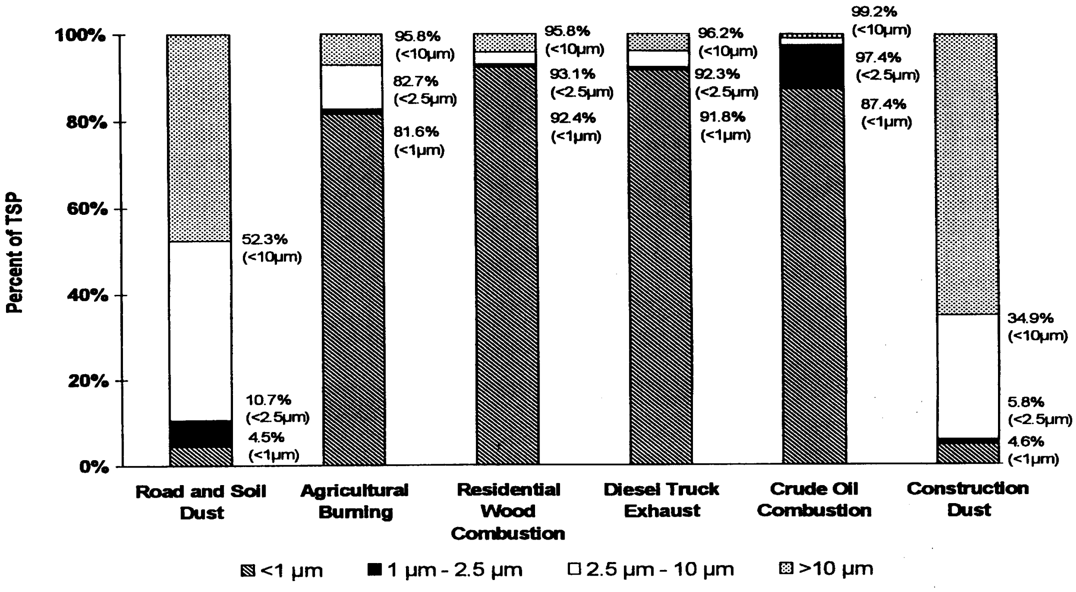

Figure 3-1. Size distributions of several particulate source emissions

3.2 Major Chemical Components and Potential Source Contributions

A variety of suspended particles can be found in the atmosphere; however, there is surprising consistency regarding the major components of suspended particles. As mentioned previously $PM_{2.5}$ is composed of a mixture of primary and secondary particles. Primary and secondary particles have long lifetimes in the atmosphere (days to weeks) and can travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over urban areas and larger regions, especially in the eastern United States. As a result, they are not easily traced back to their individual sources. The types of particles emitted directly (primary) include soil-related and organic carbon particles from the combustion of fossil fuels and biomass materials. The main sources of soil-related particles are road dusts, construction, and agriculture. The main sources of combustion-related (secondary) particles are diesel and gasoline motor vehicles, managed and open burning, residential wood combustion, and utility and commercial boilers. Combustion processes also emit primary fine particles consisting of mixtures of many trace metal compounds and sulfuric acid mists. The principal types of secondary aerosols are organics and ammonium sulfate and nitrate formed from gaseous emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) which react with ammonia. Gaseous organics from internal combustion engines as well as other combustion sources such as cooking are precursors to secondary organics. Sulfur dioxide, nitrogen oxides, and ammonia (NH_3) are important precursors to secondary aerosols (ammonium sulfate, ammonium bisulfate, ammonium nitrate) and information on their chemical abundance is useful at source and receptor locations to determine causes of high $PM_{2.5}$ levels.

Sulfate, strong acid, nitrate, organic and elemental carbon, trace elements (including metals), ammonium and water are often the major constituents of $PM_{2.5}$. Major sources of these substances are fossil fuel combustion by electric utilities, industry and motor vehicles; vegetative burning; and smelting or other processing of metals. Sulfur dioxide, NOx, and certain organic compounds are major precursors of secondary fine particulate matter. The eastern United States has a concentration of coal-burning power plants that emit significant amounts of SO_2, while the western U.S. has relatively low SO_2 emission densities (Malm, 1994). The main source of NO_x emissions are from the combustion of various fuels. Nationwide, about one-half of the NO_x is from stationary sources, while the remainder is from mobile sources such as spark-ignition and compression-ignition engines in automobiles and trucks.

Carbonaceous aerosols are a complex mixture of carbonate, elemental and organic carbon. Ambient studies have shown that carbonate carbon accounts for a negligible fraction of the total carbon in urban aerosol. Due to the great number of compounds with various volatility, the sampling of organic aerosols presents a difficult challenge. Carbonaceous aerosols are usually a major component of fine particulate mass. These particles consist of a multitude of organic and elemental carbon. Thousands of compounds have been identified in the ambient air, but in studies where individual organic compounds have been quantified, the sum of the measured compounds amount for only a few percent of the total organic mass (Bennett and Stockburger, 1994). Organic aerosols in the atmosphere may result from direct source emissions (primary) or condensation of low vapor pressure products of gas phase reactions of hydrocarbons onto existing atmospheric particles (secondary) or the reaction product of primarily emitted organic compounds with atmospheric oxidants. Elemental carbon is emitted directly from fossil fuel combustion sources.

Most of the $PM_{2.5}$ mass in urban and nonurban areas can be defined by a combination of the following components that are both primary and secondary aerosols:

- **Sulfate:** Ambient sulfate can be either a primary or secondary constituent. Ammonium sulfate, ammonium bisulfate, and sulfuric acid are the most common forms of sulfate in atmospheric particles. These compounds are water soluble and reside almost exclusively in the $PM_{2.5}$ fraction. Most fine sulfates are produced by oxidation of SO_2 gas to sulfate particles. Sources of SO_2 emissions include coal-burning power plants and copper smelters.

- **Nitrate:** Ammonium nitrate is the most abundant particulate nitrate compound resulting from a reversible gas-to-particle equilibrium between ammonia gas and nitric acid gas, and particulate ammonium nitrate. Sampling for particulate nitrate is subject to both positive and negative artifacts due to the reversible gas-to-particle phase equilibrium. Because the equilibrium is reversible, ammonium nitrate particles can evaporate into the atmosphere or after collection on a filter, due to changes in temperature and relative humidity. Sodium nitrate is found in the $PM_{2.5}$ and coarse fractions near sea coasts and salt playas where nitric acid vapor irreversibly reacts with sea salt (NaCl).

- **Ammonium:** Ammonium sulfate, ammonium bisulfate, and ammonium nitrate are the most common compounds containing ammonium. Ammonium sulfate and ammonium bisulfate result from the irreversible reaction between sulfuric acid and ammonia. Ammonium sulfate is present primarily as neutralized ammonium sulfate while ammonium bisulfate and sulfuric acid are not present in great abundance. Atmospheric ammonia (NH_3) is a primary basic gas present in the atmosphere. Significant sources of NH_3 are animal waste, ammonification of humus followed by emission from soils, losses of NH_3-based fertilizers from soils, and industrial emissions. Ammonia can absorb on wet surfaces or react with nitric acid to form ammonium nitrate.

- **Organic Carbon:** Particulate organic matter is an aggregate of thousands of separate compounds that usually contain more than 20 carbon atoms. Due to the number of organic compounds present, analysis of organic carbon presents a difficult challenge. No single analytical technique can characterize the organic compounds present in the atmosphere. Particulate organic carbon originates from combustion, geological processes, road dusts, and photochemistry. Identification of “organic carbon” is operationally defined by the sampling and analysis methods chosen. Quantification of semi-volatile components of organic carbon depends on the sampling method because the partitioning of semi-volatile compounds can change between the gas and particulate phases during sampling. In addition, accurate differentiation of high molecular weight organic compounds from the elemental carbon are method dependent as well.

- **Elemental Carbon:** Particles emitted from combustion sources contain light absorbing elemental carbon, often called “black carbon”. Particulate elemental carbon is a tracer for combustion-derived particles, whereas soil- and marine-derived aerosols contains negligible amounts of elemental carbon. Geological material contains variable abundances. Elemental carbon is present along with organic carbon, and discrimination of particulate elemental from organic carbon depends on the analytical method used. For example, thermal optical analysis methods can incorrectly estimate some of the high molecular weight organic compounds as elemental carbon, because the high molecular weight compounds require a high temperature for volatilization and combustion, and they are sometimes converted to soot before they are quantitated.

- **Sodium Chloride:** Salt is found in suspended particles near sea coasts, open playas, and after de-icing materials are applied. In its raw form, salt is usually in the coarse particle fraction and is classified as a geological material. When water of fog droplets containing sodium chloride evaporate, many of the “dry” core particles are below 2.5 μm in diameter. Particles that originally contain sodium chloride may be neutralized by nitric or sulfuric acid; the chloride is driven off and replaced by equivalent amounts of nitrate or sulfate. Such particles will be classified as nitrate or sulfate and will be deficient in chloride. Sodium chloride can constitute over 50 percent of the PM_{10} and 30 percent of the $PM_{2.5}$ at the California coast, which is 5 to 10 times higher than is usually found inland.

- **Water:** Soluble nitrates, sulfates, ammonium, sodium, other inorganic ions, and some organic material absorb water vapor from the atmosphere, especially when the humidity exceeds 70 percent. Sulfuric acid absorbs some water at all humidity levels. Particles containing these compounds grow into the droplet mode as they take on water. Some of this water is retained as the particles are sampled and weighed. The precise amount of water quantified in the $PM_{2.5}$ mass will depend on the ionic composition and the equilibration relative humidity applied prior to laboratory weighing. Highly acidic aerosols containing sulfuric acid may not give up water, even when the particles are equilibrated at lower relative humidity.

- **Geological Material:** Suspended dusts consisting mainly of oxides of aluminum, silicon, calcium, titanium, iron, and other metal oxides. The precise combination of these components depends on the geology and industrial processes of the area. Geological material typically consists of 5 to 15 percent $PM_{2.5}$ particles and could be as high as 30 to 40 percent in central California during summer months.

The value of identifying many of the chemical species is, in part, in their use to determine the origins of different air masses. The relative abundance of chemical components in an ambient $PM_{2.5}$ can indicate the chemical composition of the source emissions in the monitored environment. Chemical source profiles are fractional mass abundances of the measured chemical species relative to the primary $PM_{2.5}$ mass from source emissions. Receptor modeling has proven to be a useful method for identifying contributions of different types of sources, especially for the primary components of ambient PM. Apportionment of secondary PM is more difficult because it requires consideration of atmospheric reaction processes and rates. Results from western U.S. sites indicate that fugitive dust, motor vehicles, and wood smoke are the major contributors to ambient PM there, while results from eastern U.S. sites indicate that stationary combustion and fugitive dust are major contributors to ambient PM in the East. Sulfate and organic carbon are the major secondary components in the East, while nitrates and organic carbon are the major secondary components in the West.

Previous chemical profile compilations include chemical abundances of elements, ions, and carbon for geological material (e.g., paved and unpaved road dust, soil dust, storage pile); motor vehicle exhaust (e.g., diesel-, leaded-gasoline-, and unleaded-gasoline-fueled vehicles); vegetative burning (e.g., wood stoves, fireplaces, forest fires, and prescribed burning); industrial boiler emissions; and other aerosol sources. More modern, research-oriented profiles include specific organic compounds or functional groups, elemental isotopes, and microscopic characteristics of single particles.

As fuels, technologies, and use patterns have changed from 1970 to the present, so have the chemical profiles for many emissions sources. Lead has been phased out of U.S. and Canadian fuels, but it is still used in some Mexican gasolines that might affect $PM_{2.5}$ at border areas. Catalytic converters on spark-ignition vehicles, improved compression-ignition engines, and newly-designed wood combustion appliances have substantially reduced carbon abundances in emissions from these small but numerous sources. Similarly, process improvements and new source performance standards have resulted in changes in chemical component emissions from large industrial emitters. Source profiles must be paired in time with ambient $PM_{2.5}$ chemical species measurements to establish a reasonable estimate of what is expected in ambient air.

The spatial and temporal variability of $PM_{2.5}$ profiles are influenced by many factors, including:

- Source emissions of precursor gaseous and primary particles that are highly variable due to differences in fuel use and process operating conditions.

- Measurements of the major components discussed above for the $PM_{2.5}$ speciated monitoring network can only provide a first-order source attribution of ambient $PM_{2.5}$ concentrations to major source types. Additional measurements of precursor gases, isotopes, particle morphology, and organics need to be acquired to quantitatively assess the associated source sub-types.

- Trace metals acquired from elemental analysis of polytetrafluoroethylene (PTFE) membrane filters may be found to be abundant in both anthropogenic and geological source signature profiles. Identifying and quantifying major source contributions are not solely sufficient for source characterization; chemical speciation of ammonium, sulfate, nitrate, organic carbon, and elemental carbon are also essential.

3.3 Targeted Chemical Species

Most of the $PM_{2.5}$ mass in urban and nonurban areas can be attributed to a combination of materials as discussed above. The target species of interest for the $PM_{2.5}$ chemical speciation program are similar to those currently measured within the IMPROVE program. Their selection is based on the chemical speciation program data use objectives, primary constituents of $PM_{2.5}$, capability of current analytical methods, availability of filter types, and known analytical method performance characteristics.

The target species for this program consist of:

- anions (particulate sulfate, nitrate) and cations (particulate ammonium, sodium, and potassium);
- trace elements (about 20 elements from magnesium through lead);
- total carbon (for the purposes of this document is defined as the sum of organic, elemental, and carbonate carbon) and semi-volatile organic aerosol constituents; and
- particulate mass.

Although the target list contains chemical species that have been measured in previous studies, particulate organic carbon and semi-volatile organic species are considered to be research-oriented or non-routine in nature. Aerosols include many carbon-containing species with a wide variety of properties; however, most measurement methods identify these as either organic or elemental carbon. The measurement of organic and elemental carbon is operationally-based and dependent on the specific analytical technique used. There are currently no reference standards or standardized method for distinguishing between organic and elemental carbon; therefore, differing results can be obtained for the same sample depending on the analytical method used. Because of this issue, it is extremely important that the same analytical method be used to determine carbon at the NAMS trends sites for consistency. Although no standards are currently available for the organic and elemental carbon content of particulate carbon from a sample filter, good interlaboratory agreement (Birch, 1998) was obtained between six laboratories using the thermal-optical instrumentation on which the NIOSH method 5040 is based. In previous studies, laboratories using different analytical methodologies obtained variable results, but this can be expected with an operational-based method. The fact that a method is operationally-based does not mean it is not well-characterized or reasonably accurate. When the definition of an analyte is based solely on optical and thermal properties, the analysis is by definition an operational one. In this case, the carbon in widely different types of carbon-containing materials is collectively measured as either “organic” or “elemental” depending on these properties. A single standard is not appropriate when analytes are defined as such. Instead, the relative accuracy of different thermal methods is better addressed by examining the accuracy of total carbon measurements and ensuring that pyrolyzable organic materials used for calibration (e.g., sucrose) have no or little elemental carbon content.

Semi-volatile organic aerosols are included in the target list; however, their determination is outside the current scope of the speciation program and should not be considered on a routine basis due to the research-oriented nature of measuring these species. Promising and novel approaches for reducing artifacts due to sampling are not yet ready for routine deployment; however, research directions suggest that current and future technological developments will permit both extensive quantification of individual compounds and accurate differentiation of semi-volatile gas and particulate phase organic carbon. Therefore, speciation of individual organics and differentiation of the semi-volatile fraction from total carbon is optional. Semi-volatile organic aerosols may be considered for special studies and later added to the routine $PM_{2.5}$ speciation program as the methodology is further developed. Volatilization of semi-volatile compounds is a known source of error for species such as ammonium nitrate and many organics. Evaporative losses of semi-volatile organic compounds can be significant.

Each series of target species requires sample collection on the appropriate filter medium and chemical analysis by methods of adequate selectivity, sensitivity and reliability. The filter substrates used to collect particulate matter are chosen for compatibility with the species collected and the particular chemical analyses. Pretreated quartz fiber filters are used to collect samples destined for determination of atmospheric carbonaceous aerosol concentrations. PTFE filters are employed to obtain atmospheric particulate matter samples for mass concentration determination and for subsequent measurement of a wide variety of major and trace elements and water soluble anions and cations. The nylon filter is used to capture nitrate species. For clarity it is beneficial to think in terms of filter type, the chemical species measured on that filter type, and the analytical technique used to quantify the species. Table 3-1 provides the filter types, target species, and analytical methods used for the routine NAMS program.

3.3.1 Ions

Ionic species (sulfate, nitrate, ammonium, sodium, and potassium) can represent a large fraction of fine particulate matter, thus their determination is critical in order to meet the data analysis objectives for this program as given in Section 1.2. These ions will be measured at all NAMS speciation sites. The analysis of other important ions such as hydrogen and chloride are optional and may be included at non-routine NAMS depending upon the specific network data use objectives and availability of resources.

Table 3-1
Chemical Speciation Filter Medium, Target Species and Analytical Methods

Filter Medium	Target Species	Analytical Technique
PTFE (Teflon®) filter	Elements and mass	EDXRF (IO-3.3) and Gravimetry
Nylon filter with nitric acid denuder	Nitrate, sulfate, ammonium, sodium, and potassium	IC (National Park Service Method)
Pre-fired quartz fiber filter	Total carbon (including organic, elemental, carbonate carbon)	TOA (NIOSH 5040)

EDXRF - Energy Dispersive X-ray Fluorescence
IC - Ion Chromatography
TOA - Thermal Optical Analysis

- **Sulfate:** Sulfate is one of the most robust particulate matter species because it remains stable during and after sampling. Sulfate will be collected on nylon filters and aqueous extracts of these filters analyzed using ion chromatography (IC). It is important to utilize the appropriate denuder for SO_2 gas while making particulate sulfate measurements and to maintain the denuder for optimal efficiency while in use. Particulate sulfur is also routinely analyzed using X-Ray fluorescence (XRF). Measurements of collocated samples by ion chromatography and XRF are usually highly correlated. The typical mass ratio of [(sulfate by IC)/(sulfur by XRF)] is about 3, which indicates that almost all of the fine particle sulfur is in the form of sulfate. Therefore, for QC purposes routine comparisons may be made between the sulfate concentrations determined using ion chromatography and sulfur concentrations obtained from XRF if available.

- **Nitrate:** Accurate measurement of particulate nitrate requires the removal of gas phase nitric acid prior to particle collection. It also requires the collection of nitrate on a nylon filter, which binds the nitric acid molecules produced during the volatilization of the collected particulate ammonium nitrate. Nylon filters are slightly alkaline and can collect nitrate quantitatively. Aqueous extracts of the nylon filters will be analyzed using IC to determine the nitrate concentration. Removal of the gaseous nitric acid is achieved by using diffusion denuders coated with alkaline substances (e.g., sodium carbonate) or the use of unanodized aluminum inlets.

  Previous methods, which have used PTFE or glass fiber filters, are negatively biased due to ammonium nitrate loss during and after sampling. Loss of ammonium nitrate can be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media (Koutrakis et al., 1992). The equilibrium between particle ammonium nitrate, gaseous ammonia, and nitric acid can also be perturbed by changes in relative humidity and temperature. In addition, nitrate can be lost after sampling during sample transport and storage. To date, there is no agreement among different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling methods. If the speciation sampler relies upon metallic denuders which may be used for long periods of time (e.g., more than a couple of weeks, as with the IMPROVE network), the capacity of these denuders should be determined through laboratory and field studies.

- **Ammonium:** Aqueous extracts of nylon filters will be analyzed using IC to determine ammonium concentrations. Ammonium sulfate salts are very stable, so ammonium losses during sampling and storage are negligible. However, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage as discussed above. The extent of dissociation of ammonium nitrate depends on many parameters, including temperature, relative humidity, and face velocity of the collecting filter. It is anticipated that current sampling techniques underestimate ammonium concentrations due to the volatilization of ammonium nitrate, but fine particle mass contains many acidic compounds and consequently, a fraction of volatilized ammonium (in the form of ammonia) can be retained on a PTFE filter by reaction with the acid compounds. Therefore, it is reasonable to assume that ammonium loss will be less than the nitrate loss.

- **Potassium and Sodium:** These two cations can be used to trace wood burning and ocean sources, respectively. Similarly, as for the rest of the ions, aqueous extracts of nylon filters will be analyzed using IC to determine the concentrations of potassium and sodium. Many precautions must be taken during the filter preparation, sampling, transport, and analysis to minimize sodium contamination of the samples. Otherwise, both laboratory and field blanks will be highly variable, and sampling precision poor.

3.3.2 Elements

Elemental analysis of aerosol samples is important because it can be very helpful in identifying particle sources, and in determining the contribution of the soil and ocean sources to fine particle mass. The contribution of trace metal salts (oxides, nitrates, and sulfates) may also be determined, but typically they are expected to be negligible. To date, several analytical methods have been used to determine the elemental composition of particulate matter. X-Ray Fluorescence (Dzubay and Stevens, 1975; Jaklevic et al., 1977) and Proton Induced X-Ray Emission (Cahill et al., 1990) have been used extensively in the analysis of ambient aerosols because they are non-destructive, have multi-element capabilities, and are relatively low cost. X-Ray Fluorescence (XRF) is the analytical method chosen for the chemical speciation program. This technique is performed on PTFE (Teflon®) filters and determines the concentration of approximately forty elements (from sodium to uranium); however, for typical atmospheres, the analysis is useful only for half of these elements, including aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead.

3.3.3 Carbonaceous Aerosols

Accurate mass balance and quality assurance require determination of particulate (total) carbon (C_t), because of its abundance. Differentiation of organic (C_o), elemental (C_e), and carbonate carbon (C_c), provides more useful characterization for trends analysis and source attribution. For the purposes of this guidance document, we define total carbon as $C_t= C_o+C_e+C_c$. Semi-volatile species compose a fraction of the organic carbon which exists in the atmosphere in an equilibrium between particle and gas phases. This equilibrium depends on temperature, vapor pressures of individual species, and the amounts and types of adsorbing particle surfaces. The amount of the these species in the particulate phase collected on the filter depends on sampling conditions (e.g., filter face velocity). In this guidance, semi-volatile carbon is defined as that collected on pre-filter denuders and sorbent traps placed downstream of the collection filter on conventional samplers. At present the differentiation of C_o, from C_e and C_e from C_c are method dependent. In spite of the limitations, the first and fundamental step of carbon speciation is the semi-quantitative assessment of C_o, C_e and C_c from a quartz filter analyzed by thermal optical analysis (NIOSH 5040).

Organic compounds can represent a large fraction of fine particle mass. Organic compound speciation can provide a great deal of information regarding the sources and formation processes of carbonaceous particles. Identification of individual organic compounds is the subject of many ongoing research efforts, yet this goal is beyond the scope of the speciation program. Similarly, promising approaches for reduction of artifacts due to sampling of semi-volatile compounds are not yet ready for routine deployment; however, research directions suggest that current and future technological developments will permit both extensive quantification of individual compounds and accurate differentiation of semi-volatile gas and particulate phase organic carbon. Therefore, speciation of individual organics and accurate differentiation of semi-volatile species from C_t is optional. Although organic speciation is desirable, it is not simple to perform because there is no single analytical method that can be used to analyze all classes of organics. It may be more cost-effective to develop inexpensive methods that allow for the measurement of specific characteristic groups of organic compounds. Similar “lumping” approaches have been used successfully in ozone modeling. Attempting to obtain comprehensive spatial and temporal patterns for hundreds of organic compounds is not a cost-effective strategy.

Some species can be analyzed from more than one media and using other analytical instrumental methods. For example, PTFE filters can be extracted and analyzed for many of the same analytes as the quartz media. Also, inductively-coupled argon plasma (ICP) spectroscopy can be used to determine several trace metals, but the method is a destructive method of analysis and requires complete digestion of the filter sample. For consistency, the EPA will prescribe the use of the filter media, target species, and analytical methods identified in Table 3-1 for the 54 NAMS sites. If different target species, filter types and methods are used throughout the other 250 sites, implementation of an augmented quality control program with equivalency determinations is necessary in order to validate and evaluate the data for comparability.

4.0 NETWORK DESIGN

This section provides the recommended sites selected for the NAMS speciation network in Table 4-1, as well as outlines the general concepts to be applied when planning a $PM_{2.5}$ network outside the scope of the core NAMS speciation sites. It also important to emphasize the need for integration of field and laboratory operations at the very early stages of program design. For example, the analytical laboratory personnel should be involved in target species selection and sampler procurement or design to ensure compatibility among sampling and analysis methods, filter media, and practical quantifiable limits. A representative flow diagram of the steps involved in network design is shown in Figure 4-1, while Table 4-2 in Section 4.4 contains an example outline of typical components to incorporate in a program plan. Such a plan is essential for ensuring that all participants understand the roles and responsibilities defined for the program.

The network of stations should be designed to meet the monitoring program objectives. At a minimum, the elements outlined below should be addressed in designing a chemical speciation network and developing a program plan. For additional information on the concepts of network design, methodology for developing planning areas, selecting and evaluating monitoring sites, and usage of existing resources for network design refer to ***Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10}***, (U.S. EPA, 1997a). This reference contains information that builds upon the guidance specified for PM_{10} monitoring associated with the previous NAAQS.

4.1 Establish Monitoring Objectives

The first step in network design is to determine the overall monitoring program goals and objectives and subsequent data quality objectives. General characterization of the atmospheric aerosol, air quality trends analysis, source attribution, and control strategy development and evaluation are primary objectives of the $PM_{2.5}$ speciation monitoring program. The $PM_{2.5}$ monitoring networks producing mass concentrations for attainment determinations do not provide samples amenable to chemical analyses for all species due to the limitations of a single-filter media. Source attribution, control strategy development, and aerosol characterization require chemical speciation; therefore, additional measures must be taken to address these objectives. In addition, data from the speciation monitoring networks may be augmented for determination of metals, organics, and particle morphology for non-routine NAMS in order to meet specified data use objectives.

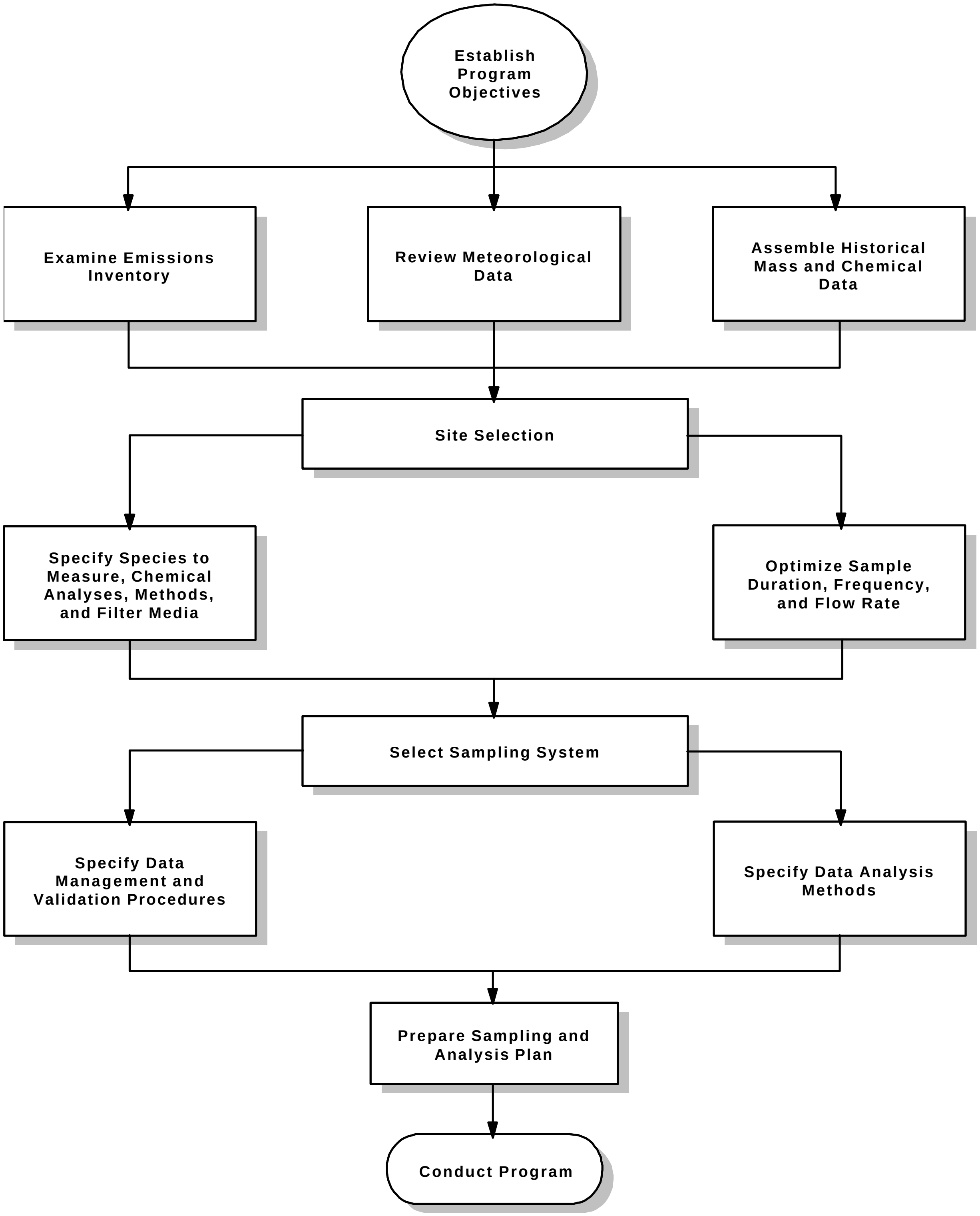

Figure 4-1. Network design flow diagram

4.2 Site Selection

Site selection is an important task in the design of a monitoring network and must result in the most representative sampling locations with characteristics that match the monitoring objectives. Proper siting requires precise specification of the monitoring objectives which usually includes a desired spatial scale of representativeness. Information from emissions inventories, meteorology data, and available historical mass and chemical data are used to determine candidate locations for sampling. This information is used in conjunction with the program objectives to determine the appropriate site selection. Specific criteria to be used in siting the NAMS monitoring stations, including spacing from roadways and vertical and horizontal probe placement can be found in Appendix E of CFR Part 58 (62 FR 38763).

Appendix D of the Part 58 $PM_{2.5}$ Regulations (62 FR 38763) provides general criteria applied in establishing networks and for choosing general locations for new monitoring stations for $PM_{2.5}$. The general requirements for chemical speciation include a national network of approximately 50 sites to include approximately 25 $PM_{2.5}$ core sites collocated at PAMS sites (1 type 2 site per PAMS area). Selection of the remaining was be based on recommendations from EPA with review and feedback from State and local agencies.

PAMS type 2 sites were established as maximum ozone precursor emission impact sites. These sites were established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions representative of a MSA/CMSA are expected to impact and are suited for monitoring urban air toxic pollutants. Generally, the type 2 sites are located immediately downwind of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district or primary area of precursor emissions mix to obtain neighborhood scale measurements.

Monitoring and sampling parameters are generally consistent among PAMS type 2 sites. For most sites, an intensive sampling period takes place during the summer (typically June-August) while a reduced set of measurements are made less-frequently during the remainder of the year. During the intensive summer period, the following sampling and monitoring parameters and minimum monitoring frequencies are measured at PAMS:

- Volatile organic compounds (VOCs) - Eight 3-hr samples daily, hourly automated measurements are typically taken at the Type 2 sites, and one 24-hour sample every 6th day year round;
- Carbonyls - Eight 3-hr samples daily, one 24-hour sample every 6th day year round;
- Ozone - Continuous sampling; and

- NO/NO_2/NOx or NO/NO_y - Continuous sampling.

In addition to VOC, carbonyl, O_3 and NO_x pollutant parameters, each type 2 site is equipped with a ten meter meteorological tower to provide surface meteorology for wind speed and direction, temperature and humidity. Each site also has access to area upper air data and surface measurement of barometric pressure, precipitation, and solar/UV radiation. Therefore, collocation of selected $PM_{2.5}$ speciation trends sites with PAMS type 2 sites offers some benefits with respect to having the ability to accumulate long-term data on organic compounds, particulate nitrate precursors, and local meteorology in conjunction with $PM_{2.5}$ mass and chemical composition data. In most cases, the existing site platforms are rugged and capable of incorporating a modest amount of additional sampling equipment. It is necessary to locate a $PM_{2.5}$ Federal Reference Method sampler at the PAMS site in addition to the speciation sampler to provide a basis for long-term comparison of particulate mass and chemical constituents.

Table 4-1 lists the recommendations for location of the 54 sites to be used to implement the speciation trends network. The current recommendation includes 20 PAMS sites and 34 other sites either identified by AIRS location or MSA. The selection of MSAs, as well as PAMS cities, was based on a balance of several factors, including:

- Location of existing PAMS and IMPROVE sites;
- Geographic location of MSAs using 1996 population statistics;
- Ozone non-attainment areas; and
- PM_{10} non-attainment areas.

The locations of existing PAMS and IMPROVE sites generally leave a large portion of the Central, Midwestern, and Southeastern US void of monitoring data that could be used for trends purposes. Therefore, we have balanced our recommendations for trends sites to specifically include major population areas in these regions which, in many cases, also include areas of higher $PM_{2.5}$ primary and precursor emissions within the region. The map given in Figure 4-2 illustrates the overall geographical coverage of the recommended speciation trends network. The IMPROVE program will also expand its total number of sites and preliminary information indicates that additional sites will be located in the Great Plains area and in New Mexico. This will further complement the integration of the IMPROVE and $PM_{2.5}$ chemical speciation network. In locating the speciation site within each of the suggested MSAs, it is suggested that a community-oriented $PM_{2.5}$ core site expecting the maximum concentrations be selected as the speciation trends site. Also, it is desirable to outfit each of the 34 MSA sites selected with a ten meter meteorological tower for collecting data on wind direction and speed, temperature, and humidity. Local siting limitations and/or unique spatial and temporal variabilities of $PM_{2.5}$ may require some balance and adjustment of the criteria outlined above to determine final site selection.

4.2.1 Target Species and Sampling Frequency and Duration

For the non-routine NAMS, the next step is to determine which chemical species beyond those specified for the routine program, are to be measured and at what concentrations they are expected to be present in the ambient air. It is imperative to include those target species required to meet the data use objectives. For example, if source attribution is an objective, it may be desirable to measure species which are present in, or indicative of, the sources which are suspected of contributing to the $PM_{2.5}$ mass.

Potential source contributions can often be determined from emissions inventory summaries in the study area. These inventories should include emissions factors for suspended particles, CO, SO_2, NO_x, VOC, and NH_3, if possible. The gaseous precursors are needed to assess whether or not secondary aerosol might contribute to elevated $PM_{2.5}$ concentrations. Some inventories may contain additional information such as the elemental or organic composition of the particulate emissions and estimates of their particle size distribution. These data, if available, are valuable in selecting sampling site locations and developing a sampling plan to consider target analytes important in a particular location.

When gridded inventories are available, or the locations of point sources are known, these should be examined to determine the locations of emissions relative to sampling locations. The closer the source, the greater the probability that some of the chemicals emitted will be detected at the receptor. Unusual or exceptional events should be identified, such as prescribed fires, wildfires, construction and demolition activities, and plant upsets. These may have a different chemical character from the sources which are listed in the inventory. Agricultural extension offices should be contacted to obtain land-use maps and soil conservation surveys. Periods of tilling, fertilizing, and grazing might be indicative of elevated emissions from these activities. Local fire departments, the National Forest Service, the Bureau of Land Management, and other fire management agencies can often supply information on local burning events.

Micro inventories are also helpful for identifying potential contributors and the chemical species which correspond to these contributions. Micro inventories include detailed surveys and locations of vacant lots, storage piles, major highways, construction sites, and industrial operations. These are plotted on a map with notes regarding the visual appearance of each potential emitter. For example, if chimneys are present in a residential neighborhood, this observation is recorded and photographs are taken. Roads in the vicinity of sampling sites are classified with respect to the type of traffic on them and whether or not they have sidewalks and paved shoulders.

Expected emissions cycles should be examined to determine sampling periods and durations. For example, residential wood burning will usually show up on samples taken during the night, whereas agricultural burning will usually show up during the daytime. While these two source types may be indistinguishable based on their chemical profiles, their diurnal cycles will provide convincing evidence that one or the other is a major contributor when both activities occur simultaneously. If local, cyclical emissions are occurring, variable sampling times (e.g., 24-hr vs. day/night 12-hr cycles) may be important in understanding the contribution of local emissions to measured $PM_{2.5}$ concentrations. The timing of other events, such as major prescribed burning or accidental wildfires, may be more difficult to predict.

Particle size is of value in separating one source from another. Particle size fractions, chemical analyses, sampling frequencies, and sample durations need to be considered because more frequent samples, or samples taken at remote locations, may require a sequential sampling feature to minimize operator costs. Shorter sample durations may require a larger flow rate to obtain an adequate sample deposit for analysis. The types of analyses and size fractions desired affect the number of sampling ports and different types of filter media needed.

Calculate the expected amount of deposit on each filter for each chemical species and compare it to typical detection limits for the analyses being considered. Urban samples acquire adequate deposits for analysis with flow rates as low as ~20 L/min for as short as 4-hour sample durations. Samples at nonurban sites may require >100 L/min flow rates for 24-hour durations to obtain an adequate deposit for chemical speciation. However, sampler flow rates as well as filter surface areas also have effects on the collection efficiency of certain target analytes.

4.3 Sampling System Selection

Select a sampling system which provides the most cost-effective and reliable means of meeting the monitoring needs. In complicated situations, especially those with many contributing sources, unknown sources, or secondary contributions, more complex sampling systems are needed. Both reference and research sampling systems have been operated side-by-side in many PM_{10} studies when this is the case, and the same practice can be applied to $PM_{2.5}$ monitoring. Refer to Section 6.0 for a discussion of the sampling methodology and candidate speciation sampler approaches for the core NAMS network.

Table 4-1
Proposed Sites for the $PM_{2.5}$ NAMS Trends Network

Region	State / Common.	MSA/Site	PAMS City Site	AIRS #
1	Connecticut		East Hartford	09-003-1003
	Maine		Kittery	23-031-3002
	Massachusetts		Lynn	25-009-2006
	Massachusetts		Chicopee	25-013-0008
	Rhode Island		East Providence	44-007-1010
	Vermont	Burlington		
2	New York		Bronx Gardens	36-005-0083
		Rochester		
	New Jersey [1]		New Brunswick	34-023-0011
	Puerto Rico	San Juan		
3	Washington DC		McMillan Reservoir	11-001-0043
	Maryland		Essex	24-005-3001
	Pennsylvania		E. Lycoming	42-101-0004
		Pittsburgh		
	Virginia	Norfolk		
4	Alabama	Birmingham		
	Florida	Miami		
		Tampa		
	Georgia		S. Dekalb	13-089-0002
	Mississippi	Biloxi		
	North Carolina	Charlotte		
	South Carolina	Charleston		
	Tennessee	Memphis		
5	Illinois [1]		Chicago-Jardine	17-031-0072
	Indiana	Indianapolis		
	Michigan	Detroit		
	Minnesota	Minneapolis		
	Ohio	Cleveland		
	Wisconsin		Milwaukee	55-079-0041

Region	State / Common.	MSA/Site	PAMS City Site	AIRS #
6	Louisiana		Capitol	22-033-0009
	Oklahoma	Tulsa		
	Texas [1]		Clinton Dr.	48-201-1035
			Hinton	48-113-0069
			Chamizal	48-141-0044
7	Kansas	Kansas City		
	Missouri	St. Louis		
	Nebraska	Omaha		
8	Colorado	Denver [1]		
	Montana	Great Falls		
	North Dakota	Grand Forks		
	Utah	Salt Lake City		
9	Arizona	Phoenix		
	California	Los Angeles		06-037-1103
		Riverside (Rubidoux) [1]		06-065-8001
			El Cajon	06-073-0003
			Simi Valley	06-111-2002
			Sacramento	06-067-0006
		Bakersfield		06-029-0014
		Fresno		06-019-0008
		San Jose		06-085-0004
	Nevada	Reno		
10	Idaho	Boise		
	Oregon	Portland		
	Washington	Seattle [1]		
Network Totals	**39 States**	**34 MSAs/Sites**	**20 PAMS Sites**	**54 Trends Sites**

[1] Selected as co-located speciation sampling sites.

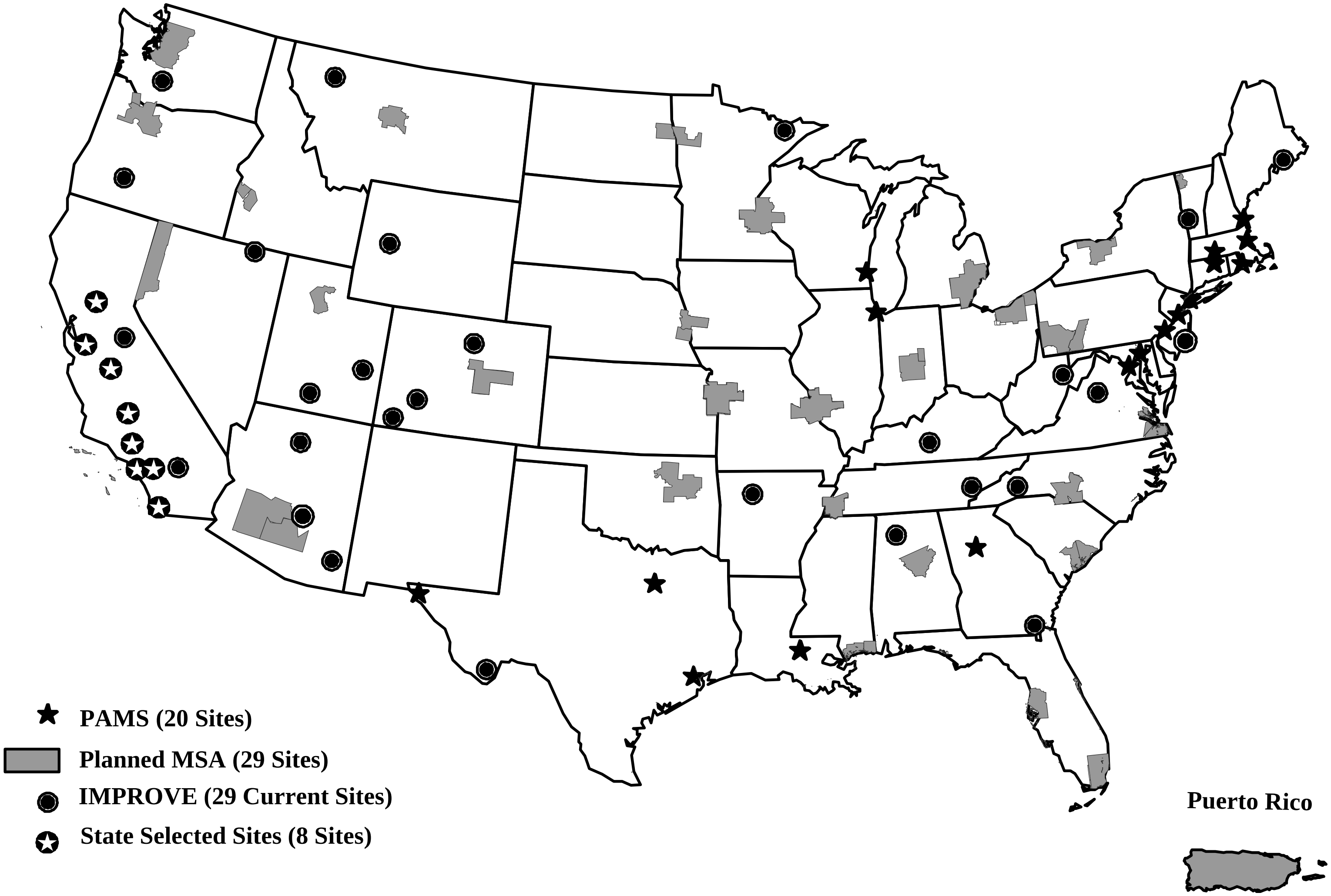

Figure 4-1. Proposed speciation trends sites and current IMPROVE sites.

4.4 Speciation Sampling and Analysis Plan Preparation

The final step is to create a written sampling and analysis plan. The plan specifies the study objectives, sampling locations, analysis methods, filter media, sampling systems, sampling frequencies and durations. Details should be included which prescribe nominal flow rates, methods and schedules for inlet cleaning, calibration and performance tests, filter transport and handling procedures, database management system, data analysis methods, and record keeping protocols. An example of an outline of the contents for a program plan is given in Table 4-2.

Table 4-2
Example of Program Plan Outline for $PM_{2.5}$ Measurements

- **1.0 INTRODUCTION**
  - 1.1 Background
  - 1.2 Objectives
  - 1.3 Overview
- **2.0 AIR QUALITY IN THE STUDY AREA**
  - 2.1 Emissions
  - 2.2 Meteorology
  - 2.3 Atmospheric Transformations
  - 2.4 Historical Air Quality Data
  - 2.5 Implications for $PM_{2.5}$ Study Design
- **3.0 DATA ANALYSIS AND MODELING**
  - 3.1 Data Evaluation
  - 3.2 Descriptive Air Quality Analysis
  - 3.3 Descriptive Meteorological Analysis
  - 3.4 Source Profile Compilation
  - 3.5 Emissions Inventory
  - 3.6 Receptor Model Source Apportionments
  - 3.7 Trajectory Modeling
  - 3.8 Secondary Aerosol Modeling
  - 3.9 Case Study Descriptions
- **4.0 PROPOSED AMBIENT MONITORING NETWORK**
  - 4.1 Sampling Sites
  - 4.2 Sampling Frequency and Duration
  - 4.3 Sampling Methods
- **5.0 EMISSIONS CHARACTERIZATION**
  - 5.1 Emissions Activities and Micro inventories
  - 5.2 Geological Source Profiles
  - 5.3 Motor Vehicle Exhaust Characterization
  - 5.4 Residential Wood Combustion Characterization
  - 5.5 Industrial Source Emission Characterization
  - 5.6 Other Source Characterization
- **6.0 LABORATORY OPERATIONS**
  - 6.1 Substrate Preparation
  - 6.2 Gravimetric Analysis
  - 6.3 Light Absorption
  - 6.4 Elemental Analysis
  - 6.5 Filter Extraction
  - 6.6 Ion Analysis
  - 6.7 Carbon Analysis
  - 6.8 Specialized Analysis
- **7.0 QUALITY ASSURANCE**
  - 7.1 Standard Operating Procedures
  - 7.2 Quality Audits
  - 7.3 Standard Traceability
  - 7.4 Performance Tests
- **8.0 DATA PROCESSING, DATA BASE MANAGEMENT, AND CHAIN-OF-CUSTODY**
  - 8.1 Data Base Requirements
  - 8.2 Levels of Data Validation
  - 8.3 Continuous Data Processing
  - 8.4 Substrate Data Processing
- **9.0 MANAGEMENT, REPORTING, AND SCHEDULE**
  - 9.1 Tasks and Responsibilities
  - 9.2 Resource Requirements
  - 9.3 Reports
  - 9.4 Schedule and Milestones
- **10.0 REFERENCES**

5.0 SAMPLING ARTIFACTS, INTERFERENCES, AND LIMITATIONS

This section discusses some of the general difficulties that may be encountered while making aerosol measurements. Particle and gas removal by inlets, nitrate particle volatilization, adsorption of SO_2 and NO_x, organic carbon adsorption and volatilization, liquid water content, electrostatic charge, and passive deposition and recirculation are discussed. Some of these biases can be avoided or counteracted with alternative sampling and filter handling techniques.

5.1 Inlet Surface Deposition

The materials from which inlets are manufactured can affect the collected aerosol, especially when gas and particle phases are being quantified for volatile species such as ammonium nitrate. Most samplers are manufactured from aluminum, plastic, or galvanized steel, due to availability and economy. These materials can absorb some gases, especially nitric acid, and can change the equilibrium between volatile particles on a filter and the surrounding air.

Nitric acid has a tendency to adhere to surfaces. Surfaces coated with perfluoroalkoxy (PFA) Teflon® can pass nitric acid with 80 percent to 100 percent efficiency. Aluminum surfaces common to many samplers and inlets have a large capacity (60-70 percent) for absorbing nitric acid vapor while transmitting particles with high efficiency. If measurement of nitric acid is important to the non-routine NAMS component of the speciation program, then coating of the inlet is necessary. Denuders are often used as part of, or located immediately behind, size-selective inlets to remove gases that might interfere with the aerosol measurement. See Section 5.2.2 for a more detailed discussion of denuders.

Plastic surfaces can acquire an electrical “static” charge which might attract suspended particles, although the dimensions of most ambient sampling system inlets are sufficiently large that the attraction is negligible.

5.2 Nitrate Particle Volatilization

Nitrate losses during and after sampling have been reported. At temperatures greater than 30 C, most nitrate will be in the gas phase as nitric acid (HNO_3), while at temperatures lower than 15 C, most nitrate will be in the particle phase as ammonium nitrate (NH_4NO_3). There will be varying amounts of nitric acid and ammonium nitrate at the intermediate temperatures. Relative humidity and concentrations of ammonia and nitric acid gases also affect this equilibrium, but temperature is by far the most important variable. When air temperature changes during sampling, some of the ammonium nitrate already collected on the filter can volatilize. Nitrate volatilization is minimized when ambient temperatures are low and with proper ventilation of the sampler housing.

Volatile compounds can also leave the filter after sampling and prior to filter weighing or chemical analysis. Losses of nitrate, ammonium, and chloride from glass and quartz-fiber filters that were stored in unsealed containers at ambient air temperatures for 2 to 4 weeks prior to analysis exceeded 50 percent (Witz et al. 1990). Storing filters in sealed containers and under refrigeration will minimize these losses.

5.3 Organic Carbon Volatilization

The collection and determination of particulate organic material is complicated by changes in equilibrium between organic material in the gas and particulate phases during sample collection. Volatilization of individual semi-volatile organic species depends on both temperature and filter face velocity due to flow rate. Gas phase organic molecules in the sample stream or on the particulate matter may either be adsorbed by the quartz filter or pass through the filter during sampling (Figure 5-1). If corrections are not made for collection of gas phase components by the quartz filter, the amount of carbonaceous material determined from the analysis of the filter for carbon may result in a positive bias (Cui et al., 1997). Also, a larger negative error results from the loss of 20-80 percent of the particulate phase organic material during sampling (Eatough et al., 1993).

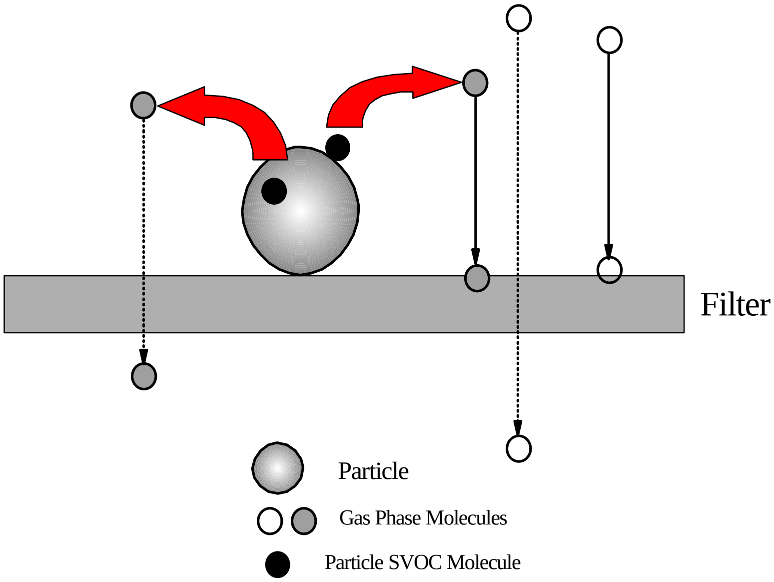

Figure 5-1. Artifacts associated with collection of particulate carbonaceous material (Adapted from Cui et al. 1997)

Volatilization of organic carbon is typically addressed by sampling with two quartz filters in series and correcting the carbon found on the first filter by the amount of carbonaceous material found on the second filter (Eatough et al., 1995, Appel et al., 1989, McDow et al., 1990).

However, it is difficult to distinguish between the gas phase organic compounds collected on the particulate filter and the backup filter.

In addition to collection of gas phase organics by the particle collecting filter, particulate semi-volatile organic compounds (SVOCs) can volatilize from the collected particles during sampling (Cui et al., 1997). These SVOCs can be absorbed by the filter or pass through the filter and be lost (Figure 5-1). If only a fraction of the SVOCs which can be adsorbed by the quartz filter is adsorbed by the first filter, then the second filter may contain either gas phase organic compounds, SVOC lost from particles and subsequently adsorbed, or both (Eatough et al., 1995).

The capability for determination of semi-volatile organic aerosols will be added to the routine speciation program as the technology further develops and is validated for routine use. The approach to be used for the routine NAMS speciation program to correct for these artifacts during the collection of particulate organic carbon, is to incorporate the use of a diffusion denuder to remove the gas phase organic compounds (including volatile organic and semi-volatile organic compounds) prior to the collection of particles on a single quartz filter. A post-filter sorbent material like XAD-4 will also necessary to collect the gas phase semi-volatile organic compounds volatilized from the particulate and the filter medium. The candidate speciation samplers have been designed to accommodate the necessary components as they are developed.

If the determination of semi-volatile organics is required to fulfill the objectives of the non-routine NAMS network, the analysis of the gas-phase semi-volatile organics collected by the denuder, in addition to the quartz filter and post-filter sorbent will be necessary. However, determination of semi-volatile organic aerosols is considered non-routine and research oriented in nature as discussed in Section 2.1.

5.4 Sample Moisture

The importance of liquid water content in ambient aerosol is recognized. As ambient relative humidity exceeds 70 percent, particle growth due to accumulation of moisture becomes significant. Theoretical calculation or experimental measurement of aerosol liquid content is complicated because growth rates vary with aerosol composition, ambient relative humidity and surface tension.

The current $PM_{2.5}$ NAAQS FRM for mass measurements requires filter equilibrium at a relative humidity between 30 and 40 percent prior to weighing. If samples are collected in a very humid environment where soluble particles tend to aggregate in liquid water molecules, and then are equilibrated in a laboratory environment where the relative humidity is controlled at 30 percent, a difference in mass concentrations may occur depending on particle and filter composition. When samples are collected in an environment rich in sulfuric acid or ammonium sulfate, this bias could be as high as 15 percent to 20 percent. Therefore, to minimize the effect of liquid water on measured particles, it is recommended that relative humidity equilibration ranges be kept at the low end of the 30 to 40 percent range for filter weighing.

5.5 Electrostatic Charge

One problem that occurs when using a microbalance for filter weighing is electrostatic charge. Electrostatic charge is also referred to as static, static electricity, static charge and triboelectric charge. Electrostatic charge is the accumulation of electrical charges on a nonconductive, dielectric surface such as the surface of a Teflon®-membrane or polycarbonate-membrane filter. Residual charge on a filter can produce an electrostatic interaction that induces non-gravimetric forces between the filter on the microbalance weighing pan, and the metal casing of the electrobalance, thereby biasing mass measurements. As electrostatic charges build up during the weighing session, the readout of the microbalance becomes increasingly unstable (e.g., noisy).

To minimize the static charge during gravimetric analysis, it is necessary to place a radioactive antistatic strip inside the microbalance chamber prior to weighing. It may also be necessary to pass each filter near, but not touching, the antistatic strip prior to weighing. The most commonly used low-level radioactive antistatic strips contain 500 picocuries of polonium-210 (Po^{210}). Polonium strips are commercially available and have a half-life of 138 days. Polonium strips neutralize electrostatic charges on items within an inch of the strip surface. Antistatic solutions can also be used to coat the interior and exterior nonmetallic surfaces of the weighing chamber. This coating increases surface conductivity and facilitates the draining of electrostatic charges from non-metallic surfaces to metallic surfaces.

Charge neutralization may take longer than 60 seconds for situations in which a high amount of charge has developed on collected particles due to their origin, or the particle loading on the filter is large. Electrostatic charge build up becomes greater when the air becomes drier. A 60-second charge neutralization may be sufficient in ambient indoor air conditioned to 37 percent relative humidity and 23 C. Earth-grounded conductive mats should also be placed on the weighing table surface and beneath the analysts feet to reduce electrostatic charge buildup.

5.6 Passive Deposition

Passive deposition of windblown dust on the filter prior to, and following sampling, can positively bias PM measurements. This deposition is minimal and dependent on local conditions during the specific collection time. Bias due to deposition can be minimized by more frequent sample filter changing (i.e., reduce the passive deposition period), pre-loading filters in the laboratory, and transporting unexposed and exposed filter cassettes in covered cassette holders.

Recirculation of the sampling pump exhaust is not expected to have an effect on $PM_{2.5}$ mass measurements. However, it can effect carbon and trace metal speciation measurements when pump and armature wear are entrained in the exhaust. This contamination can be minimized by filtering pump exhausts or ducting them away from nearby sampling inlets. Even though $PM_{2.5}$ pumps may be adequately filtered, nearby high volume samplers for PM_{10} or TSP can still affect the $PM_{2.5}$ measurements and require filtration or ducting.

For sampling, it is recommended that field blanks be periodically placed in the sampling system, without air being drawn through them, to estimate the magnitude of passive deposition during the period of time that filters are exposed in the sampler (24 hours). A field blank should be collected for each filter medium used. These blanks may also be used as trip blanks to evaluate the level of contamination during transport. Since field blanks values are dependent on local conditions, it is not appropriate to perform blank correction. The results are used to demonstrate that the contribution of passive deposition was negligible under the normal conditions of sampling.

5.7 Contamination Due to Handling

In order to avoid measurement errors due to damaged filters or a gain or loss of collected particles on the filters, careful handling of the filter during sampling, transport, equilibration, and weighing is necessary. When filters are handled, the analyst should wear gloves that are antistatic and powder-free to act as an effective contamination barrier. Gloves that are packed in a box can carry an electrostatic charge and should be discharged by touching a good electrical ground after putting them on. The filters should be handled carefully by the support ring, if present, rather than the filter material using smooth, non-serrated forceps only for this purpose. It is a good idea to mark the forceps to distinguish them from forceps used for other purposes, such as handling mass reference standards. Forceps should be cleaned with alcohol and lint-free wipes before handling filters and then should be allowed to air dry. These precautions reduce the potential effect of body moisture or oils that may contact the filters and subsequently affecting the analytical results.

5.8 Filter Media Artifacts

It is important to utilize the appropriate denuder for acid gases while making particulate speciation measurements and to maintain the denuder for optimal efficiency while in use. A regular denuder replacement schedule must be incorporated into any $PM_{2.5}$ speciation program. Sampling filters can collect gases as well as particles onto the surface, or onto the particles collected on the surface, constituting an artifact. This process may change the weight of the filter, causing artifacts that significantly alter the estimated concentration. Artifacts can be formed by oxidation of acid gases (e.g., SO_2, NO_2) or by retention of gaseous nitric acid on the surface of alkaline (e.g., glass fiber) or other filter types. The magnitude of the effect is dependent on the concentration of the gases and also affected by the sampling period, filter composition and pH, and relative humidity. The magnitude and significance of the artifact is variable and dependent on local conditions and can be minimized or eliminated by use of an acid gas denuder. However, if the denuder is not properly maintained or replaced on a regular preventative schedule, acid gas breakthrough and the potential for artifact formation may occur.

Conversion of SO_2 on nylon filters has been shown to be highly variable and dependent on sampling conditions (Chan et al., 1986). The extent of the conversion of SO_2 to sulfate on Nylasorb nylon filters was found to depend on both the concentration of SO_2 and the relative humidity. The conversion was higher at lower SO_2 concentrations. More recent work (Batterman 1997) done to test the sorption of SO_2 on various filter types has shown the artifact formation for Teflon and quartz fiber filters to be insignificant. This study also showed the change in mass concentrations due to SO2 sorption on nylon filters at the secondary 3 hour SO2 NAAQS of 0..5 ppm to be small. The study did not directly address the potential for bias of sulfate measurements and examined the sorption on only clean filters without the presence of particles. Other work has shown there to be no statistical difference in measured sulfate on nylon filters with and without a denuder (Ashbaugh 1998).

Nitrate lost from inert filters (e.g., Teflon®) by volatilization and reaction with acidic materials also presents the potential for negative artifacts as discussed in Section 5.2 above.

6.0 SAMPLING METHODOLOGY

This section describes the sampling methodology for use in the NAMS chemical speciation $PM_{2.5}$ program. For the routine component of the program, specific guidance for sampler selection and operation is provided to ensure consistency across the network for comparison of spatial data and trends analyses. To allow flexibility for speciation sampling at non-routine NAMS sites, State and local agencies can tailor sampling methodologies to their individual program needs. However, these non-routine speciation sites will be subject to a balance between the competing need for national consistency and the flexibility needed to address regional and local issues.

The chemical speciation program involves both sampling and analysis components. The "National $PM_{2.5}$ Sampler Procurement Contract" includes the provision for the purchase of over 300 speciation monitors, including accessories, for establishing the speciation monitoring network. In some cases, the speciation sampler design is flexible and can include additional filter collection media best-suited for the analysis of specific components. The 40 CFR Part 53 requirements for designation of reference and equivalent methods for $PM_{2.5}$ do not require designations for speciation monitors (U.S. EPA, 1997f). However, it is imperative that all non-reference or equivalent methods incorporate particle inlets and size fractionators with equivalent particle size efficiency curves to the reference method for $PM_{2.5}$.

Desirable features of a speciation sampler include the following:

- The inlet cut-point and separation profile must be comparable to the WINS, FRM. A number of laboratory and field tests should be conducted to demonstrate that the fine particle mass collected by the speciation monitor and the FRM are in good agreement (for example, have a slope of 1 ± 0.1 and r^2 better than 0.90).
- The sampler should use proven denuder technology to obtain nitrate and anion/cation measurements. The nitric acid denuder should be tested for its capacity and efficiency as a function of exposure time and relative humidity. If it is proposed that a denuder will be used for more than one sampling day, it will be important to demonstrate the collection efficiency over time.
- The sampler should collect samples at a face velocity and sample volume similar to that of the FRM with 46.2-mm diameter filters.
- The sampler must be reliable, rugged, and employ field-proven monitoring approaches.

There are several samplers which employ multiple channels and the appropriate filter media for use by State and local agencies in implementing the $PM_{2.5}$ routine NAMS speciation program. The samplers mainly differ by inlet design and approach to collection of particles less than 2.5µm. More recent designs include the capability to collect semi-volatile organic aerosol particles using diffusion denuders followed by quartz fiber filters and solid sorbent traps. Three candidate sampler designs described in Section 6.2 are being made available through the EPA's National $PM_{2.5}$ Sampler Procurement Contract.

6.1 Sampler Intercomparison Study

Several different speciation sampler designs could be used in the overall sampling program. Therefore, studies are needed to collect data which show intercomparisons between the samplers relative to the performance of the FRM inlet, chemical species, and corresponding mass measurement. EPA's goal for the intercomparison study is to determine if there are differences between the three $PM_{2.5}$ speciation samplers available under the EPA National Contract, other samplers historically used for $PM_{2.5}$ and the FRM.

Development of chemical speciation samplers for the National PM Sampler Contract was based on performance, rather than design criteria. This has allowed innovation in the development of these samplers and resulted in development of three slightly different approaches for meeting the performance criteria. Also as a result of review by the Speciation Expert Panel, the recommendation was made for an intercomparison among the chemical speciation samplers. The intercomparison will also include other historically accepted samplers (e.g., the IMPROVE sampler) and the FRM. The chemical species to be determined during the intercomparison study include only a subset of those specified for the routine NAMS speciation program.

6.1.1 Study Objectives

The objective of the intercomparison study is to determine if there are differences among the three chemical speciation samplers and how these samplers compare relative to other historical samplers, and to the FRM. While the FRM is considered the "gold" standard for mass, there are no such standards for the chemical components of $PM_{2.5}$. Thus, this intercomparison can only establish the relative equivalence of the samplers to each other on a species-by-species basis. For semi-volatile species (those in dynamic equilibrium between the gas and particle phases), the FRM which uses a PTFE filter provides only a lower limit of these species on the expected mass loading, since there is potential for loss of nitrate and SVOCs from the inert PTFE filters. For stable species (e.g., sulfate), the FRM should provide an accurate estimate of the mass loading for those species. Historical chemical speciation samplers like the Versatile Air Pollution Sampler

(VAPS) developed under an EPA contract, the Caltech gray box sampler (Solomon et al., 1989), or the South Coast Air Quality Management District's PTEMP sampler (SCAQMD, 1996) should provide a less biased value for semi-volatile species and provide an additional set of samples for comparison.

6.1.2 Overview of the Intercomparison

Collecting atmospheric particulate matter using the FRM with PTFE filters can result in negative sampling artifacts associated with the collected sample. Potential artifacts include the loss of volatile species, such as ammonium nitrate and semi-volatile organic compounds. Use of other filter media may result in negative or positive sampling artifacts. The magnitude of these potential artifacts depends upon the atmospheric concentration of the species being affected, the temperature, relative humidity, and, other variables. The chemical speciation samplers have been designed to overcome these potential biases or artifacts by the use of denuders to remove gas phase species and reactive substrates to collect species volatilized from the inert filters collecting the aerosol. Therefore, to evaluate the performance of these chemical speciation samplers they must be able to properly determine the chemical components of $PM_{2.5}$ under a variety of atmospheric conditions, each of which will place different stresses on the performance of the sampler designs. This can be accomplished by sampling at different locations throughout the country, since the composition of the atmospheric aerosol is not identical across the country. For example, some areas have high nitrate and low sulfate level, while others have relatively high sulfate and low nitrate. Still, other areas are dominated by aerosol rich in organic compounds derived from automobile exhaust, by organic aerosol derived from wood smoke combustion, or from by organic aerosol derived from natural biogenic emissions. Some areas of the country are highly influenced by crustal material. In actuality, several of these conditions exist simultaneously, with one or two components being higher then the others.

A variety of atmospheric chemical conditions also may be observed at one location during different seasons. For example, sulfate is likely highest in the east during the summer when photochemistry is high, while nitrate is highest in the west in the winter when cool temperatures drive the ammonium nitrate equilibrium with nitric acid and ammonia to the aerosol phase. Due to time constraints, the study will be conducted over about an eight week period at four different locations to obtain as wide a difference in chemical atmospheres as possible. These constraints, however, result in limitations and follow-on studies will have to occur to fully test the equivalency of these samplers. For example, by sampling in the winter in the east, we are missing the highest sulfate concentrations, we are not sampling at a site with high wood smoke emissions, and we are sampling in Phoenix for crustal material in the winter when highest concentrations are likely to be observed in the summer.

Due to time and resource limitations, the study design is being conducted in two phases, the latter phase dependent on additional available resources. Phase I will be centered on sampling in areas with the following atmospheric conditions: high sulfate and low nitrate, high nitrate and low sulfate, and high crustal material. A fourth site was chosen locally EPA's laboratories in Research Triangle Park to allow for a more thorough evaluation of the samplers and their in-field operational performance. Phase II will include collecting samples at other locations where $PM_{2.5}$ aerosols are thought to contain significant levels of wood smoke or biogenic carbon, or at key locations during summer months to evaluate high sulfate or crustal component conditions.

The time schedule for Phase I of the study dictates that sampling occur more frequently than every 6th day, as the results are needed by OAQPS by early March for input into the decision process for choosing chemical speciation monitors for the NAMS network. Therefore, samples will be collected every-other-day. The statistical design requires a minimum of 10-15 samples. To ensure that a sufficient number of samples are collected to meet that objective, 16 sampling periods will be attempted with a contingency of four additional sampling periods for a total maximum of 20. Samples will be analyzed for the major chemical components using standard analytical techniques. Data analysis will provide a robust test of the similarity of the samplers studied and, within the limitations of the study, reasons for differences among the methods tested.

6.1.3 Study Design

The design of this program is constrained by time limitations and resources available to complete the program (e.g., number of samplers, personnel, and funding). However, the statistical design was prepared understanding these limitations and the design chosen will provide a robust evaluation of the samplers relative to each other, to several samplers used historically to obtain similar data, and to the FRM. A secondary objective of this study is to evaluate the operational performance or practicality of the samplers in the field, that is, reliability, ruggedness, ease of use, and maintenance requirements. There are two major scientific hypotheses to be addressed by this intercomparison study.

- One is associated with reconstructing the FRM mass.

- The second is associated with inter-comparing the concentrations from the various speciation samplers, which consist of two parts:
  1. The first part is associated with examining differences among the samplers, without regard to why there are differences, if they exist. This will be addressed through analysis of variance (ANOVA).

2. The second part will examine why there are differences, if they exist. Some are expected due to the different methods employed. This will be primarily addressed using the Student's t-Test.

- A third set of hypotheses is given dealing with the potential affect of different analytical methods on measured concentrations of the chemical components of $PM_{2.5}$. These include the effect of vacuum XRF or atmospheric pressure XRF on nitrate concentrations measured on PTFE filters and the effect of thermal optical reflectance (TOR) vs. thermal optical transmittance (TOT) on OC/EC concentrations.

The first two hypotheses are predicated on the assumption that the cut points for the samplers in this study are the essentially the same. This is a required assumption to address the following hypotheses. Also, it is important to establish the precision of the instruments and this will be done by collocating samples at one site. While this provides only a limited assessment of the precision, it will provide a first cut estimate of the precision for the statistical analysis to be performed here. If for example, the precision is estimated at 50%, then determining differences among samplers will not be as informative as if the precision were 10-15%. As a benchmark, the coefficient of variation for the differences in concentrations from collocated FRM instruments is required to be less than 10%, according to 40 CFR Part 58, Appendix A. Depending on the species, a range of precision from less than 10% to about 30% is anticipated (Solomon et al., 1998).

6.2 Available Candidate Sampling Approaches

The candidate sampling approaches to chemical speciation include the Reference Ambient Air Sampler (RAAS™), Mass Aerosol Speciation Sampler (MASS), Spiral Ambient Speciation Sampler (SASS™) and IMPROVE. At a minimum, the speciation monitors used for these approaches contain PTFE, nylon, and quartz filter media and provide for the collection of the target analytes of interest. The PTFE filter will be used for mass and elements; quartz will be used for total, organic, elemental, carbonate carbon, and semi-volatile organic aerosols; and nylon will be used for the collection of nitrate and other cations and anions. The sampling system must also be capable of collecting a 24-hour $PM_{2.5}$ sample. The candidate speciation monitor designs differ in their approach and are configured either as a multi-channel device operating from a single inlet, or a series of separate inlets or instruments, each with its own particulate separator mechanism. In any case, the monitor design must have the capability of collecting particles with an aerodynamic diameter equal to or less than 2.5 μm in a manner comparable to the FRM.

6.3 Operating Principle

The principle of operation involves several common components. Most fine particulate samplers have a size-separation device to separate particles so that only fine particles (those of approximately 2.5 microns) are collected onto the sample filter. Air is drawn through the sample filter at a controlled flow rate by a pump located downstream of the sample filter. The systems have two critical flow rate components for the capture of fine particulate: 1) the flow of air through the sampler must be at a flow rate to ensure that the size cut at 2.5 microns occurs; and 2) the flow rate must be optimized to capture the desired amount of particulate loading with respect to the analytical method detection limits. Other components such as a flow rate measurement device, denuder, temperature and barometric pressure probe and microprocessor control are also typical components of a speciation sampler. Key components of the candidate samplers for the speciation program are discussed below.

6.3.1 Particle Size Inlets

The inlet cut-point and separation profile must be comparable to the WINS, FRM inlet and be capable of removing particles which exceed the aerodynamic particle diameter of fine particulate matter. Size selective inlets typically use a variety of means to remove particles larger than the specified aerodynamic size and the size cutoff is based on sample flow rate. In the IMPROVE and RAAS, a cyclone is used. The SASS™ uses a spiral inlet and the MASS uses the $PM_{2.5}$ FRM WINS assembly.

6.3.2 Denuder

Denuders are used immediately behind the size-selective inlet to remove gases that interfere with the aerosol measurements, or to quantify the concentrations of gases that are precursors to secondary aerosols. Denuders take advantage of the fact that gas molecules diffuse through air much more rapidly than small particles. Denuder surfaces are made of, or coated with substances that absorb the gases of interest while letting the particles pass through. Denuder geometries can be rectangular, cylindrical, honeycomb, or annular; the annular designs provide higher gas collection efficiencies than coated cylinders. The annular denuder design is well characterized for a wide range of applications involving acidic aerosols, ammonia, formaldehyde, and other chemical species. Honeycomb designs are composed of an array of narrow cylinders that combine high surface area with compact size. When the walls of the denuder are coated with substances that absorb the gases, the denuders may be washed and the extract submitted for special chemical analyses. This method is often used to measure nitric acid, sulfur dioxide, and ammonia gases along with suspended particles. These gases are common precursors to secondary sulfate and nitrate compounds.

For the chemical speciation program, denuders are part of the sampler design primarily for the collection of nitrate on the nylon filter and organic carbon on the quartz filter. For removal of nitric acid, denuders coated with sodium carbonate or magnesium oxide will be used. For other applications, sodium carbonate denuders are also used to remove SO_2, HCl, HF, and HNO_2 from the air stream. For semi-volatile organics, technology for the routine removal of gas-phase semi-volatile organics has not been fully developed. The EPA and research community expect this capability to become available in the near future and employ the use of coated XAD-4 denuders. At this time, denuders will not be extracted and analyzed for vapor phase components as part of the routine NAMS.

Denuders have specific efficiencies and capacities depending on the design and coating materials used. It is recommended that acid gas denuders be recoated or replaced every 3 months, depending on the anticipated acid gas concentrations for each site or recommendations from the denuder manufacturer. For a detailed discussion regarding the use of annular denuder technology in the determination of acidic and basic gases (including sulfate, nitrate, and ammonium) of atmospheric fine particles refer to ***Compendium Chapter IO-4*** (U.S. EPA, 1997b).

6.3.3 Filter Types

Filter media include polytetrafluoroethylene (PTFE), quartz, and nylon. Other filter media types may be used in the non-routine NAMS component of the speciation network. Refer to Table 3-1 of this document for a matrix of filter types, target analytes and analytical methods used. Some physical and chemical characteristics of the filter media are given in Table 6-1. Also, Section 7 includes a brief discussion of the filter medium sample preparation procedures for lab analyses. Filter holders are expected to be made of an inert material. Since many of these materials are expected to be polymers, consideration should also be given to static electricity problems.

6.3.4 Flow Rate Measurement

Flow measurement and control for the speciation network are expected to be similar to the $PM_{2.5}$ FRM requirements stated in 40 CFR, Appendix L to Part 50. The sampling system shall have a sample air flow rate control capable of providing a sample air volumetric flow rate, measured over intervals of not more than 5 minutes over a 24-hour period, that shall not vary

Table 6-1
Physical and Chemical Characteristics of Speciation Filter Media

Filter Type	Physical Characteristics	Chemical Characteristics
PTFE	Thin film of PTFE attached to ring without adhesive	Usually low blank levels
	White surface, nearly transparent	Made of carbon-based material, so inappropriate for carbon analysis
	Minimal diffusion or transmitted light	Inert to adsorption of gases
	High particle collection efficiency	Low hygroscopicity
	Cannot be accurately sectioned	Low blank weight
	Melts at approx. 60 C	
	High flow resistance	
Nylon	Thin membrane of pure nylon	High HNO_3 collection efficiency
	White opaque surface, diffuses transmitted light	Passively adsorbs low levels of NO, NO_2, PAN, and SO_2
	Melts at approximately 60 C	Low hygroscopicity
	High flow resistance	Low blank weight
Pure quartz-fiber	Mat of pure quartz fibers	Pre-washed during manufacturing
	White opaque surface, diffuses transmitted light	Low blank levels for ions
	High particle collection efficiency	Contains large and variable quantities of Al and Si; May contain other metals
	Soft, friable edges that have tendency to flake	Passively adsorbs organic vapors; Adsorbs little HNO_3, NO_2, and SO_2
	Melts at >900 C	Low hygroscopicity
	Moderate flow resistance	

more than ± 5 percent from the manufacturer's specified flow rate over the entire sampling period. Having tight control of sampler flow rate is a critical component of the speciation program since calculations of ambient air concentrations require knowing the volumetric flow rate through the sampler. Deviations from the expected flow rate that cannot be quantified reduce data quality.

6.3.5 Filter Temperature Measurement

Filter temperature measurement and control is an important element of the $PM_{2.5}$ chemical speciation network. This is due to the characteristics of the aerosols that are being captured. If sampler performance resulted in significantly higher temperature at the sample media compared to the ambient temperature, then volatile chemical species may be underestimated. If filter media were colder than ambient temperature, as may be the case during a rapid temperature rise in the morning under conditions of a very low dew point, then more volatile chemical species may be trapped in the sample media than otherwise would occur under normal conditions. This would not necessarily invalidate data, however, it should be appropriately qualified. For these reasons, it is necessary for the sampler to provide a means to limit the temperature fluctuations and to monitor both ambient and filter media temperatures.

6.3.6 Barometric Pressure Measurement

The sampler must have the capability to measure barometric pressure and record the maximum, minimum, and mean measurements over the sampling period. The barometric pressure measurement is used for the purpose of computing the actual sample collection volume.

6.3.7 Relative Humidity Measurement

Particle growth due to accumulation of moisture is recognized in Section 5.4. When relative humidity is above 70%, particle growth due to accumulation may start to become significant. The capability for the sampler to measure ambient relative humidity is useful for input of this data into the overall data interpretation process.

6.4 Candidate Monitor Configurations for NAMS

The following is a description of candidate chemical speciation monitor configurations that may be used for both routine and non-routine NAMS sites. In addition, a very brief description of single channel, continuous, saturation and special purpose monitors also appropriate for use in non-routine NAMS or special studies is provided. Table 6-2 provides a comparison of the sampler designs, filter types and target species analyzed.

Table 6-2
Target Analytes Associated with Filter Type and Sampler Design

Sampler Design	Teflon®	Nylon	Quartz
IMPROVE	Mass, elements	$SO_4^=$, NO_3^-, NH_4^+, Na^+, K^+	Carbonaceous aerosols
Met One SASS	Mass, elements	$SO_4^=$, NO_3^-, NH_4^+, Na^+, K^+	Carbonaceous aerosols
Andersen RAAS	Mass, elements	$SO_4^=$, NO_3^-, NH_4^+, Na^+, K^+	Carbonaceous aerosols
URG MASS400/MASS 450	Mass, elements, $SO_4^=$, NO_3^-, NH_4^+, Na^+, K^+	NO_3^-	Carbonaceous aerosols

6.4.1 IMPROVE

Each IMPROVE sampling module consists of an inlet stack; a cyclone to provide particle size cut based on flow rate; filter media for sample collection; a critical orifice that provides the proper flow rate for the desired size cutoff; a vacuum pump to produce the flow; and solenoids for exposing two filters. IMPROVE samplers consist of up to four parallel modules (three modules for $PM_{2.5}$ and one for PM_{10}) and a common controller. A programmable clock, located in one of the filter modules or in a separate module, controls pump and solenoid switching for all filter modules. The pump(s) is housed separately. A schematic diagram of the IMPROVE sampler $PM_{2.5}$ modules configuration is shown in Figure 6-1. Each of three modules utilizes a cyclone operating at a flow rate of 22.7 L/min to provide for a cut point of 2.5μm.

One $PM_{2.5}$ module uses a PTFE membrane filter to collect aerosols for mass measurement and subsequent analysis for trace elements. A second module is equipped with a sodium carbonate denuder and nylon filter to measure total particulate nitrate, anions and cations. The third module contains two pre-fired quartz-fiber filters in series to measure organic and elemental carbon on the first filter and to assess the extent of organic artifacts on the backup filter. The flow rate is monitored by two independent magnehelic gauges which measure pressure drop across the cyclone and filter. A secondary measurement, using a pressure gauge behind the filter, provides a quality assurance check and ensures that the cassettes are properly seated. Flow control is maintained by a critical orifice between the filter and pump.

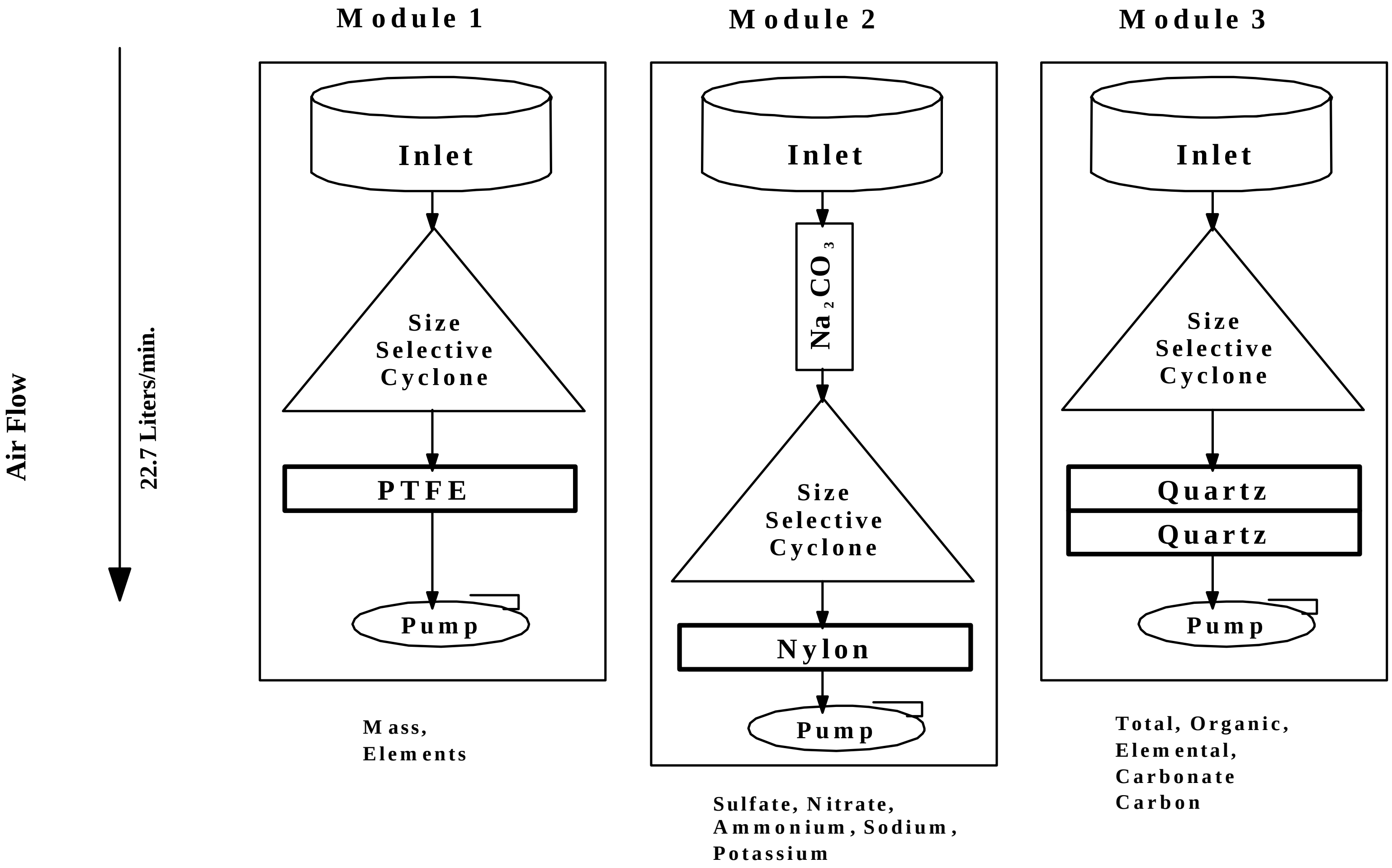

Figure 6-1. Schematic of the IMPROVE sampler modules.

IMPROVE samplers have historically been used at regional background and transport sites to fulfill SLAMS requirements. They were developed to quantify PM chemical components that affect visibility at Federal Class I areas that include national parks, national monuments, and wilderness areas.

6.4.2 Mass Aerosol Speciation Sampler (MASS)

The MASS consists of two stand-alone samplers. These samplers are identical except the MASS400 has a sodium carbonate coated denuder followed by a two stage Teflon® and nylon filter pack, while the MASS450 has a single stage quartz filter pack. On the MASS 400 the air stream travels through a sodium carbonate-coated denuder which removes HCl, HNO_2, HNO_3 and SO_2. The air stream then passes through a citric acid-coated denuder which removes NH_3. The remaining particulate passes through a 46.2-mm PTFE-filter which is analyzed for mass, elements, anions and cations. The PTFE filter is followed by a nylon filter which captures volatilized nitrate. The MASS 450 is designed for collection of carbon species. The MASS 450 may be retrofitted with a XAD-4 denuder and a PUF/XAD-4 sorbent trap to collect semi-volatile organic aerosols as the technology becomes available for routine application.

To obtain the fine particulate matter, the sample air inlet particle size separator is as specified in 40 CFR Part 50 Appendix L and identical to the FRM WINS. This provides an identical cut point and efficiency curve. These samplers use active volumetric flow rate control which is designed to meet FRM specifications and, therefore, has the same accuracy of flow as an FRM sampler. One modification of the inlet is a high capacity sodium carbonate annular denuder placed between the PM head and WINS inlet.

Perfluoroalkoxy (PFA) Teflon® coating of the inlet is an option that is available. This would allow particles and gases to pass through the inlet with high efficiency. If an accurate measurement of nitric acid is desired, then PFA-Teflon® coating is needed. Coated surfaces can pass nitric acid with 80 percent to 100 percent efficiency. Other materials, such as aluminum, can absorb some gases, particularly nitric acid, that may change the equilibrium between volatile particles on a filter an the surrounding air. Coating also minimizes oxidation of inlet internal and external surfaces, thus extending the life of the sampler.

The sampler configuration for both the MASS400 and MASS450 is shown in Figure 6-2. While an aluminum inlet will remove some of the nitric acid, it is not 100 percent efficient. Nitric acid is removed by using an annular denuder coated with sodium carbonate that quantitatively removes the acidic gases, including HNO_3, from the air stream. If NH_3

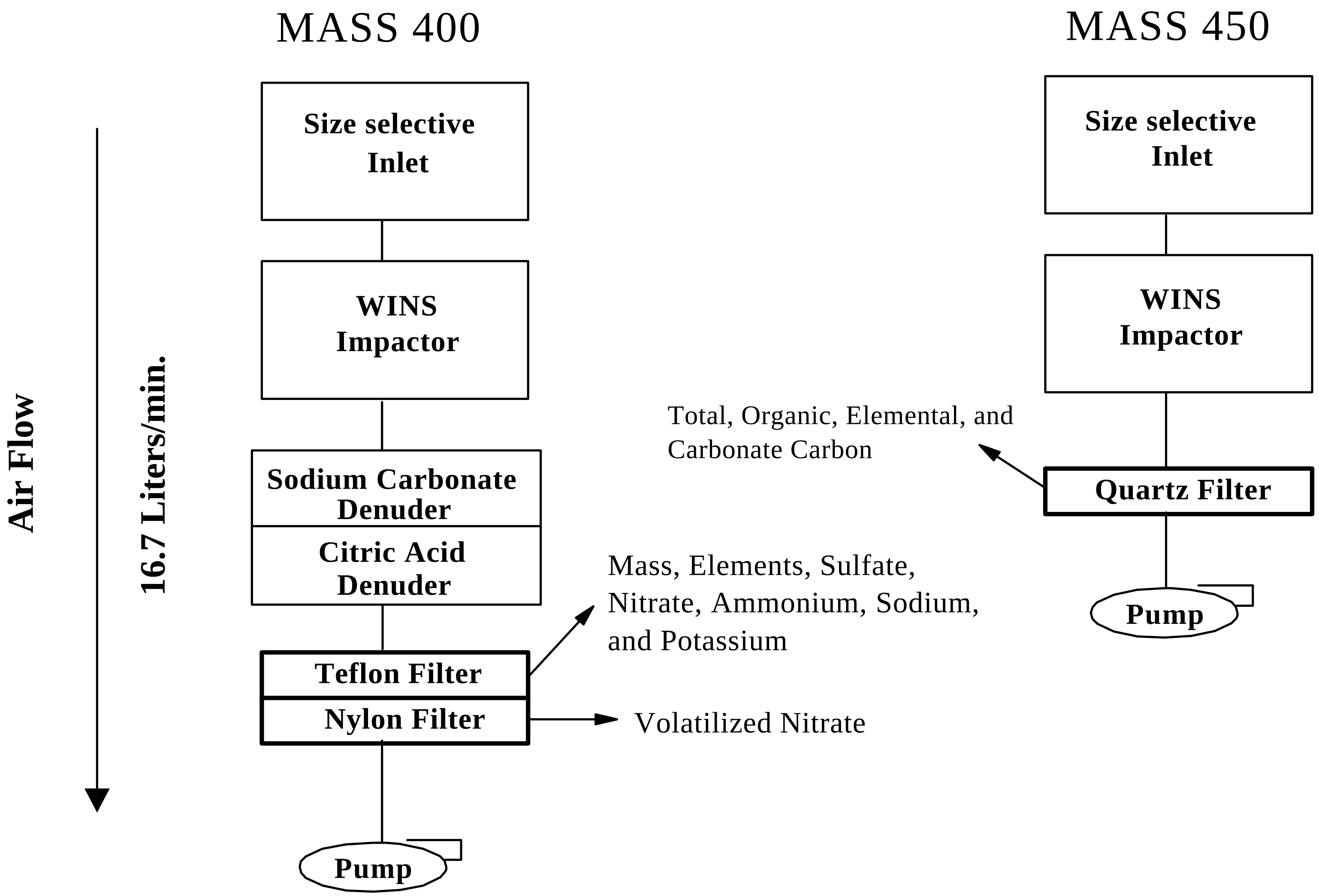

Figure 6-2. Schematic diagram of the MASS 400 and MASS 450 sampling systems

measurements are needed in conjunction with the aerosol measurement the denuder may be extracted and analyzed for ammonium ion content. In addition, if ammonia reacts with acid sulfates this effect. to differentiate between SVOC's in gas phase and the SVOC's that evaporate (negative artifacts) during sampling. Quartz filters have some affinity for gas phase SVOC's, thus, removing these species from the air stream minimizes their adsorption (positive artifact).

The PUF/XAD-4 trap will quantitatively collect the semi-volatile organic species that evaporate from the particles during collection of the sample. These organic species can be quantified by GC/FID/MS analysis of the XAD/PUF extracts or by evaporating the extract and weighing the residual materials. on the filter, a positive mass artifact would result.

6.4.3 Reference Ambient Air Sampler (RAAS™)

Ambient air is pulled through a wind direction and speed insensitive inlet and through an inert inlet line that is insulated from direct heating by the sun. The inlet has no size selective function. The air sample is directed via the sample downtube to a primary sample flow splitter into two streams. Each of the two flow streams in turn move through a AIHL-design cyclone separator which removes coarse particles with diameters larger than 2.5 μm. The cyclone requires a precise flow of 24 liters per minute to produce the correct cut point for sample collection. Following one side after splitting, the remaining particulate and gases are split again through the sample manifold into one, two or three outlet channels. The flow streams are then directed through the sample filters. The flow rate through each filter holder is controlled by a critical orifice that can be changed if a different sampler configuration flow rate is desired for special studies. The other half of the primary flow stream duplicates this flow path. A total of six channels are available for various speciation sampling objectives. For the routine chemical speciation program a total of 4 channels are used as shown in the schematic in Figure 6-3.

All inlet, manifold, connector and cyclone parts are fabricated from polytetrafluoroethylene (PTFE)-coated aluminum. Any combination of reactive annular denuders or filter materials can be attached with consideration for the flow requirements and species to be measured. In normal sampling, the combined flow rate to both filter holder assembles is 24 liters per minute, which is divided into one 16.7 and one 7.3 liter per minute subdivisions. Two of these sampling lines collect fine particles on standard 46.2-mm diameter PTFE filters for subsequent chemical analysis. Two PTFE filters are used because samples intended for X-ray fluorescence analysis may be placed in a vacuum chamber during analysis leading to the expected loss of volatile aerosol components, thereby making it desirable to use a second PTFE filter for analysis for ionic species.

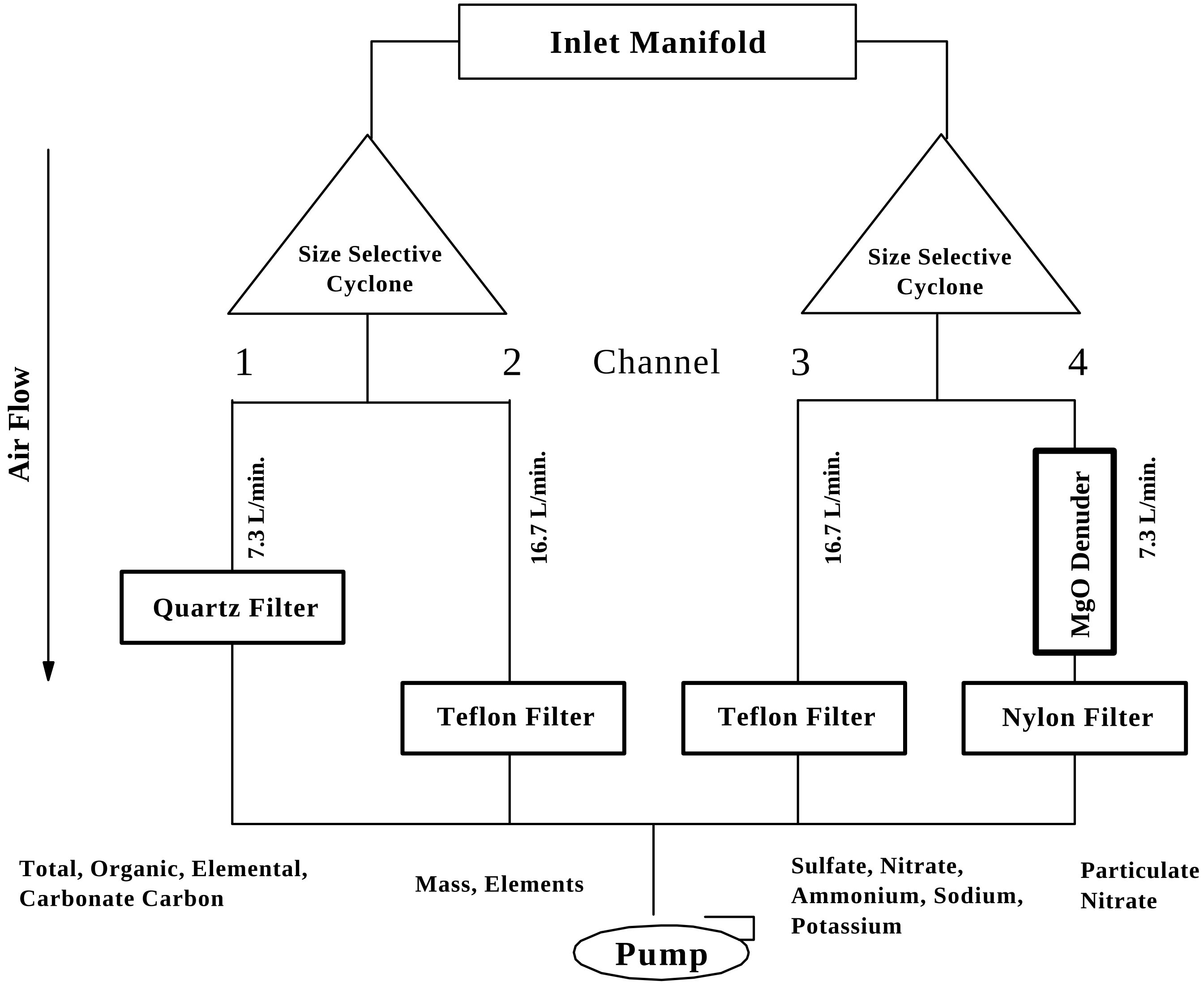

Figure 6-3. Schematic of the RAAS™ sampling system

A third filter holder is used to collect particles on a quartz fiber filter from which carbonaceous species can be measured by thermal optical analysis. If semi-volatile species are to be determined, a diffusion denuder coated with XAD to remove gaseous semi-volatile organics from the incoming air stream and a backup trap using polyurethane foam (PUF) or XAD resin to capture any semi-volatile organic components evaporating from the particulate captured on the filter may be used.

The fourth filter is a nylon filter located downstream from a magnesium oxide (MgO)-coated diffusion denuder. The diffusion denuder removes nitric acid vapor from the air stream while allowing fine particulate nitrate to pass through the denuder; then the nylon filter captures the fine particulate nitrate. The nylon filter is used because it has a high affinity for nitric acid. The nitrate content of any particulate ammonium nitrate (NH_4NO_3) that dissociates during sampling will be retained by the nylon filter. This system eliminates the well known negative sampling artifact for nitrates that can occur in locations such as Los Angeles and many cities in the West, that experience significant fine particle ammonium nitrate concentrations. A single denuded nylon filter is used rather than a nylon filter downstream from one of the PTFE filters to guard against the evaporative loss of ammonium nitrate (NH_4NO_3) from the PTFE filter after sampling has ceased but before samples are retrieved from the field. An optional PTFE-coated filter holder equipped with a nylon filter can be located in parallel with those filters that are directly downstream of the cyclone separator which will permit nitric acid concentrations to be measured by the denuder difference technique.

The relative humidity, barometric pressure, orifice pressure, ambient temperature, manifold temperature, meter temperature, and cabinet temperature are measured by the RAAS control unit. The control unit uses a microprocessor to control the various aspects of the system operation. An RS-232 serial port is provided to allow for retrieval of sampling data using a personal computer or other data storage device.

6.4.4 Spiral Ambient Speciation Sampler (SASS™)

This sampler provides five parallel sample cassettes as shown in Figure 6-4. Each cassette has its own spiral size-selective $PM_{2.5}$ inlet, denuder (if applicable), and tandem filter holder. The five cassettes are mounted in an aspirated radiation shield that maintains the sampler temperature close to ambient. Cassette inlets point downward. The sampling head has five independent sampling channels, each operated at a sample flow rate of about 6.0 liters per minute. Ambient air enters each independent sampling inlet and the particle size separated by a

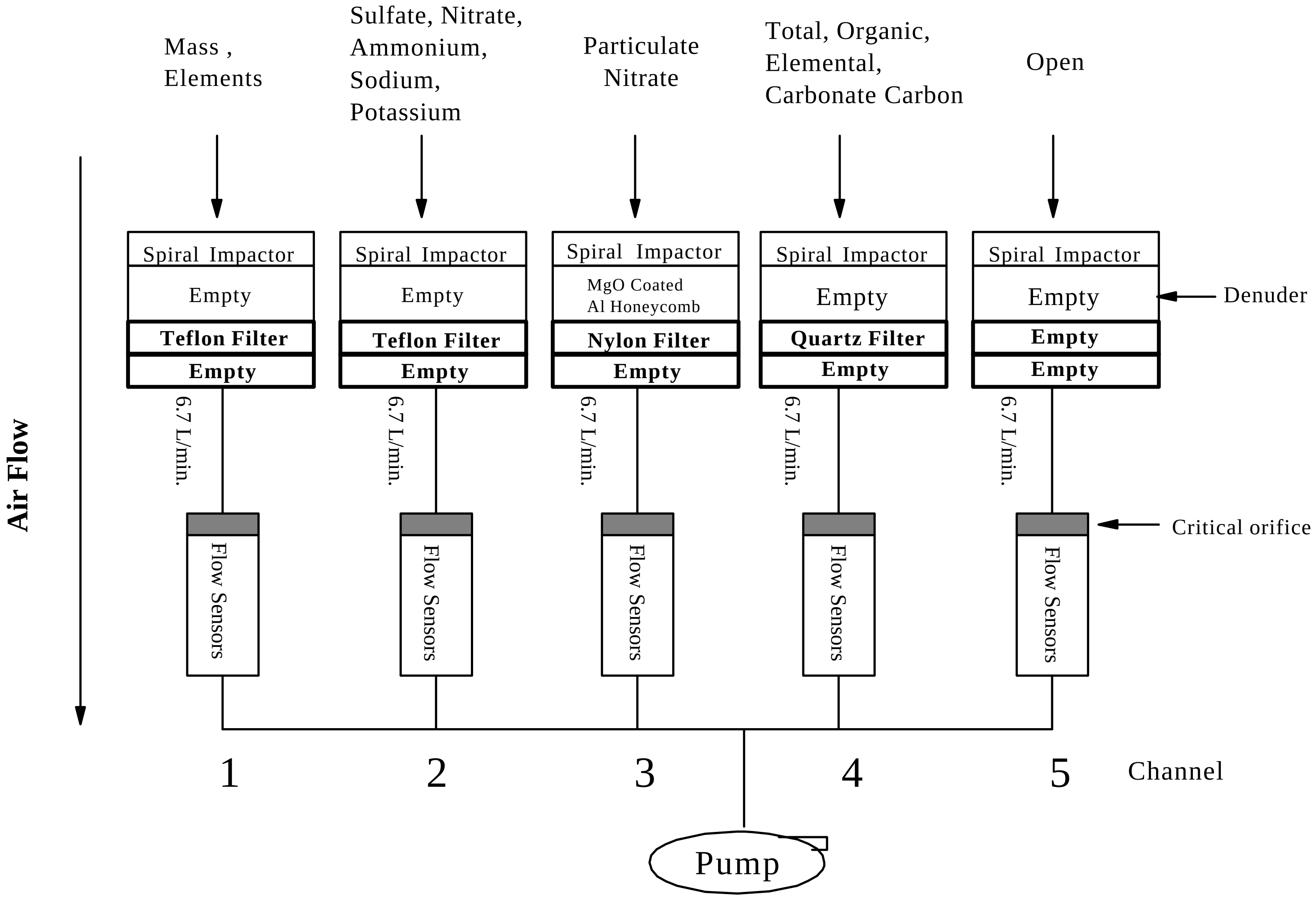

Figure 6-4. Schematic diagram of the SASS™ sampling system configuration.

spiral inlet (John 1997). The particle separator does not require the use of grease or oil anti-bounce agents. The spiral inlet is built into the cassette which allows the inlet to be cleaned in the laboratory before or after each sample event to ensure accurate performance. The sampler does not use a plenum or sample tube which requires field maintenance.

Two types of denuders of multi-cell configuration are provided. The nitric acid denuder is made of aluminum and is coated with magnesium oxide. The carbon denuder, used for collection of semi-volatile species, is made using activated carbon. These denuders remove interfering gases but are not designed to be extracted for direct analysis.

The five cassettes provided with the sampler can be used in multiple configurations. For the routine speciation trends program, the suggested configuration for the five cassettes incorporates:

- a Teflon® filter for mass and trace elements;
- MgO-denuder followed by a nylon filter for particulate nitrate;
- a second Teflon® filter for anions and cations;
- a quartz filter for carbon; and
- an additional filter channel of choice for replicate sampling or field blank collection.

Any cassette can be configured with one or two filters or a denuder followed by one or two filters. The filter cassette temperature is monitored and the data logged. The fan aspirated solar radiation shield houses the five individual cassettes and maintains the cassette filter temperature during a sample event to less than 5 C above ambient temperature. A shielded ambient temperature sensor mounted to the control module logs the ambient temperature.

The flow from each cassette passes through a critical orifice, a mass flow sensor, a valve and then to a common pumping manifold. The critical orifice controls the sample flow rate. The valve located downstream of the filter can be used to close sample lines not in use. The mass flow sensors are used for flow measurement. The flow rate sensors send a signal to the microprocessor which takes the ambient temperature and barometric pressure readings to calculate and display the current volumetric sample rate of each channel. The pumping manifold pressure is read by a mechanical differential pressure gauge leading to a control valve prior to the vacuum pump. The pump uses a rotary carbon vane rated for 20,000 to 30,000 hours of use between vane replacement. The pump is mounted in its own separate enclosure to minimize heat, vibration, isolate power and protect the sampling system from re-entrained dust.

6.5 Other Monitor Types

The monitor types briefly discussed below can also be considered in configuring a non-routine NAMS speciation network. Selection of these monitor types are dependent on the monitoring network and data use objectives.

6.5.1 Single Channel Monitors

Single channel (single inlet assembly and filter medium), FRM samplers are not expected to be routinely used in speciation sampling. A designated FRM or FEM sampler, operated with the appropriate filter media, can be used to collected a sample that may be subsequently analyzed for targeted chemical species. This approach may be used in cases where chemical speciation analyses are performed on a Teflon® filter, after gravimetric analyses has determined a high fine particulate loading. In the case of a Teflon® filter media, the sample can be analyzed for trace elements. The single channel sampler could also be used with other filter media to collect fine particulate for other targeted chemical species. Multiple FRM/FEMs with multiple filter media would be needed to cover the entire group of target chemical species. Alternatively, a uniquely designed sampler could be used to capture fine particulate on nylon and quartz filters, and a FRM sampler used to capture fine particulate on a Teflon® filter.

6.5.2 Continuous Monitors

The EPA encourages the use of continuous monitors as part of the non-routine NAMS speciation monitoring program. Continuous monitors should only be considered for use at routine NAMS as the technology develops and is demonstrated as adequate for use to meet the program and data quality objectives. Continuous monitoring data can be used to provide more timely data reports to the public and collection of data on a more real time basis. Continuous monitors can be used to characterize diurnal patterns of exposure and emissions and are extremely useful in collecting samples during extremely high or low particulate periods.

Currently available continuous monitors for mass include the Tapered Element Oscillating Microbalance (TEOM®), Piezoelectric Microbalance, Beta Attenuation Monitor (BAM), and the Pressure Drop Tape Sampler (CAMMS). Chemical-specific particle monitors include single particle mass spectrometers, a particulate carbon monitor, sulfur analyzer with Flame Photometric Detection (FPD), nitrate analyzers, and elemental analyzers. Precursor gas continuous monitors include a chemiluminescence ammonia analyzer, fluorescence ammonia gas analyzer, and nitric acid analyzers. Refer to the ***Guidance for Using Continuous Monitors in $PM_{2.5}$ Monitoring***

Networks (U.S. EPA, 1998b), for additional guidance regarding the use of continuous in-situ measurements of suspended particles, their chemical components, and their gaseous precursors.

6.5.3 Saturation Monitors

EPA encourages State and local air pollution control agencies to conduct short-term, multi-site pollutant monitoring studies using a technique known as saturation monitoring. Saturation monitors are non-reference method, small portable samplers which are readily set-up, operated, and easy to site. Also, because they are relatively inexpensive, it is possible to "saturate" an area with these monitors to assess air quality in areas where high concentrations of pollutants are possible. Saturation monitors are expected to be used to determine “hot spots” of fine particulate. This information can be used to help air pollution control agencies gather preliminary information for speciation sampler siting and evaluate and develop their monitoring networks. Saturation monitoring may also be conducted to characterize the spatial distribution of pollutant concentrations or to evaluate the contributions of sources in support of receptor modeling.

6.5.4 Special Purpose Monitors

A strength in the design of the speciation program is sufficient flexibility to accommodate coordination between the user’s needs and advances in sampling technology as they become available. Hence, there is a provision for special purpose monitors (SPMs) as part of the $PM_{2.5}$ program. These monitors can serve a variety of uses including research, regulatory support (i.e., SIPs) and others. The SPMs will not be used as NAMS samplers; they may be collocated with NAMS speciation and FRM samplers. The SPMs may be utilized as part of the speciation program in the sense that subsequent laboratory analysis of the captured particulate may be performed as part of the speciation program, if resources are available.

Special purpose monitors are a separate component of the $PM_{2.5}$ network and as such are not part of the 1,500 network sites. The use of special purpose monitors is expected to complement or be complemented by the use of speciation monitors. Specific requirements of special purpose monitors are not prescribed, so that study designers may tailor monitoring components to the end user needs. Any use of a special purpose monitor should take into consideration the design of the speciation components of the PM fine network and how data can be evaluated.

6.6 Sampling Procedures

Published sampling procedures from several sources are expected to be utilized for compiling the sampling procedures used in the speciation component of the $PM_{2.5}$ program. Sources may include, but are not limited to: sampler manuals, section 2.12 of the QA handbook (U.S. EPA, 1998a), and other sampling methods published from the peer-reviewed literature.

7.0 SAMPLE ANALYSIS

With the goal of ensuring data quality for several thousand filter analyses per year, which will utilize a range of analytical methods for the species required, it is critical to establish an analytical laboratory framework which is consistent to support these needs. One key aspect of the framework is the establishment of standardized SOPs for the routine NAMS speciation analyses. The SOPs will be based on analytical methods with proven application to the analysis of ambient particulate matter filter samples as specified in Table 3-1 of Section 3. In addition to guidance on sampling and handling, the EPA will also develop guidance and documentation for SOPs on the laboratory analysis of the target analytes. The guidance will include laboratory quality assurance guidelines specific to the methods of analysis and guidelines on standardized data reduction, validation, sample handling, chain-of-custody, and reporting formats. The EPA plans for the speciation data to be submitted to the Aerometric Information Retrieval System (AIRS) data base. The EPA is developing laboratory SOPs that are complementary to the techniques used by various agencies and research groups operating ambient air particulate matter speciation programs.

The operational schedule for providing the speciation laboratory support services began with development of a program team of EPA Office of Air Quality Planning and Standards (OAQPS) and Regional Office personnel. The OAQPS has provided the development of the required guidance information and the SOPs with input from the Office of Research and Development (ORD), EPA Regional Offices, and the $PM_{2.5}$ monitoring technical community. Initial deployment of the approximately 50 speciation monitors for the routine trend network is projected for the third quarter of calendar year 1999. Allowing for time by site operators to be trained in the use of the monitors, we project that the laboratory services support portion of the National $PM_{2.5}$ Speciation Program will be in place by July of 1999. The speciation analytical guidelines developed by EPA can also be used by State laboratories with appropriate facilities to provide local support, if appropriate, for an individual State-level monitoring network. In addition EPA is studying the process of evaluating alternative test methodology which may be proposed by States. In such a process, an equivalency methodology guideline would have to be developed that can be used by States to prove that their proposed method performs well as defined by the guidelines.

The methods used for analyses of the filter media include gravimetry (electro-microbalance) for mass and various instrumental methods for determining the chemical composition of the particles. In addition to chemical analyses, special measurement needs may include determining particle size and morphology through optical and/or electron microscopy.

A national laboratory services support program consisting of contracted services with up to three qualified laboratories capable of providing consistent laboratory service support for all of the target analytes will be developed. The extent of the services will depend upon capacity needed, as well as the level of participation by State and local government laboratories for providing analytical services. Analytical support from the contract laboratories will be accessed through three EPA Regional Project Officers or Delivery Order Project Officers (DOPOs).

The contractor shall designate a Services Program Manager (SPM) for work performed under this contract. The SPM shall be responsible for the performance of work issued under this contract in accordance with the terms of the contract. The SPM shall provide information on the status and progress of laboratory services requests to the Project Officer (PO) and Delivery Order Project Officer (DOPO) as needed and submit contract-required reports to the PO/DOPO. The SPM shall notify the PO/DOPO regarding any problems encountered in the performance of work and implement PO/DOPO guidance in the resolution of problems. The SPM shall be responsible for maintaining technical and financial integrity in performance of the requested services, in accordance with EPA-issued delivery orders and contract terms and conditions. A flow diagram of the sample analysis Delivery Order process is given in Figure 7-1.

Analytical needs requests are initially submitted by a state to the corresponding EPA Regional Speciation Coordinator (RSC). The RSC consolidates all analytical requests received from states within their Region and submits them to the appropriate EPA DOPO. The DOPO, in turn, consolidates analytical requests from several regions. The Contracting Officer, as necessary will issue delivery orders to the Contractor's Laboratory. The Contract Laboratory prepares the appropriate filter media for sampling and delivers the media to the appropriate state. After sample collection, the state returns the samples along with sampler information to the Contract Laboratory. In addition, selected field quality assurance samples will be collected by the states and submitted to an appropriate EPA Region QA laboratory for analysis. The Contract Laboratory performs analysis, Level 0 and Level I data validation on all data sets and enters the data into AIRS. After Level I validation and AIRS data entry has been completed, the contractor submits the data sets in both hard copy and electronic format to the appropriate state requesting service. After each data set is submitted to the State, the contractor submits copies of the Level I data validation checklists and hard copies of the monthly analytical data reports to the appropriate EPA DOPO for review, acceptance, and recommendation for payment to the PO.

The most commonly applied aerosol analyses methods can be divided into the following categories: mass, elements, ions, and carbon. It is possible to obtain several different analyses from the same substrate, but not possible to obtain all desired chemical species from a single substrate; therefore, the appropriate filter media, sampling hardware, and analysis methods must be combined. Depending on the study objectives and sources in an area, different chemical species may need to be added or omitted. A flow diagram of filter processing and analysis activities for the NAMS is shown in Figure 7-2.

The following sections outline the filter analysis methods for the target chemical species categories of elements, ions, and organic carbon.

7.1 Elements

Energy dispersive X-ray fluorescence (EDXRF) by Method Inorganic Compendium of Methods IO-3.3 (U.S. EPA, 1997d) is the method chosen to characterize the elemental composition of the aerosol deposits on PTFE filters for the routine $PM_{2.5}$ NAMS chemical speciation program. Interest in elemental composition is commonly derived from concerns about health effects and the utility of these elements to trace the sources of suspended particles or source characterization. Since sample filters often contain very small amounts of particle deposits, preference is given to methods that can accommodate small sample sizes and require little or no sample preparation or operator time after the samples are placed into the analyzer. X-ray fluorescence (XRF) meets these needs and leaves the sample intact after analysis so it can be submitted for additional examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF typically places the filters in a vacuum which may cause volatile compounds (nitrates and organics) to evaporate. Volatilization will not be an issue for the NAMS sampling systems where the PTFE filters are not subsequently analyzed for volatile species.

In XRF the filter deposit is irradiated by high energy X-rays which causes the ejection of inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent X-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are determined by comparing photon counts for a sample with those obtained from thin-film standards of known concentration.

The type of filter is important and thin membrane filters (PTFE) are required so that the background is low and penetration of particles into the matrix of the filter is small. XRF provides rapid, simultaneous, and nondestructive detection of the target elements from Al to Pb. Advantages of using XRF are the quantitative analysis of bulk elemental composition, the ability to perform trace level particulate analysis with sensitivity to ppm levels, and the availability of instrumentation. The XRF method of analysis employs an energy dispersive spectrometer. Analysis atmospheres are selectable with choices of helium or air; helium is used for all target elements except Gd where air is employed because it gives a lower background.

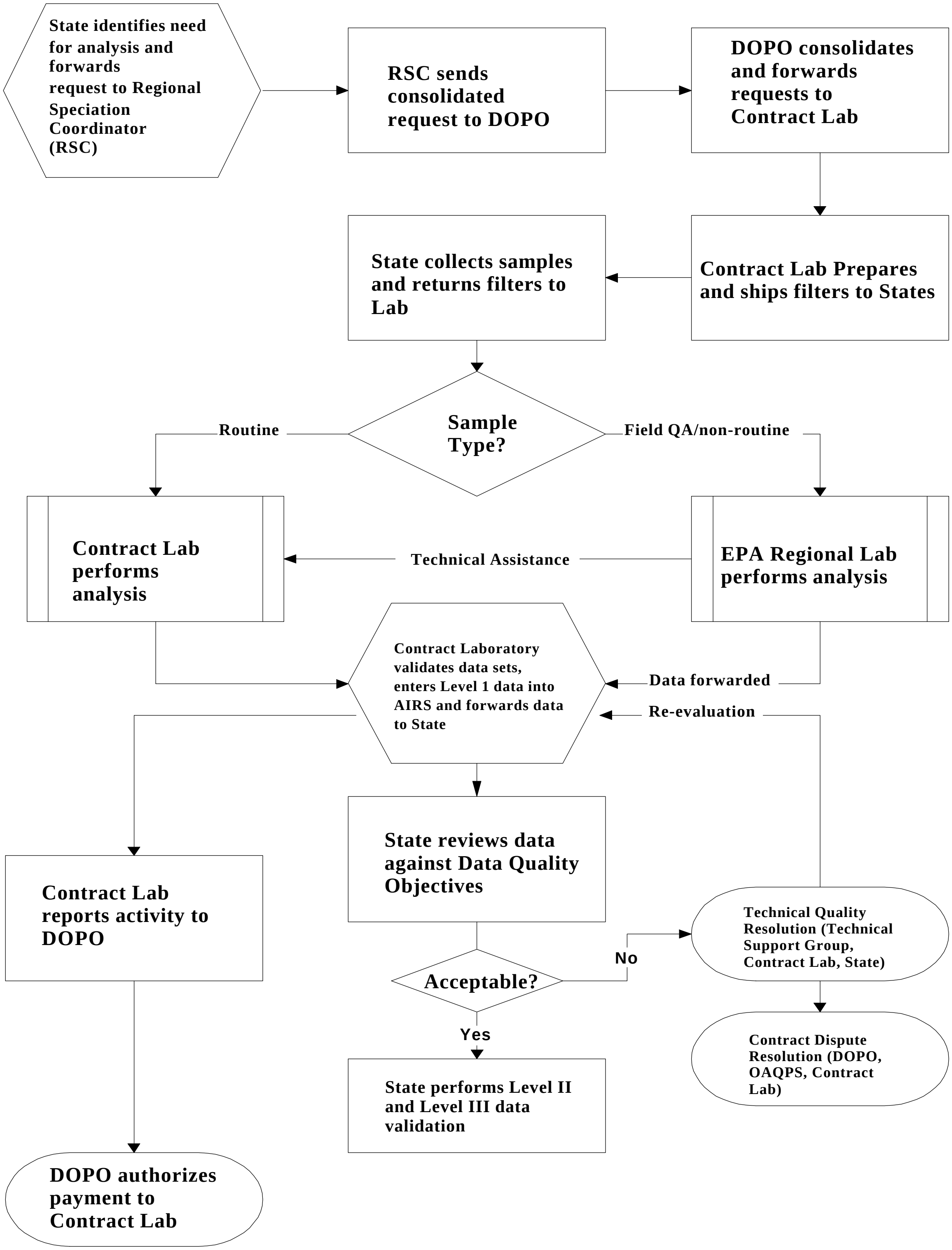

Figure 7-1. Flow diagram of the sample analysis Delivery Order process

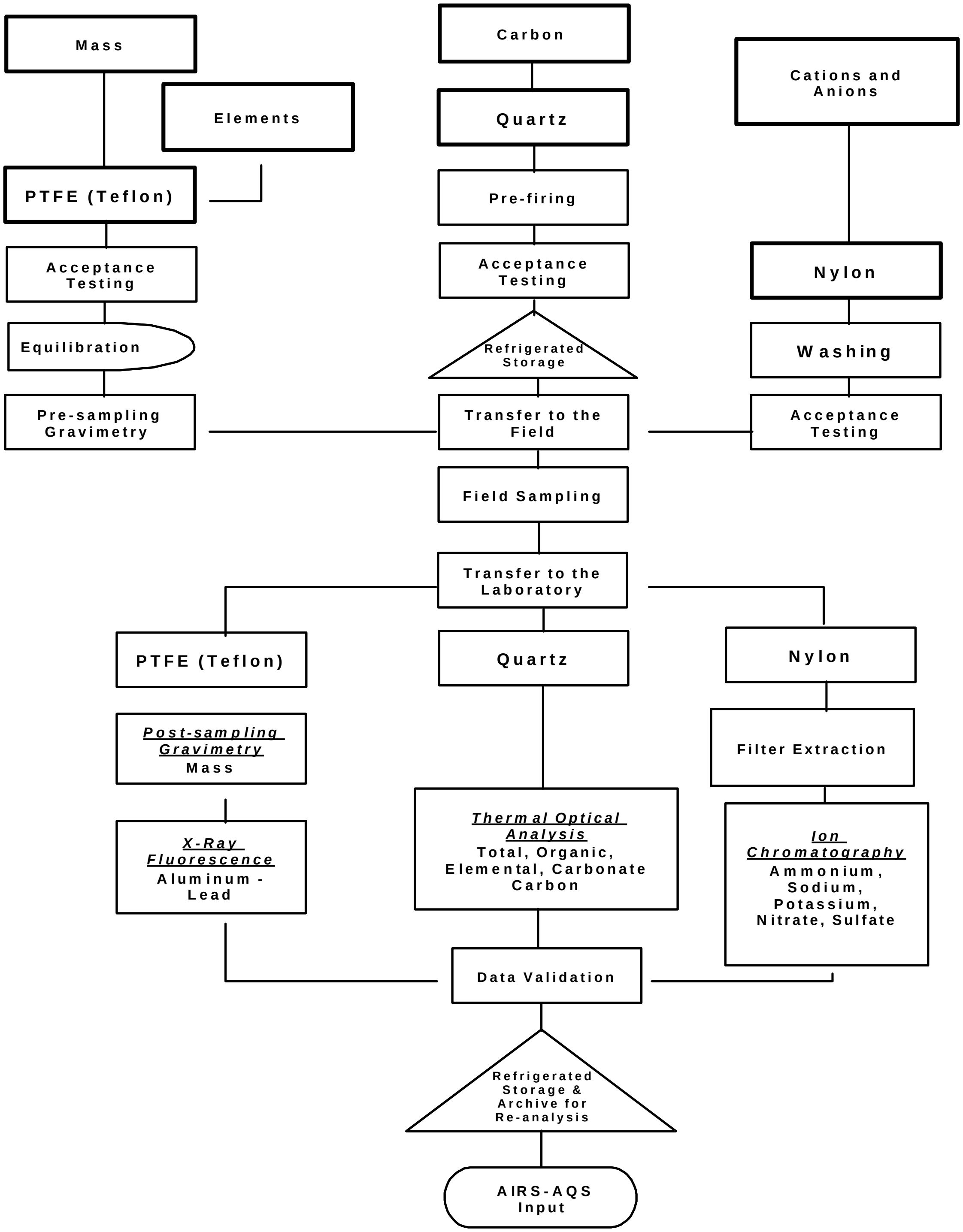

Figure 7-2. Flow diagram of filter processing and analysis activities

Calibration is by far the most complicated task in the operation of the XRF. Recalibration is only performed when a change in fluorescers or x-ray tubes is made or a serious instrument malfunction occurs. Three types of XRF standards are available for calibration: vacuum deposited thin film elements; polymer films; and NIST thin-glass films. The vacuum deposited thin film standards are available for almost all elements analyzed and are used to establish calibration curves. Some standards have high inherent volatility and do not serve well as calibration standards. These are selenium (Se), bromine (Br), mercury (Hg), and elemental arsenic (As). The same set of standards is used every time the spectrometer is calibrated. These standards are sufficiently durable to last many years. Polymer films contain two elements in the form of organo-metallic compounds dissolved in the polymer as described in Dzubay et al., 1988. These standards are available for elements with atomic numbers above 21 (Titanium or heavier). The polymer films and NIST standards are typically used for quality control measures. NIST produces reference materials for iron, lead, potassium, silicon, titanium, and zinc (SRM 1833).

The sensitivity of this method is on the order of few ng/m_3 for 24-hour samples (flow rates of 10-20 liters per minute). This may be a potential issue for the SASS samplers which operate at a flow rate of 6.7 liters per minute for the PTFE filter. Nonetheless, quite often environmental samples have elemental measurements below the detection limit of this method. Thus, analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. It should be mentioned that, during the analysis using XRF, the sample is typically introduced into a chamber that is evacuated and the sample is slightly heated due to the absorption of X-rays or protons. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during the analysis. This volatilization is important if the PTFE filter is to be subjected to subsequent analyses of volatile species.

7.2 Ions

Aerosol ions refer to chemical compounds which are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and nonsoluble fractions as in the case of soluble potassium. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material.

Polyatomic ions such as sulfate, nitrate, and ammonium are quantified by methods such as ion chromatography (IC). Simple ions, such as chloride, and fluoride may also be measured by IC along with the polyatomic ions. When the aerosol deposit is suspected of being acidic, its hydrogen ion content can be determined by a pH electrode or by micro titration. It is important to keep the filter away from ammonia sources, such as human breath, to minimize neutralization of the acidic compounds.

Applied to aerosol samples, the anions and cations are most commonly analyzed by IC. IC can be used for anions (fluoride, phosphate, chloride, nitrate, sulfate) and cations (potassium, ammonium, sodium) by employing separate columns. All ion analysis methods require a fraction of the filter to be extracted in deionized distilled water and then filtered to remove insoluble residues prior to analysis. The extraction volume should be as small as possible to avoid over-diluting the solution and inhibiting the detection of the desired constituents at levels typical of those found in ambient $PM_{2.5}$ samples. IC is the method used for IMPROVE and chosen for the $PM_{2.5}$ NAMS speciation program for the analysis of the target cations (ammonium, sodium, and potassium) and anions (nitrate and sulfate).

A major sampling requirement for analysis of water-soluble species is that the filter material be hydrophilic, allowing the water to penetrate the filter and fully extract the desired chemical components. A nylon filter is used for volatilized and particulate nitrate and sulfate anions and the ammonium, sodium, and potassium cations. The anions and cations are extracted with ultrapure deionized water. A small amount of ethanol may be used to help wet the nylon filter and improve analyte recovery.

In IC, the sample extract passes through an ion-exchange column which separates the ions for individual quantification, usually by a electroconductivity detector. The anions are separated when passed through a resin consisting of polymer beads coated with quaternary ammonium active sites. The separation is a result of the different affinities of the anions for these sites. After separation and prior to detection, the column effluent and anions enter a suppressor column where the cations are exchanged for H^+ ions. Species are then detected as their acids by a conductivity meter. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. The IC is especially desirable for particulate samples because it provides results for several ions with a single analysis, low detection limits, and uses a small portion of the filter extract.

The cations are analyzed in the same manner except the sample extract passes through a surface-sulfonated ion exchange resin where separation occurs. After separation and prior to detection, the cations enter a suppressor column where all the anions are exchanged for OH^- ions. The species are then detected as their bases (hydroxides) by a conductivity meter. Concentrations of ions and cations are proportional to the conductivity changes.

7.3 Carbonaceous Aerosols

Three classes of carbon are typically measured in ambient aerosol samples collected on pre-fired quartz-fiber filters: 1) organic, volatilized, or non-light absorbing carbon; 2) elemental or light-absorbing carbon; and 3) carbonate carbon. Carbonate-source carbon [i.e., potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$)] may be specifically determined from a second filter section after acidification. Without acidification, the determination of carbonate carbon is not specific and is detected as either organic or elemental carbon.

Two thermal-optical methods currently are in use for the analysis of carbonaceous aerosols. The measurement principle is fundamentally the same, but the methods differ with respect to calibration, analysis time, temperature ramping and settings, types of carbon speciated, and pyrolysis correction technique. The method's pyrolysis correction feature allows correction for the char that forms on the filter during analysis of some materials (e.g., cigarette smoke). Correction for pyrolysis is made by continuously monitoring the filter transmittance (NIOSH Method 5040) or reflectance (TOR) throughout the analysis.

For the NAMS chemical speciation program, total, organic, elemental, and carbonate carbon will be determined by thermal/optical instrumentation specified in NIOSH Method 5040 (NIOSH, 1996, 1998) and described in the literature (Birch and Cary, 1996). Method 5040 was developed for occupational monitoring of diesel particulate, but its evaluation also included a round-robin study involving a variety of carbonaceous aerosols (Birch, 1998). The thermal-optical method is applicable to nonvolatile, carbon-containing species only. Thermal-optical analyzers are practical, economical, and are routinely used for environmental and occupational monitoring of carbonaceous aerosols. Although the number of commercial laboratories currently is limited, an adequate number (3 in the U.S.) are available to cover the analytical demands of this program.

A schematic of the thermal-optical analyzer evaluated by NIOSH researchers is shown in Figure 7-3; an example of the instrument's output, called a 'thermogram,' is given in Figure 7-4. The traces appearing in the thermogram correspond to temperature, filter transmittance, and detector response of the flame ionization detector. Thermal-optical analyzers operate by liberating carbon compounds under different temperature and oxidation environments. A small portion (or punch) is taken from a quartz-fiber filter sample and placed in the sample oven. The oven is purged with helium and the temperature is then stepped to a preset value. Volatilized compounds are converted to carbon dioxide (CO_2) in an oxidizer oven (MnO_2 at 870 C or higher), the CO_2 is subsequently reduced to methane (CH_4) in a methanator (nickel-impregnated firebrick heated to ~550 C in a stream of hydrogen), and CH_4 is quantified by a flame ionization detector (FID). In the second part of the analysis, an oxygen-helium mix is introduced and the remaining carbon is removed through combustion and quantified in the same manner.

In NIOSH Method 5040, the sample oven is purged with helium and the temperature is stepped (to 250, 500, 650 and 850 C) to volatilize the organic and carbonate-source carbon. It is critical to ensure that trace oxygen is not present during the first part of the analysis. Potential sources of oxygen include leaks and inadequate helium gas purification. If present, trace oxygen will cause organic carbon to be overestimated and elemental carbon correspondingly underestimated. In the second part of the analysis, the temperature is lowered, a 2% oxygen/98% helium mix is introduced, and the temperature is then stepped to a maximum of 940 C. At the end of the analysis, a calibration gas standard (CH_4) is injected. Correction for pyrolysis is made by continuously monitoring the filter transmittance throughout the analysis. The point at which the filter transmittance returns to its original value is defined as the split between organic and elemental carbon. Designation of the split in this manner allows assignment of pyrolyzed organic carbon to the organic fraction.

In general, thermal-optical methods classify carbon as ‘organic’ or ‘elemental.’ Organic carbon is non-light absorbing carbon that is volatilized in helium as the temperature is stepped to a preset maximum (850 C). Elemental carbon is light-absorbing carbon and any non-light absorbing carbon evolved after pyrolysis correction. Depending on the sampling environment, carbonates [e.g., potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$)] also may be present in the sample. Carbonate-source carbon is quantified as organic by NIOSH Method 5040, wherein the sample is exposed to 850 C during the first part of the analysis (i.e., in helium only). Under these conditions, thermal decomposition of carbonate occurs. To quantify carbonate carbon, a second portion of the filter sample is analyzed after its acidification. Carbonate is taken as the difference between the pre- and post-acidification results (Note: the approach assumes a homogeneous filter deposit). Alternatively, carbonate carbon in a simple carbonate (i.e., not a bicarbonate) can be estimated by integrating the carbonate peak (typically the fourth peak in ‘thermogram’). The carbonate peak can be integrated separately within the instrument’s calculation software. This approach normally is taken when higher loadings of carbonate are present. In the case of the TOR method, carbonate in a filter portion is determined through on-line measurement of the carbon dioxide (CO_2) evolved upon acidification. Acid (0.04 M HCl) is injected directly onto the filter portion through an injection port. The sample oven is kept at ambient temperature while CO_2 is evolved, reduced to methane and quantified. (Note: This approach is subject to potential interference of adsorbed CO_2). Typically, carbonate carbon is not speciated in environmental samples because it

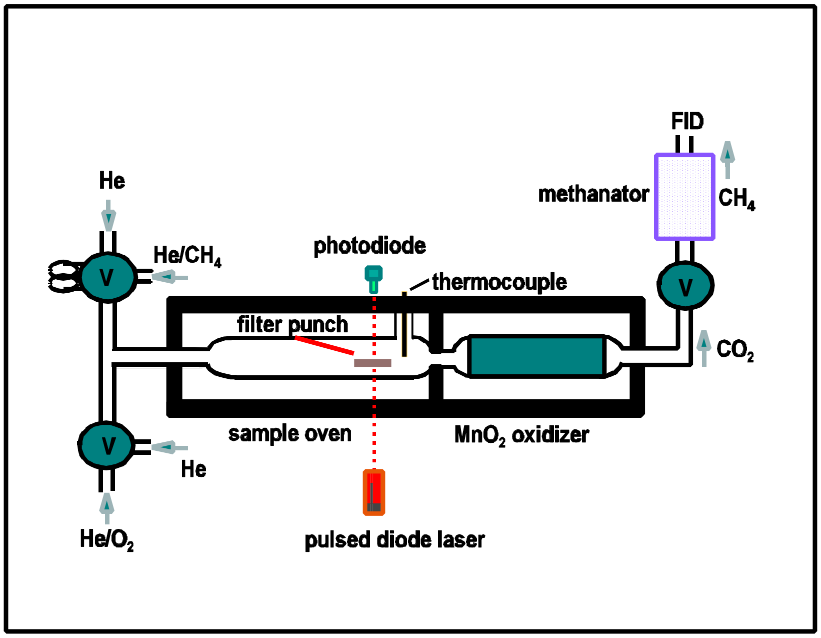

Figure 7-3. Schematic of a Thermal-Optical Analyzer

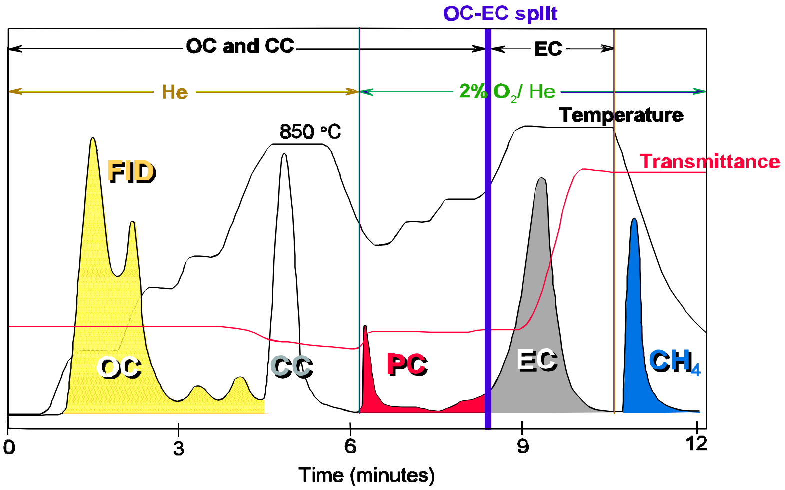

Figure 7-4. Thermogram for a sample containing organic, carbonate, pyrolytic and elemental carbon (OC, CC, PC and EC). The last peak is the methane calibration peak.

has been found to constitute less than 5 percent of the total carbon in most samples (Chow et al., 1993).

It is important to remember that elemental and organic carbon have meaning only in the operational sense. That is, results reflect the method used and the appropriateness of a method depends on its purpose. Operational methods differ from those used for specific, identifiable analytes (e.g., sulfate or sulfur), where a well-defined entity is quantified and laboratory standards are available for its determination. Because elemental and organic carbon are defined operationally, the details of the measurement method must be rigorously prescribed.

Only one organic and one elemental carbon fraction are reported in NIOSH 5040 (total carbon is the sum of these two) and carbonate carbon as simple carbonate (i.e., not a bicarbonate) can be estimated by integrating the carbonate peak (typically the fourth peak in 'thermogram'). In contrast, four types of organic carbon and three types of elemental are defined by the TOR technique. In both instances, different classes of carbon are evolved from the sample during the analysis. In the case of Method 5040, the division into two fractions reflects the purpose of the method (i.e., occupational monitoring of diesel particulate). For other applications (e.g., source apportionment), additional fractions may be appropriate provided that the applied temperature program is repeatable over time. Otherwise, relative information will not be meaningful because non-constant analytical parameters can affect the classification of carbon types.

7.4 Semi-volatile Organic Aerosols

Semi-volatile organic aerosols should not be considered on a routine basis due to the non-routine and research-oriented nature of measuring these species. Identification of the ideal denuder, filter combination, and sorbents and development of routine sampling and analytical methods is complicated due to the number and variety of semi-volatile organic aerosol compounds in the atmosphere and their varying absorptive properties.

The collection of particulate organic matter can be accomplished using particulate sampling instruments equipped with quartz fiber or Teflon®-impregnated glass fiber filters. However, since many organic compounds are distributed between the gas and particle phases, additional sampling techniques are required to measure the particle phase semi-volatile organics. This methodology is susceptible to negative (desorption of semi-volatile compounds from the particles on the filters) and positive (adsorption of gases by the filter material) artifacts. Considerable experimental and theoretical effort has been expended to understand and correct for these vaporization and adsorption effects. Denuder technology has been employed to provide a less artifact-encumbered approach for accurate determination of semi-volatile species because the gas phase is removed prior to the particulate phase. A sorbent or denuder after the filter may also be employed to collect any semi-volatile material desorbed from the filter.

For quantitation of individual organic compounds the denuder, filter, and sorbent is extracted individually with a suitable organic solvent (or a combination of solvents). The extract is then analyzed by gas chromatography (GC) combined with mass spectrometry (MS) or with other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also used.

8.0 QUALITY SYSTEM REQUIREMENTS FOR PM$_{2.5}$ SPECIATION SAMPLING AND ANALYSIS

The quality system is a structured and documented management system describing how and by whom an organization assures quality in its work. The Quality System was established by EPA Order 5360.1 (EPA Order 5360). The order requires all environmental programs conducted by the EPA, or on behalf of the EPA, to be supported by a mandatory Quality System (previously referred to as a Quality Assurance Program). The EPA is responsible for developing the quality system for the PM$_{2.5}$ chemical speciation program. As the standard, EPA has adopted the American National Standard ANSI/ASQC E4-1994, ***Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs***. When properly designed, a quality system encompasses both quality assurance and quality control through a quality management process by which quality system specifications are planned, implemented, and assessed. To collect data of the right type, quality and quantity to support decisions regarding the chemical speciation component of the National PM$_{2.5}$ Monitoring program, adequate planning and management of a quality system that integrates QA and QC requirements consistent with good field and laboratory practices is necessary.

To communicate the requirements and policies of EPA's Quality System to the Agency's internal organizations, the Quality Assurance Division (QAD) developed the EPA Quality Manual. For the organizations external to EPA (States, Regions, etc.), QAD developed the EPA ***Quality System Requirements for Environmental Programs*** (EPA QA/R-1). This document and other requirement and guidance documents are available from the EPA QAD homepage at http://es.epa.gov/ncerqa/qa. The Quality Manual describes how EPA organizations should implement the policies and requirements of the Quality System as defined in the Order. EPA QA/R-1 should be used to determine general requirements, then external organizations should consult the specific requirements (R-series) documents and guidance (G-series) documents for implementation.

The EPA used the Data Quality Objectives (DQO) process to develop the QA system for the PM$_{2.5}$ program. Meeting the objectives of the PM$_{2.5}$ program requires a combination of QA and QC procedures to evaluate and control measurement uncertainty. As a result, EPA has developed a quality system specifically for PM$_{2.5}$ which incorporates procedures to quantify total measurement uncertainty, as it relates to total precision and total bias. Total bias, precision, and accuracy are defined in 40 CFR Part 58, Appendix A (62 FR 38763). Total bias is defined as systematic or persistent distortion of a measurement process which causes errors in one direction. Total precision is defined as a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of standard deviation. Accuracy is defined as the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. Various QA tools to quantify measurement uncertainty include collocation of monitors at various sites; use of operational flow checks; and implementation of an independent technical systems audit.

The measurement system represents the entire data collection activity. This includes initial filter acceptance testing and equilibration, weighing, and transport; sampling instrument calibration, maintenance and operation; filter handling; laboratory analysis; storage and archival; and finally data analysis and reporting. Detailed QA procedures and guidance for all operational aspects of the PM2.5 program using the FRM for mass determinations is detailed in the ***QA Guidance Document 2.12***, (U.S. EPA, 1998a).

A quality system must be developed to permit maximum flexibility yet ensure that the measurement uncertainty is known and under control. To ensure consistency in the application of the Quality System, organizations must implement several components at the organization/program level:

- Each EPA organization collecting data must prepare a Quality Management Plan (QMP) that details the organization’s responsibilities;
- Data Quality Objectives (DQOs) will be developed to determine the data collection needs and sampling plan;
- One mandatory component at the project level is the Quality Assurance Project Plan (QAPP);
- Standard Operating Procedures (SOPs) are developed and documented in the QAPP for use during data collection;
- Technical System Audits and Reviews; and
- Following the implementation and planning stages of the program, the Data Quality Assessment (DQA) is performed to determine if the data collected is meeting the intended uses.

The development of data quality objectives and quality assurance project plans support the planning needs of monitoring studies. The implementation phase of a study is carried out using the quality assurance project plan and standard operating procedures. Assessment and redirection, if necessary, of activities within a study are performed by conducting management system reviews, technical assessments and audits, data quality assessment, and data validation.

8.1 Quality Management Plans (QMPs)

A properly developed quality management plan QMP encompasses all QA-related activities, procedures, and responsibilities. The EPA, OAQPS has developed a ***Quality Management Plan*** for intramural and extramural environmental data operations (U.S. EPA, 1996d). There are 10 elements the QMP should contain to ensure consistency. Most of the elements are mandatory, however, some elements may not apply in certain situations. The QMP is the responsibility of senior management within the organization administering the monitoring activities and incorporates the following 10 elements:

- Management and organization;
- Quality system description;
- Personnel qualifications and training;
- Procurement of items and services;
- Documentation and records;
- Computer hardware and software;
- Planning;
- Implementation of work processes;
- Assessment and responses; and
- Quality improvement.

8.2 Data Quality Objectives (DQOs)

An important concern in the collection and evaluation of ambient air monitoring data is the level of uncertainty of the data. Uncertainty arises due to temporal and spatial variability in the ambient air, variability in the samplers, and variability in the laboratory analyses. The DQO process is a seven-step systematic approach for defining the criteria that the $PM_{2.5}$ speciation data collection design should satisfy, including when to collect samples, where to collect samples, how many samples to collect, and the tolerable level of decision errors. By using the DQO process, EPA will assure that the type, quantity, and quality of the data will be appropriate for the intended application, while guarding against committing resources to data collection efforts that do not support a defensible decision. The outputs of the DQO process are used in developing a sampling design for data collection and preparing the QAPP. In addition, DQO outputs and assumptions are examined and applied during the DQA process.

A $PM_{2.5}$ speciation Work Group of EPA and State participants was convened to complete the DQO process for the $PM_{2.5}$ speciation program. More detailed information on the DQOs and measurement quality objectives is provided in Section 1.2.2 of this document.

8.3 Quality Assurance Project Plans (QAPPs)

The QAPP is a critical planning document for any environmental data operation. The QAPP documents how data operations are planned, implemented, and assessed with respect to the quality of the data required. The purpose of the QAPP is to define how specific QA and QC activities will be performed. The ***EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations***, EPA QA/R-5 and ***EPA Guidance for Quality Assurance Project Plans***, EPA QA/G-5 are documents that should be consulted in the preparation of the QAPP. The QAPP is composed of 25 elements grouped into four classes: 1) project management; 2) measurement and data acquisition ; 3) assessment and oversight; and 4) data validation and usability. Not all elements are addressed for every project; however, other projects may require additional elements not contained in the original 25. The final decision on the elements to be included in the QAPP is made by the overseeing EPA organization. **QAPPs are required for all environmental data operations that acquire, generate, or compile data and are performed by or on behalf of the EPA. A QAPP must be in place prior to the start of data collection.**

A stand-alone QAPP will be developed by the EPA for the $PM_{2.5}$ chemical speciation trends network. QA issues for filter preparation, sample handling and transport for mass measurements will be comparable to those stated in the of the ***QA Guidance Document 2.12*** (U.S. EPA, 1998a). Place holders will be included for sampler specific SOPs to be incorporated based on the sampler type chosen. With exception of the sampler specific SOPs, the QAPP will be equally applicable to the entire chemical speciation program. Prior to data collection, a QAPP is required to be prepared by each organization implementing a non-trends NAMS network.

During the planning phase, DQO outputs are documented int the QAPP in the form of measurement performance criteria and QA/QC procedures. SOPs are also included or referenced in the QAPP. Development of the QAPP provides a transition from planning to implementation. During implementation, data are collected in accordance with the QAPP. During the assessment phase, data are verified and validated according to procedures and criteria specified in the QAPP, and DQA analyzes the data to determine if the assumptions and criteria documented in the QAPP were met.

The QAPP is a planning document for environment data collection operations that describe the necessary quality assurance (QA) and quality control (QC). Quality assurance is an integrated system of management activities to ensure that a process or service is of the type and quality needed and expected by the end user (e.g., State or local regulatory agencies, EPA, general public, etc.). Quality control is defined as the overall system of technical activities that compares performance against defined standards to verify that stated requirements are met.

Every measurement consists of measurement quality objectives that refer to values of precision, accuracy, and validity. Quality control and quality auditing establish the precision, accuracy, and validity of measured values. Quality assurance integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. The results of quality assurance are data values with specified precision, accuracy, and validity. Quality auditing is performed by personnel who are independent of those performing the procedures. A separate quality assurance officer performs these audits.

Quality control is the responsibility of each operator and is intended to prevent, identify, correct, and define the consequences of difficulties which might affect the precision and accuracy, and or validity of the measurements. The QC activities include: modifying standard operating procedures (SOPs) to be followed during sampling, chemical analysis, and data processing; equipment overhaul, repair, acceptance testing, and spare parts; operator training, supervision, and support; periodic calibrations and performance tests, which include blank and replicate analyses; and quality auditing.

8.4 Standard Operating Procedures (SOPs)

SOPs document the specific procedures necessary to carry out routine or repetitive technical or administrative activities. SOPs are specific to the organization or facility where they will be used and ensure that the procedure is conducted in a standardized and reliable manner. SOPs provide standardization and consistency of methods and protocols used to ensure data comparability, credibility, defensibility and quality. The SOPs codify the actions which are taken to implement a measurement process over a specified time period. State-of-the-art scientific information is incorporated into the SOP with each revision.

SOPs are developed at the organizational level and applied at the project level. SOPs provide input to the QAPP, used for implementation of the data collection activities, and used as a specification during technical systems audits. SOPs are an important part of the personnel training program and must be kept current to be effective. For $PM_{2.5}$ chemical speciation sampling and analysis, SOPs are needed which effectively detail major field sampling and laboratory operations. Guidance for the preparation of SOPs is given in EPA QA/G-6, ***Guidance for the Preparation of Standard Operating Procedures***. Each SOP should include the following basic elements:

- A brief summary of the measurement method, its principles of operation, scope and applicability, expected accuracy and precision, and the assumptions which must be met for it to be valid.

- A list of materials, equipment, reagents, and suppliers. Specifications are given for each expendable item.
- Definition of terms (acronyms, abbreviations).
- Health and safety warnings indicating operations that could result in personal injury or loss of life and an explanation of what will happen if the procedure is not followed.
- Cautions indicating activities that could result in equipment damage, degradation of samples or possible invalidation of results.
- Personnel qualifications and designation of the individual to be responsible for each part of the procedure.
- A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification.
- Start-up, routine, and shut-down operating procedures and an abbreviated checklist.
- Copies of data forms with examples of filled-out forms.
- Routine maintenance schedules, maintenance procedures, and troubleshooting tips.
- Internal calibration and performance testing procedures and schedules.
- External performance auditing schedules.
- References to relevant literature and related standard operating procedures.
- Data and records management.

The ***Quality Assurance Guidance Document 2.12*** (U.S. EPA, 1998a), ***Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part 1*** (U.S. EPA, 1998g), and the ***Model QAPP for the $PM_{2.5}$ Ambient Air Monitoring Program at State and Local Air Monitoring Stations***, EPA-454/R-98-005, has been issued by the EPA to address $PM_{2.5}$ mass monitoring with designated FRMs. Table 8-1 gives an example of the SOPs that may be required for $PM_{2.5}$ chemical speciation. SOPs should be reviewed and updated annually to ensure that procedures specified in the SOPs are actually being followed in field and laboratory operations.

8.5 Technical Systems Audits and Performance Evaluations

The quality auditing function consists of technical systems audits and performance evaluations. Technical systems audits include an on-site review and inspection of a State or local agency’s monitoring program to assess compliance with established regulations that govern the collection, analysis, validation and reporting of the air quality data. Technical systems audits of the agencies operating the SLAMS chemical speciation program shall be conducted at least every 3 years by the EPA Regional QA laboratories. Detailed information regarding the performance of technical system audits is found in ***Quality Assurance Handbook for Air Pollution Measurement Systems*** (U.S. EPA, 1998g). A systems audit should consist of three phases: 1) pre-audit activities; 2) on-site audit activities; and 3) post-audit activities. Systems audits start with the preparation of an audit plan which documents items such as the audit scope, purpose, criteria, activities, and time line. A review of the operational and QC procedures are performed to assess whether they are adequate to ensure that data meet the specified levels of accuracy and precision. After reviewing the procedures, the auditor examines all phases of the measurement or data processing activity to determine that the procedures are being followed and the operational staff are properly trained. The findings of the audit are documented in a technical systems audit report. The systems audit is intended to be a cooperative assessment resulting in improved data rather than a judgmental activity.

Performance Evaluations (PEs) are a means of independently verifying and evaluating the quality of data from a measurement process, or overall measurement system. Performance audits establish whether the predetermined specifications are being achieved in practice. The performance audit challenges the measurement/analysis system with known standards traceable to a primary standard. These samples can be used to control and evaluate bias, accuracy, and precision and to determine whether the measurement quality objectives and DQOs are satisfied. Performance evaluation samples can also be used to determine inter- and intra-laboratory variability and temporal variability. For data processing, the performance audit consists of independently processing sections of the data and comparing the results. Performance objectives should be specified for the field or laboratory instruments on which performance audits are conducted. Audit findings are compared against these values to decide whether or not remedial action is needed.

An example of field and laboratory performance audit observations is given in Table 8-2. Performance audits for field operation will be addressed in the EPA's Quality Assurance Project Plan for NAMS trend sites, therefore only laboratory performance audits are discussed here. The quality audit function is incorporated into the chemical speciation monitoring network to ensure the accuracy, precision, and validity of mass and chemical speciation measurements.

The laboratory performance audit consists of the submission of known standards to routine laboratory procedures and of an interlaboratory comparison of those standards. Gravimetric analysis can be audited by weighing independent Class M or NIST-traceable standard weights and Teflon®-membrane filters, which will be pre-weighed and post-weighed at the primary laboratory and the audit laboratory for comparison. To audit the analysis of soluble species on quartz-fiber filters, a solution containing sulfate, sodium, nitrate, ammonium, and potassium is prepared and deposited in known amounts on quartz-fiber filters. Samples at a minimum of three concentrations are submitted to the routine chemical analyses for nitrate, ammonium, potassium, and sulfate by ion chromatography. To audit the analysis of the elements by x-ray fluorescence (XRF) on Teflon®-membrane filters, several thin film micromatter pure-element deposits are submitted for routine XRF analysis.

Table 8-1
Examples of Standard Operating Procedures

Subject	Observation/Method	Standard Operating Procedure
Chain-of-Custody	**Filter Pack/Cassette Handling**	**Assembling, Disassembling, and Cleaning Procedures**
	Shipping and Receiving	**Sample Shipping, Receiving, and Chain-of-Custody**
	Nylon Filter Cleaning	**Preparation of Nylon Filters for Nitric Acid or Total Nitrate Sampling**
	Quartz Filter Pre-Firing	**Pre-firing of Quartz Fiber Filters for Carbonaceous Material Sampling**
Chemical Analysis	**Sample Sectioning**	**Sectioning of Teflon® and Quartz Filter Samples**
	Filter Extraction	**Extraction of Ionic Species from Filter Samples**
	Mass	**Gravimetric Analysis Procedures**
	Elements (Al to Pb)	**X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples**
	Nitrate NO_3) **Sulfate (SO_4^{2-})**	**Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography**
	Ammonium (NH_4^+)	**Analysis of Filter Extracts for Ammonium by ion chromatography**
	Soluble Sodium (Na^+) **Soluble Potassium (K^+)**	**Analysis of Filter Extracts by ion chromatography**
	Total Organic Carbon (OC) **Total Elemental Carbon (EC)** **Total Carbon (TC)**	**Thermal Optical Carbon Analysis of Aerosol Filter Samples**
Aerosol Data	**Data Validation**	**Field, Mass, and Chemical Data Processing and Data Validation**

At the present time there are no widely accepted standards for elemental and organic carbon. Potassium acid phthalate solutions can be deposited on quartz-fiber filters to create organic carbon standards. A minimum of three sets of analyses at each concentration level and three blank filters should be analyzed for each audited chemical species.

8.6 Data Quality Assessment (DQA)

A DQA is the scientific and statistical evaluation of the data obtained to determine if those data are of the right type, quality, and quantity to support the intended use. The DQA is broad reaching and encompasses an evaluation of all aspects of the program from DQOs through data reporting. A very important aspect of the DQA is that it provides a measure of the quality of data which is important for data analyses and data use. The five steps of the DQA process are shown in Figure 8.1. Although the steps of the DQA are presented in a linear sequence, the process is iterative in nature. The DQA is designed to promote an understanding of how well the data satisfy their intended uses. The DQA approach parallels the activities typical of analyzing a data set for the first time. The five step procedure is not intended to be a definitive analysis of a project or problem, but instead to provide an initial assessment on the "reasonableness" of the data that have been generated. The QA guidance available in EPA QA/G-9, ***Guidance for Data Quality Assessment***, is directed towards the analysis of relatively small data sets containing data that have been collected in a relatively simple fashion.

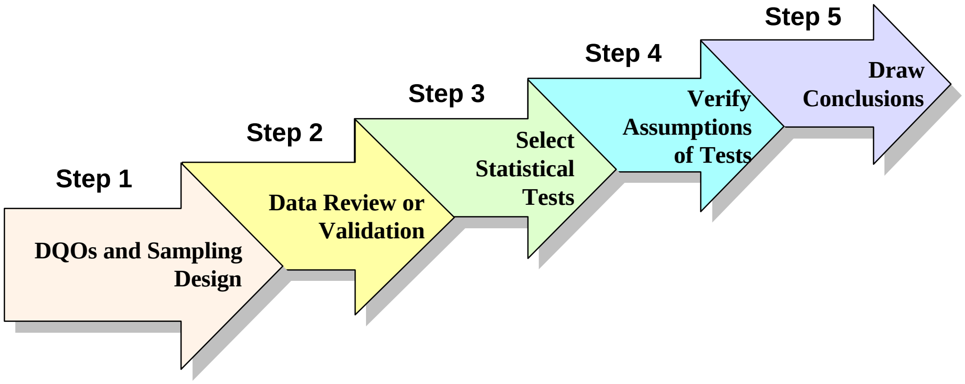

Figure 8-1. Five steps of the Data Quality Assessment

The DQA process is built on a fundamental premise that data quality as a concept is meaningful only as it relates to the intended use of the data. One must know in what context the data set will be used in order to establish a relevant yardstick for judging whether the data set is adequate. The steps of the DQA are described in more detail below.

1. **Review of the Data Quality Objectives (DQOs) and Sampling Design:** The DQOs are reviewed to assure that they are still applicable. If DQOs have not been developed, as may be the case for SPMs or non-routine NAMS monitors, specify DQOs before evaluating the data. Review the sampling design and data collection documentation for consistency with the DQOs.

2. **Preliminary Data Review:** Review QA reports, calculate basic statistics, and generate graphs of the data. Use this information to learn about the structure of the data and identify patterns or potential anomalies. In addition to the review of the QA reports by the State and regional data analysts, OAQPS/EMAD will prepare a report showing the quality of the data as the data begin to be reported. The purpose of the report is to summarize the quality of the data and to identify potential QA concerns. For example, certain speciation monitors may show more variability than others or certain seasons may show more variability. Such information is necessary for evaluating the data and providing direction for improvements in the $PM_{2.5}$ speciation network.

3. **Determination of Appropriate Statistical Test:** Select the most appropriate statistics for summarizing and analyzing the data based on review of the DQOs, the sampling design, and the preliminary data review. Identify key underlying assumptions about the data that must hold true for the statistical procedures to be valid.

4. **Verification of the Assumptions of the Statistical Test:** Evaluate whether the underlying data assumptions hold, or whether departures are acceptable, given the actual data and other information about the study.

5. **Conclusions Drawn from the Data:** Perform statistical tests and document the inferences drawn from those tests and evaluate performance of the sampling design.

The DQA process will be conducted by the EPA and reveal whether the decisions for which the data were collected can be made with the desired confidence, given the quality and quantity of the monitored data. If the data provide evidence strongly in favor of one conclusion, then the decision maker can proceed knowing that the decision will be supported by unambiguous data. However, if the data do not provide strong evidence, then the decision maker has the information needed to determine whether to proceed with the decision, despite the reduced level of confidence, or whether to collect more or different data with the goal of increasing the confidence level. The strength of the DQA process is in the design which promotes an understanding of how well the data satisfy their intended use by progressing in a logical and efficient manner.

The DQA needs to be conducted at the spatial resolution of a State or smaller geographical area. The reason for this is that the overriding objective of the speciation network will vary spatially, as may the quality of the monitored data. An exception to this is the network of 50 NAMS sites deployed with the primary objective of monitoring national trends in the constituents of $PM_{2.5}$. For these 50 sites, the objective is the same and SOPs need development to minimize the variability in the quality of the collected data.

8.7 Regional Laboratory QA

Four EPA and Regional labs will comprise the Laboratory QA support group. This group is responsible for providing routine QA support to the chemical speciation program, which includes conducting QA sample analyses, analyses for special studies, and technical QA support to the contract laboratories, States and EPA. The link of the Regional QA labs to the overall contact laboratories and the filter analysis and data processing in discussed in Section 7.0. Each EPA region is responsible for resolving Contractor laboratory QA issues, analysis of QA samples (field duplicates, round robin samples, audit samples), performing technical systems audits, and providing technical support for QA. QA support for field duplicates, collocated samples, and special studies will be provided for all routine speciation target analytes using the same methods as those used by the contract laboratories.

Table 8-2
Examples of Laboratory Performance Evaluation Procedures

Parameter	**Measurement Device**	**Performance Test Frequency**	**Performance Standard**	**Calibration Frequency**	**Calibration Standard**	**Audit Frequency**	**Audit Standard**	**Primary Standard**
Aerosol Sample Flow	**Candidate Chemical Speciation Sampler**	**Once per day**	**Calibrated Rotameter**	**At the Beginning and End of one-month Sampling Period or When Performance Tests are Out of Specification**	**Calibrated Rotameter**	**Once every 2 months**	**Mass Flow Meter**	**Certified Roots Meter**
$PM_{2.5}$	**Electromicro-balance**	**1/10 Samples** **3/10 Samples**	**NBS Class M Standard Weights** **Replicate**	**At Beginning of Weighing Session**	**NBS Class M Standard Weights**	**Once every 2 months**	**NBS Class M Standard Weights**	**NBS Class M Standard Weights**
$PM_{2.5}$	**XRF Analyzer**	**1/15 Samples** **1/15 Samples**	**NBS Thin Film Standards** **Replicate**	**Quarterly**	**Micromatter Thin Film Standards**	**Once every 2 months**	**Prepared Standard Deposit**	**Thin Film Standard**
$PM_{2.5}$ anions and cations	**Chromatographic Analyzer**	**1/10 Samples** **1/10 Samples**	**Solution Standards** **Replicate**	**At Beginning of Each Run**	**ACS Certified Standard Solutions**	**Once every 2 months**	**N/A**	**ACS Certified Chemicals**
$PM_{2.5}$ Carbon	**Thermal/Optical Carbon Analyzer**	**1/10 Samples** **1/10 Samples**	**Methane Gas** **Replicate**	**Once/2-months or When Performance Test Tolerances Not Met**	**Methane, CO_2, Gas and ACS Certified KHP**	**Once every 2 months**	**Standard KHP Solutions**	**ACS Certified Chemicals**

9.0 DATA VALIDATION AND DATA MANAGEMENT

This section provides a general discussion of the general specifications relative to data validation, data base requirements, substrate data processing and AIRS. EPA plans to develop specific data validation guidance for use by States, Regions, and laboratories implementing the NAMS speciation program. This guidance is slated for completion by the third quarter of 1999.

9.1 Data Validation

Data validation is the most important part of the overall data generation and processing system. The data must be reviewed and validated to assure the overall quality of the measurement prior to inclusion into the Aerometric Information Retrieval System -Air Quality Subsystem (AIRS-AQS) data base. Data validation is used in conjunction with the program objectives, DQOs, and program QA/QC to remove inconsistencies in the data set and to improve data quality. Data validation consists of systematic procedures developed to identify deviations from measurement assumptions and procedures. Timely data validation is required to more easily resolve data issues and unusual events and take the necessary corrective actions to minimize the generation of additional data that may be invalid or suspect. Four levels or categories generally apply to validation of monitoring data:

Level I)	Routine checks made during the initial data processing and generation of data, including proper data file identification, review of unusual events, review of field data sheets and result reports, instrument performance checks and deterministic relationships.
Level II)	Tests for internal consistency to identify values in the data which appear atypical when compared to values of the entire or whole data set.
Level III)	Comparison of the current data set with historical data to verify consistency over time. This level can be considered a part of the data interpretation or analysis process.
Level IV)	Tests for parallel consistency with data sets from the same population (region, period of time, air mass, etc.) to identify systematic bias. This level can also be considered a part of the data interpretation or analysis process.

Level I validation establishes the traceability of the integrated data set and takes place mainly in the field and in the laboratory. Level I validation consists of flagging samples when significant deviations from measurement assumptions have occurred. Computer file entries are verified against data sheets; values are eliminated for measurements which are known to be invalid because of instrument malfunctions; and measurement values are adjusted due to quantifiable calibration or interference biases.

Level II validation takes place after data from various measurement methods have been assembled in the master data base or LIMS (Laboratory Information Management System). Level II applies internal consistency tests based on known physical relationships between variables of the assembled data. Several internal consistency checks can be applied to evaluate validity when different particle size fractions are measured and submitted to chemical analyses. These include comparisons between collocated measurements; comparisons between mass concentrations and the weighted sum of chemical species; checks for physical and chemical consistency; and charge balances between anions and cations. As discovered, data adjustments for quantifiable biases can be made in Level II validation..

Level III validation is part of the descriptive data analysis or data interpretation process. Level III validation can include time series analysis, correlation matrices, material balance, quantitative statistical analyses, and modeling. The first assumption upon finding a measurement inconsistent with physical expectations is that the unusual value is due to a measurement error. After tracing the path of the measurement, if nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are identified during the data interpretation process as extreme values or outliers.

Level IV validation is typically performed as part of data interpretation and consists of tests for consistency with data sets from the same population. Level IV validation in done after the data is placed in the AIRS-AQS data base and can include the same interpretive analyses discussed in Level III validation. Data sets from the same region, air mass, or period of time are analyzed for consistency.

Given that there are separate field sampling, laboratory analysis, QA and data analysis components of the speciation program, various pieces of each level of validation will logically fall under each of these areas. No one area will contain the responsibility for an entire level of data validation. For example, components of Level I data validation will be done independently but not be duplicated by both the field and lab personnel. The State data analyst of laboratory personnel may perform certain components of Level II and Level III validation.

9.2 Data Base Requirements and AIRS

Substrate data processing is a very important part of the overall data management process. Data base requirements exist for the managing and processing data at the field and laboratory level, prior to submitting the data to the AIRS-AQS data base. Aerosol data processing consists of six general tasks:

1. **Record Keeping** - All relevant information obtained at the time an operation is performed is registered on field data sheets, the data logger, or other transfer medium.

2. **Input -** The data are transferred from the recording medium into computer-accessible files or an electronic data base.

3. **Merging -** Data from various files pertaining to an individual sample or sampling day are retrieved and related to each other.

4. **Calculations -** Data items are combined in mathematical expressions to yield a desired concentration result. These include the pollutant concentration, which must be reported in $\mu g/m^3$, accuracy, and precision.

5. **Data Validation** - Data are validated according to the Level I through IV data validation steps as described above.

6. **Output -** Data are arranged into the desired format for input to the AIRS-AQS and subsequently formatted for data interpretation and modeling software.

Aerosol data processing requires the assignment of identification (ID) codes to filter substrates. Field data records should include a recording of the IDs and their corresponding sampling sites, sampling dates, sampling times, sampling duration, sample flow rates, and deviations from normal sampling procedures. Laboratory records should contain instrument recordings of analytical outputs. Data validation is performed and should provide for formatting and reporting of concentrations in $\mu g/m^3$ and all data validation activities.

Field data can be entered into computerized data forms. Substrate IDs can be bar-coded and then entered with a scanner rather than being typed. The screen forms have limits that do not allow entry of values lying outside a certain range. Every data item entered is verified against the original data sheet by the data processing supervisor. A data base structure, which contains fields for chemical concentrations and a level of uncertainty is formed. Each record should contain sample IDs, sample volumes, sample times, sampling sites, and sampling dates, which are integrated into this structure from the field records. All other fields contain the missing data default value. These defaults are replaced by the result data as they become available. In this way, it is possible to determine which analyses have been completed and which have not.

The laboratory chain-of-custody is used to track the disposition of each sample and can be consulted to determine the fate of missing values in the master data base. This independent tracking is needed to prevent sample IDs from being mixed up or samples being lost.

Laboratories having the capacity to analyze a high volume of samples, usually employ a LIMS to acquire, record, manipulate, store, and archive their data. Not all automated laboratory systems are LIMS. Automated laboratory systems that record data but do not allow changes to the data are not LIMS. For example, an instrument that measures weights and produces or maintains a read-out of the weight is not a LIMS, if the true reading cannot be adjusted if needed prior to recording. If data entered into automated laboratory systems can be manipulated or changed in any way by the action of a person prior to being recorded, then that automated laboratory system is a LIMS. The EPA has developed guidance on Good Automated Laboratory Practices (GALP), ***Good Automated Laboratory Practices*** (U.S. EPA, 1995b), which addresses principles for ensuring data integrity in automated laboratory operations. In summary, the following areas are addressed:

Laboratory Management - Following the collection, analysis, and processing of LIMS data, laboratory management shall ensure the overall quality of the data provided. Laboratory management ensures that personnel understand their roles; the QA unit monitors LIMS activities; resources are adequate and available; corrective action is promptly taken; and SOPs are approved.

Personnel - Personnel must have adequate education, training, and experience to perform assigned LIMS functions; and have a current summary of their training, experience, and job description, including their knowledge relevant to LIMS design and operation, maintained at the facility.

Quality Assurance Unit – The QA unit inspect the LIMS at intervals adequate to ensure the integrity of the LIMS Raw Data.

LIMS Raw Data - Procedures and practices to verify the accuracy of LIMS raw data are documented and included in the laboratory SOPs, and managed.

Software - SOPs are established, approved, and managed for the software used to collect, analyze, process or maintain the LIMS raw data.

Security - Laboratory management shall ensure security practices to assure the integrity of LIMS data are adequate. EPA laboratories and those of its agents (contractors) shall comply with EPA's information security policy.

Hardware - LIMS hardware shall be of adequate design and capacity, and a description of the hardware documented and maintained. The hardware shall be installed and operated in accordance with the manufacturer's recommendations and be adequately tested, inspected, and maintained.

Comprehensive Testing - When LIMS raw data are collected, analyzed, processed, or maintained, laboratory management shall ensure that comprehensive testing of LIMS performance is conducted, at least once every 24 months or more frequently as a result of software or hardware changes/modifications. These tests shall be documented, and the documentation shall be retained and available for auditing when appropriate.

Record Retention - The retention of LIMS raw data, documentation, and records pertaining to the LIMS will comply with EPA contract, statute, or regulation; and SOPs for retention are documented, maintained, and managed.

Facilities - The environmental conditions of the facility housing the data are regulated to protect against data loss, and the facility has adequate environmental storage capability for retention of raw data, storage media, documentation, and records.

Standard Operating Procedures - Each SOP should be readily available and current. SOPs are periodically reviewed at a frequency adequate to ensure that they describe the current procedures. A historical file of SOPs shall be maintained.

After data for a record have been assembled, data validation comparisons should be conducted as discussed in Section 9.1. A data validation summary is maintained and associated with each record to provide traceability for data adjustments, replacements, or deletions. Field and laboratory data validation flags are assigned as part of the data validation process. Data validation summaries accompany the final data base. This data base must be converted to AIRS-AQS format for subsequent submission to the AIRS-AQS. All $PM_{2.5}$ chemical speciation data must be entered into AIRS. The EPA, OAQPS, Information Transfer and Program Integration Division (ITPID) administers the AIRS-AQS. The AQS contains data submitted by States, local and reporting organizations. The AIRS-AQS includes descriptions of air monitoring sites, monitoring equipment, measured concentrations of pollutants and related parameters.

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Particulate Matter "Supersites" Program

U.S. Environmental Protection Agency

A joint research solicitation of EPA's Office of Air and Radiation and the Office of Research and Development

Opening Date: March 1, 1999 Closing Date: August 4, 1999

This solicitation document contains the following sections:

1.0 SUMMARY

This request for applications (RFA) solicits proposals to support development of a "Particulate Matter (PM) Supersites" monitoring program that will provide information of value to the atmospheric sciences, human health, and human exposure research communities. The PM Supersites Program will be implemented through individual projects in as many as five study areas of the United States. Each of these individual projects will be an ambient atmospheric measurement study which is designed to address and integrate objectives of the atmospheric sciences, health, and exposure research communities. These objectives are documented in several reports which are discussed in Section 3 of this solicitation.

Applications which respond to this solicitation will be accepted (1) from single research institutions and (2) from consortia which include more than one research institution. Each application must propose to develop a Supersite project in a distinct geographic study area of the United States (e.g., locations with potential for significant PM exposures, distinct atmospheric chemistry or transport regimes, proximity to important population centers or contaminant sources). Single research institutions and consortia may propose to develop a Supersite project in more than one study area; however, a separate application must be submitted for each study area.

The PM Supersites Program will be implemented through as many as five cooperative assistance agreements; each will have a duration of up to five years. Total funding for this solicitation is $18.5 million; awards for individual cooperative assistance agreements are anticipated to be $3.5 million or less. Applications may be submitted by domestic not-for-profit research institutions such as universities, research institutes, and state research laboratories.

2.0 KEY DATES

The deadline for receipt of applications that respond to this solicitation is Wednesday, August 4, 1999. EPA requests that all potential applicants refrain from approaching any individuals with requests to serve on advisory boards or steering committees until after the award of these cooperative assistance agreements has been announced.

EPA has established a solicitation time frame for this RFA that responds to Congressional guidance for timely allocation of PM resources, and National Academy of Sciences guidance (see Section 3) for coherent planning across the atmospheric sciences, health and exposure research communities. Accordingly, EPA anticipates that the competitive scientific evaluation of applications which respond to this RFA will be finished by the end of September 1999. Negotiations for award of final agreements resulting from this solicitation will occur during October and early November 1999 in Research Triangle Park, N.C. It is essential that the principal investigator for each application being considered for award be available during October and early November to participate in these negotiations. Final award for the cooperative assistance agreements is anticipated by the end of November 1999, with the initiation of studies and associated field activities to be phased in over a period that will not exceed approximately 18 months from award. This post-award phase-in period is intended to allow for adequate detailed planning and coordination across scientific disciplines, and to optimize the potential for integration with related ongoing and planned studies.

To foster interaction among potential applicants across a spectrum of scientific disciplines, EPA has organized a discussion session on the evening of June 7, at the Durham Marriott at the Civic Center, in Durham, N.C. Further information about this meeting will be posted on two EPA Internet web sites: www.epa.gov/ttn/amtic/supsites.htm and www.epa.gov/ncerqa/rfa. The meeting occurs at the site of the Third Colloquium on Particulate Air Pollution and Health. This colloquium will be held from June 6-8, 1999. Potential applicants are encouraged to attend the Colloquium, but registration for the Colloquium is not required to participate in the June 7th discussion session with EPA. For further Colloquium information contact Ms. Toni Moore (914) 351-2300, email: moore@charlotte.med.nyu.edu.

3.0 PARTICULATE MATTER SUPERSITES PROGRAM DESCRIPTION

3.1 BACKGROUND INFORMATION

Based on an extensive review of the scientific criteria and standards for PM, on July 18, 1997, the EPA Administrator published revised National Ambient Air Quality Standards (NAAQS) for PM and added standards for PM2.5. In taking this action, the Administration recognized the scientific uncertainty associated with effects, exposure, concentrations, and source-receptor relationships, as well as management alternatives for PM2.5. These revised standards and the associated scientific findings and uncertainties have stimulated national concern about exposure to, and health effects from, PM. This concern has resulted in Executive and Congressional direction and funding to EPA.

On July 18, 1997, President Clinton issued a memorandum and implementation plan for the revised NAAQS to the EPA Administrator [Federal Register: July 18, 1997, (Volume 62, Number 138), pages 38421 - 38432]. This memorandum and plan (1) identified the need for additional research to address the scientific uncertainties, and (2) distinguished between this research and environmental measurements that may be needed for the NAAQS assessment and NAAQS reevaluation procedures (see, for example, page 38427).

Congress also has distinguished between research and regulatory support in its direction to EPA. In its direction, Congress called for a broad spectrum of research by parties within and outside EPA based on recommendations prepared by the National Research Council (NRC) and funds appropriated by Congress for EPA. The success of much of the intended research depends on the availability of air pollution samples and data obtained through ambient air quality monitoring. In its direction, Congress emphasized that the Agency is to be guided by the National Research Council's Committee on Research Priorities for Airborne Particulate Matter and the Committee's recommendations contained in the March 1998 report ***Research Priorities for Airborne Particulate Matter I: Immediate Priorities and a Long-Range Research Portfolio*** (Electronic copies of this document can be obtained from www.nap.edu).

To plan and prioritize activities, EPA has developed a particulate matter "Supersites Conceptual Plan" (U.S. EPA, Office of Air Quality Planning and Standards and Office of Research and Development). The Supersites Conceptual Plan benefitted from scientific discussions held during a public PM Measurements Research Workshop held in Chapel Hill, N.C. on July 22 and 23, 1998, which was attended by about 200 members of the atmospheric, exposure, and health effects research communities. The report of this workshop, entitled "Atmospheric Observations: Helping Build the

Scientific Basis for Decisions Related to Airborne Particulate Matter," and the Supersites Conceptual Plan, are available electronically at www.epa.gov/ttn/amtic/supsites.htm. These documents are of central importance as reference documents for potential applicants to this RFA.

3.2 PURPOSE

As discussed in the "Supersites Conceptual Plan," the objectives of the Supersites Program are:

(1) Characterize particulate matter: to obtain atmospheric measurements to characterize PM, its constituents, precursors, copollutants, atmospheric transport, and source categories that affect the PM in any region. This information is essential for understanding source-receptor relationships and the factors that affect PM at a given site (e.g., meteorology, sources, transport distances). This information is also essential for improving the scientific foundation for atmospheric models that investigate exposure and risk management questions.

(2) Support health effects and exposure research: to obtain atmospheric measurements to address the research questions and scientific uncertainties about PM source-receptor-exposure-effects relationships. Examples of these questions include, "What is the relationship between sources, ambient PM concentrations, human exposures, and health effects such as respiratory tract disease and mortality?" and "What is the biological basis for these relationships?"

(3) Conduct methods testing: to obtain atmospheric measurements that will compare and evaluate different methods of characterizing PM (e.g., emerging sampling methods, routine monitoring techniques, and federal reference methods). Testing new and emerging measurement methods ultimately may advance the scientific community's ability to investigate exposure and effects questions significantly.

In essence, each PM Supersites project should obtain the ambient measurements and support the associated analyses needed to address the objectives stated above. A Supersite project can consist of a single ambient measurement platform at one location or multiple platforms located purposefully throughout the study area, including measurements at the surface and aloft.

Supersites Program funds are not to be used to collect indoor, personal exposure, or health related (e.g. measures of lung function) measurements. Instead, the ambient measurements and analyses obtained in the Supersites Program are intended to support the scientific objectives identified above. PM Supersites projects are encouraged to establish liaisons with health effects, exposure, and atmospheric science researchers supported by other funding, thus leveraging the information obtained from the PM Supersites Program. For example, EPA expects that measurements from this Supersites Program will be relevant to source-receptor and model evaluation studies, but Supersites Program resources are not to be used for explicit tasks of model development and evaluation. Augmenting Supersites work with up-coming or-ongoing ambient measurement programs, particularly measurements associated with the national PM2.5 and PM10 compliance networks and the national chemical speciation network, is also highly desirable.

EPA expects that each applicant will consider the following scientific elements in formulating a proposal for a Supersites project:

* the high priority objectives identified above;

* specific hypotheses that could/will address the activities proposed by the applicant and the explicit relevance of each activity to the high priority objectives cited above;

* the basis for selecting the proposed geographic study area in the United States (e.g., locations with potential for significant PM exposures, distinct atmospheric chemistry or transport regimes, proximity to important population centers or contaminant sources).

* the air quality measurements, data analyses, quality assurance, and quantitative interpretation relevant to the objectives cited above;

* a protocol that identifies data validation steps and the structure of the database which will be developed for each project; and

* research collaboration with other organizations that may help to investigate the hypotheses [e.g, collaboration with state and local air pollution agencies and their criteria air pollutant monitoring programs, EPA's Atmospheric Sciences Research Centers and the yet to be named Particulate Matter Research Centers (www.epa.gov/ncerqa/rfa) and other ongoing or planned research activities by other public and private research organizations] and the contribution provided by each of these collaborating organizations.

In the long-term, the data collection and data analyses that result from the Supersites Program will create improved scientific information to investigate source-receptor-exposure-effects relationships at community-, state-, regional-, and national-scales. Thus, organizations that will benefit from the Supersites Program include state and local agencies, industries, universities, technical associations, public interest groups, and Federal agencies.

4.0 MECHANISM OF SUPPORT AND FUNDING AVAILABLE

In preparing this solicitation, EPA has determined that the principal purpose of the Supersites Program described above is consistent with the use of a cooperative assistance mechanism. This determination is required by EPA extramural management policy and the Federal Grant and Cooperative Agreement Act. This mechanism is administered by the Environmental Protection Agency in accordance with 40 CFR Parts 30 or 35 and 40, and with EPA's Policies and Procedures on Cooperative Agreements. The anticipated total funding for all cooperative assistance agreements awarded under this solicitation will be approximately $18.5 million for total (direct plus indirect) costs, depending on the availability of funds. Awards for individual cooperative assistance agreements are anticipated to be $3.5 million or less of total funding. The anticipated duration of each cooperative assistance agreement is up to five years.

5.0 ELIGIBILITY REQUIREMENTS

Academic and not-for-profit institutions located in the U.S., and state or local governments, are eligible under all existing authorizations. Profit-making firms are not eligible to receive cooperative agreements from EPA under this program. Federal agencies, national laboratories funded by federal agencies (Federally Funded Research and Development Centers, FFRDCs), and federal employees are not eligible to submit applications to this program and may not serve in a principal leadership role on these awards.

Applications will be accepted (1) from single research institutions and (2) from consortia that include more than one research institution. An application must propose to develop a Supersite project in a single geographic study area of the United States. Single research institutions and consortia may submit applications to conduct research in more than one study area; however, a separate application must be submitted for each study area.

FFRDC employees may cooperate or collaborate with eligible applicants within the limits imposed by applicable legislation and regulations. They may participate in planning, conducting, and analyzing the research directed by the principal investigator, but may not direct projects on behalf of the applicant organization or principal investigator. The principal investigator's institution may provide funds through its cooperative assistance agreement from EPA to a FFRDC for research personnel, supplies, equipment, and other expenses directly related to the research. However, salaries for permanent FFRDC employees may not be provided through this mechanism.

Federal employees may not receive salaries or in other ways augment their agency's appropriations through cooperative agreements with this program. However, the nature of the cooperative assistance agreement mechanism which will be used to support the Supersites Program explicitly contemplates collaboration between scientists in EPA laboratories and centers and the applicant's institution or consortium. EPA scientists will collaborate with specific Supersites awardees through on going or planned research. The discussions about EPA collaboration will occur during the final negotiation phase **(see Section 10.0 SELECTION, NEGOTIATION, AND AWARD)**. Do not discuss potential collaborations with EPA in the application.

6.0 INSTRUCTIONS FOR SUBMITTING AN APPLICATION

This section contains a set of specific instructions on how applicants should apply for a cooperative agreement under this program.

6.1 SORTING CODE

In order to facilitate proper assignment and review of applications, each applicant is asked to identify this topic area in the application. **It is the responsibility of the applicant to correctly identify the proper sorting code.** Failure to do so will result in an inappropriate peer review assignment. At various places within the application, applicants are asked to identify this topic area by using the appropriate Sorting Code.

The Sorting Code must be placed at the top of the abstract (as shown in the abstract format), in Box 10 of Standard Form 424 (as described in the section on SF424), and should also be included in the address on the package that is sent to EPA (see the section on **How to Apply**). The sorting code for this solicitation is 99-NCERQA-X1.

6.2 PREPARING THE APPLICATION

The initial application is made through the submission of the materials described below. **It is essential that the application contain all the information requested and be submitted in the formats described.** If an application is considered for award, (i.e., after external peer review and internal review) additional forms and other information will be requested by the Project Officer. **The application should not be bound or stapled in any way.** The Application contains the following:

A. Standard Form 424: The applicant must complete Standard Form 424 (see attached form and instructions). This form will act as a cover sheet for the application and **should be its first page**. Instructions for completion of the SF424 are included with the form. The form must contain the original signature of an authorized representative of the applying institution. Please note that both the Principal

Investigator and an administrative contact should be identified in Section 5 of the SF424.

B. Key Contacts: The applicant must complete the Key Contacts Form (attached) as the **second page** of the submitted application.

C. Abstract: The abstract is a very important document. Prior to attending the peer review panel meetings, some of the panelists may read only the abstract. Therefore, it is critical that the abstract accurately describe the research being proposed and convey all the essential elements of the research. Also, in the event of an award, the abstracts will form the basis for an Annual Report of awards made under this program. The abstract included in the application should not exceed two pages in length, should summarize the activities that will be accomplished during the performance period, and explain how these activities respond to the high priority objectives in the documents cited in this solicitation document. The abstract should include the following information, as indicated in the example format provided:

1. Research Category and **Sorting Code:** Enter the full name of the solicitation to which your application is submitted and the correct sorting code 99-NCERQA-X1.

2. Title: Use the exact title as it appears in the rest of the application.

3. Investigators: Start with the Principal Investigator. Also list the names and affiliations of each co-investigator who will significantly contribute to the project.

4. Institution: List the name and city/state of each participating university or other applicant institution, in the same order as the list of investigators.

5. Project Period: Provide the proposed project dates.

6. Project Cost: Provide the total request to EPA for the entire project period.

7. Project Summary: This should summarize: (a) the **objectives** of the project (including any hypotheses that will be tested), (b) the **approach** to be used (which should give an accurate description of the project as described in the proposal), and (c) the **expected results** of the project and how they address the research needs identified in the solicitation.

8. **Supplemental Keywords:** A list of suggested keywords is provided for your use. Do not duplicate terms already used in the text of the abstract.

D. Project Description: This description must not exceed thirty (30) consecutively numbered (center bottom), 8.5x11-inch pages of single-spaced standard 12-point type with 1-inch margins. The description must provide the following information:

1. **Objectives**: List the objectives of the proposed research, the hypotheses being tested during the project, and the explicit relevance of each hypothesis to the high priority objectives cited in section 3.2. This section can also include any background or introductory information that would help explain the objectives of the project.

2. **Approach**: Describe the methods, analyses, approaches, and techniques that you intend to employ in meeting the objectives stated above.

3. **Site Selection**: Describe the basis for selecting the area of the United States proposed for this activity (e.g., distinct atmospheric chemistry or transport regimes, proximity to important population centers or contaminant sources, the potential for significant PM exposures).

4. **Expected Results or Benefits**: Describe the results you expect to achieve during the project and how the public and non-governmental scientific community will benefit from these results.

5. **Collaboration**: Describe the collaboration with other organizations which may help to investigate the hypotheses (e.g., EPA's Particulate Matter Research Centers or other public or private research organizations) and the contribution provided by each of these collaborating organizations.

6. **General Project Information**: Discuss other information relevant to the potential success of the project. This should include facilities, personnel, project schedules, proposed management, interactions with other institutions, etc.

7. **Important Attachments**: If necessary, tables, figures, attachments, appendices, and reference lists may be included at the end of the project narrative and will be considered to be outside the thirty-page limitation.

The following sections are in addition to the 30-page Project Description.

E. Resumes: The resumes of all principal investigators and important co-workers should be presented. Resumes must not exceed two consecutively numbered (bottom center), 8.5x11-inch pages of single-spaced standard 12-point type with 1-inch margins for each individual page.

F. Current and Pending Support: The applicant must identify any current and pending financial resources that are intended to support research related to that included in the proposal or which would consume the time of principal investigators. This should be done by completing the appropriate form (see attachment) for each investigator and other senior personnel involved in the proposal. Failure to provide this information may delay consideration of your proposal.

G. Budget: The applicant must present a detailed, itemized budget for the entire project. This budget must be in the format provided in the example (see attachment) on 8.5x11-inch pages with 1-inch margins. Please note that institutional cost sharing is not required and, therefore, does not have to be included in the budget table. However, if you wish to cost-share, a brief statement concerning cost sharing can be added to the budget justification. If cost-sharing is proposed, the estimated dollar amounts should be included in the appropriate categories in the budget table.

H. Budget Justification: Supplemental budget information and a brief supporting narrative are requested which clearly and simply describe the applicant's funding plan for each year of up to the five-year period of performance. If the applicant proposes to provide funding from other sources to contribute to the research under this cooperative agreement (e.g.,. EPA Particulate Matter Research Centers), the magnitude, duration, and use of such funding should be identified clearly. At a minimum, the supplemental budget information should present and explain concisely how the proposed annual expenditures for such items as personnel, significant equipment costs (e.g., site setup, instrument procurement and calibration), travel, measurements, analyses, database preparation, and quality assurance will accomplish the solicitation's research goals. Format and length should be determined by the applicant, but should not exceed 10 pages.

I. Quality Assurance Narrative Statement: Since these projects involve data collection or processing, conducting surveys, environmental measurements, and/or modeling, or the development of environmental technology (whether hardware-based or via new techniques) for pollution control and waste treatment, a statement on how quality processes or products will be assured is required. This statement should not exceed 10 consecutively numbered, 8.5x11-inch pages of single-spaced standard 12-point type with 1-inch margins. This is in addition to the 30 pages permitted for the Project Description. The Quality Assurance Narrative Statement should, for each item listed below, either present the required information or provide a justification as to why the item does not apply to the proposed research. For awards that involve environmentally related measurements or data generation, a quality system that complies with the requirements of ANSI/ASQC E4, "Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs," must be in place. Also, there are EPA requirements (R-series) and guidance (G-series) documents available for potential applicants which address in detail how to comply with ANSI/ASQC E4. These may be found on the Internet at es.epa.gov/ncerqa/qa/qa_docs.html. R-5 "EPA Requirements for Quality Assurance Project Plans" and G-4 Guidance for the Data Quality Objectives Process" are particularly pertinent to this RFA's QA requirements.

1. The activities to be performed or hypothesis to be tested (reference may be made to the specific page and paragraph number in the application where this information may be found); criteria for determining the acceptability of data quality in terms of precision, accuracy, representativeness, completeness, comparability. (Note: these criteria must also be applied to determine the acceptability of existing or secondary data to be used in the project.)

2. The study design, including sample type and location requirements and any statistical analyses that were used to estimate the types and numbers of samples required for physical samples or similar information for studies using survey and interview techniques.

3. The procedures for the handling and custody of samples, including sample identification, preservation, transportation, and storage.

4. The methods that will be used to analyze samples or data collected, including a description of the sampling and/or analytical instruments required.

5. The procedures that will be used in the calibration and performance evaluation of the sampling and analytical methods used during the project.

6. The procedures for data reduction and reporting, including a description of statistical analyses to be used and of any computer models to be designed or utilized with associated verification and validation techniques.

7. The intended use of the data as they relate to the study objectives or hypotheses.

8. The quantitative and or qualitative procedures that will be used to evaluate the success of the project.

9. Any plans for peer or other reviews of the study design or analytical methods prior to data collection.

ANSI/ASQC E4, "Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs" is available for purchase from the American Society for Quality Control, phone 1-800-248-1946, item T55.

J. Postcard: The Applicant must include with the application a self-addressed, stamped 3x5-inch post card. This will be used to acknowledge receipt of the application and to transmit other important information to the applicant.

7.0 HOW TO APPLY

The original and fifteen (15) copies of the fully developed application and one (1) additional copy of the abstract (16 in all), must be received by NCERQA no later than **4:00 P.M. EDT** on the closing date, **Wednesday, August 4, 1999**. A postmark or date stamp does NOT constitute compliance with these instructions.

The application and abstract must be prepared in accordance with these instructions. Informal, incomplete, or unsigned proposals will not be considered. The application should not be bound or stapled in any way. The original and copies of the application should be secured with paper or binder clips. Completed applications should be sent via regular mail to:

U.S. Environmental Protection Agency
Peer Review Division (8703R)
Sorting Code: 99-NCERQA-X1
401 M Street, SW
Washington DC 20460

For express mail or courier-delivered applications, the following address must be used:

U. S. Environmental Protection Agency
Peer Review Division (8703R)
Sorting Code: 99-NCERQA-X1
1300 Pennsylvania Avenue, NW
Room B-10105
Washington, DC 20004

Phone: (202) 564-6939 (for express mail applications)

The sorting code must be identified in the address (as shown above).

8.0 GUIDELINES, LIMITATIONS, AND ADDITIONAL REQUIREMENTS

Among the scientific elements included in the proposal, each applicant should consider the following special requirements in formulating the proposal.

Applicants are encouraged strongly to consider including a small set of data collection objectives that would enable comparisons across Supersite projects nationwide. Highly recommended minimum data collection objectives include:

(a) PM2.5 mass using an FRM or equivalent method;

(b) Continuous PM2.5 mass (or mass surrogates through optical, pressure differential, or other approaches) through available technologies;

(c) PM2.5 chemical composition for species determined in the National Chemical Speciation Monitoring Network, including at a minimum, PM2.5 mass, sulfate, nitrate, ammonium, organic carbon, elemental carbon, and trace elements by XRF, Instrumental Neutron Activation Analysis (INAA), Particle-Induced X-ray Emission (PIXE), or other method that would provide an estimate of the crustal component of the collected aerosol;

(d) Coarse particle mass (PM10-2.5) and the chemical composition of the coarse particles;

(e) Surface meteorological data including scalar and vector wind speed and direction, relative humidity, and solar radiation.

Each applicant should include in the budget funds for two meetings each year with EPA to discuss research progress and develop plans to coordinate activities. For planning purposes, assume that each meeting will be held in Research Triangle Park, N.C., will require the attendance of principal investigators and co-principal investigators (a maximum of three representatives from each Supersites award), and will be up to four days in length, exclusive of travel time.

EPA has been directed by Congress to ensure that key data from each Supersite project are made available to the public in an easily accessible fashion. For the purposes of this solicitation, EPA's interpretation of this direction is that a defined set of data will be assembled according to a protocol that will apply to each Supersite. This protocol will include a mandatory schedule, agreed upon by all awardees, which addresses intellectual property rights and provides adequate lead time for interpretation of the data by each awardee. The EPA is recommending that Supersites data be submitted to a national data archive, the NARSTO Permanent Data Archive (see: the NARSTO Quality Systems Management Plan, www.cgenv.com/narsto). Each applicant is expected to include a budget to accomplish this objective at the applicant's site. During the negotiation step of this solicitation, EPA will organize a meeting of all principal investigators to consider and adopt a protocol, schedule, and mechanism by which the data will be made available to the public. However, based on the outcome of this meeting, EPA may permit budget modifications from each applicant to ensure adequacy of funding.

In addition, several types of reports may be required during the course of the Supersites Program for each location. A final quality assurance project plan must be prepared by each awardee and approved by the EPA project officer before sampling and analysis begin. If several different projects will be conducted under the auspices of the cooperative agreement, the consortium or group will need to develop a quality management plan. Semiannual progress reports are required with sufficient detail to allow the EPA project officer to understand what progress has been made and if any problems exist that may delay the project or result in budget overruns. Other required reports may include: a data report that describes the data base structure and contents before each project's data become part of the national data archive; a final quality assurance report describing the procedures used to quality assure the field measurements, laboratory measurements, and the data base, including data validation procedures and results; and a final report, or several final reports describing the data analyses results and how they addressed the original objectives. It is expected that Principal Investigators and staff will publish papers in peer-reviewed journals and present papers at conferences during the second and future years of the program. All publications reflecting activities supported by the Supersites Program must acknowledge EPA cooperative agreement funding. The final cooperative assistance documents prepared for each award will specify precisely the nature and frequency of all required reports.

The full notice of this solicitation appears at two EPA Internet web sites: www.epa.gov/ttn/amtic/supsites.htm and www.epa.gov/ncerqa/rfa. The Internet addresses for obtaining electronic copies of the reference material cited in Section 3 of this document are www.epa.gov/ttn/amtic/supsites.htm and www.nap.edu.

Proprietary Information: By submitting an application in response to this solicitation, the applicant grants EPA permission to share the application with technical reviewers both within and outside of the Agency. Applications containing proprietary or other types of confidential information will be returned to the applicant without review.

9.0 REVIEW OF APPLICATIONS

All grant applications are initially reviewed by EPA to determine their legal and administrative acceptability. Acceptable applications are then reviewed by an appropriate technical peer review group. This review is designed to evaluate each proposal according to its scientific merit. In general, each review group is composed of non-EPA scientists, engineers, social scientists, and/or economists who are experts in their respective disciplines and are proficient in the technical areas they are reviewing. The reviewers use the following criteria to help them in their reviews:

1. The originality and creativity of the proposed **activities**, the appropriateness and adequacy of the methods proposed, and the appropriateness and adequacy of the Quality Assurance Narrative Statement. Is the approach practical and technically defensible, and can the project be performed within the proposed time period? Will the activities contribute to scientific knowledge in the topic area of the solicitation? Is the proposal well-prepared with supportive information that is self-explanatory and understandable?

2. The qualifications of the principal investigator(s) and other key personnel, including research training, demonstrated knowledge of pertinent literature, experience, and publication records. Will all key personnel contribute a significant time commitment to the project?

3. The availability and/or adequacy of the facilities and equipment proposed for the project. Are there any deficiencies that may interfere with the successful completion of the project?

4. The responsiveness of the proposal to the needs identified for the topic area. Does the proposal adequately address all of the objectives specified for this topic area?

5. Although budget information is not used by the reviewers as the basis for their evaluation of scientific merit, the reviewers are asked to provide their view on the appropriateness and/or adequacy of the proposed budget and its implications for the potential success of the proposed research. Input on requested equipment is of particular interest.

10.0 SELECTION, NEGOTIATION, AND AWARD

Once the review for scientific merit has been completed, the most meritorious proposals are forwarded to senior EPA officials for selection and recommendation for award. These evaluations form the basis for EPA to select the most meritorious application(s) for award.

In developing recommendations for award, EPA officials will consider a number of criteria, including:

1. Regional distribution of Supersites. EPA intends to select for award a suite of applications which together offer broad coverage of distinct geographic areas (e.g., locations with potential for significant PM exposures, distinct atmospheric chemistry or transport regimes, proximity to important population centers or contaminant sources). Priority will be given to geographic areas that have not been the subject of intensive PM atmospheric studies.

2. Responsiveness to address objectives in Section 3. EPA intends to select for award those applications which respond to the high priority objectives discussed and cited in this solicitation.
3. Collaboration and resource leveraging. EPA intends to select for award those applications which integrate collaborative contributions from other PM researchers when the proposed collaboration strengthens the ability to investigate high priority objectives. NOTE: consideration of collaboration at this stage does NOT include collaboration with EPA research scientists.

After EPA officials develop recommendations for award, all applicants will be notified and the EPA Project Officer will begin negotiations with the recommended applicants to develop final cooperative agreement(s) that will form the legal basis for the award of assistance funding. EPA anticipates that these negotiations will occur during October and November 1999 and that one or more mandatory meetings at Research Triangle Park will be necessary to successfully complete these negotiations. Issues to be included in the negotiation at this juncture include: formal identification of key personnel; modification to the applicant's plan that respond to written peer panel evaluations regarding weaknesses that can be improved; **negotiations about the nature of the collaboration by the principal investigator(s) with EPA scientists, engineers, and experts associated with the National monitoring networks, and incorporation of this collaboration into the final cooperative agreement plan**; negotiations about implementing the special requirements discussed in Section 8 of this document; and final budgets and terms of the agreement. The purpose of this final negotiation step is to ensure that all planning, application, and award paperwork--as well as implementation procedures--have been documented properly and are clearly understood by the affected parties.

The anticipated date of award for the cooperative agreements is November 30, 1999, depending on the availability of funds. Funding decisions are the sole responsibility of EPA. The cooperative agreements are selected on the basis of technical merit, relevancy to the research priorities outlined, program balance, and budget. A summary statement of the scientific review by the peer panel will be provided to each applicant.

11.0 INQUIRIES

Additional general information on the grants program, forms used for applications, etc., may be obtained by exploring our Web page at **www.epa.gov/ncerqa**. EPA does not intend to make mass-mailings of this announcement. Additional information may be obtained by calling the contacts or by leaving a message or the hotline listed below:

U.S. Environmental Protection Agency
National Center for Environmental Research and Quality Assurance (8703R)
401 M Street, SW
Washington DC 20460

Phone: 1-800-490-9194

In addition, a contact person has been identified below for this RFA. This individual will respond to inquiries regarding the solicitation and can respond to any technical questions related to your application.

* Technical Contact
Richard D. Scheffe 919-541-4650
scheffe.richard@epa.gov

* Administrative Contact
Robert Menzer, Ph.D.
menzer.robert@epa.gov 202-564-6849

Atlanta SuperSite '99 Study Protocol
(Version 1.0 – June 7, 1999)

prepared by
Susanne Hering, Atlanta SuperSite Sampling Protocol Officer
Aerosol Dynamics

Overview

In August 1999 many emerging and/or state-of-the-science measurement methods for fine, airborne particles will be deployed at one site in Atlanta GA for a period of four weeks. These measurements are being made as part of the first of the regional "Supersites" being established by the Environmental Protection Agency for advanced investigations of outstanding issues related to $PM_{2.5}$. The Atlanta Supersite is being coordinated by the Southern Oxidants Study (SOS) in collaboration with the numerous universities and agencies that comprise SOS as well as a number of other programs and agencies including the Southeastern Aerosol Research Characterization / Aerosol Research Inhalation Epidemiology Study (SEARCH/ARIES) and the Southern Center for the Integrated Study of Secondary Aerosols (SCISSAP).

The purpose of this document is to provide the pertinent information for participants in the August field operations.

Objectives

Goals of the Atlanta SuperSite study are twofold: first, to provide a platform for testing and contrasting some of the newer particle measurement techniques, and second, to provide data to advance our scientific understanding of atmospheric processes regarding atmospheric particles. Specific objectives are:

1. to characterize the performance of emerging and/or state-of-the-science "PM Measurements[1]."

2. to compare and contrast similar and dissimilar PM Measurements;

3. to evaluate the precision, accuracy, and completeness of information that can be gained from the planned EPA "PM mass and chemical composition" networks;

4. to evaluate the scientific information gained by combining various independent and complementary PM Measurements; and

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[1] "PM Measurements" includes methods to determine the physical and chemical characteristics of PM, identify their chemical precursors and meteorological driving forces, and ultimately understand the public-health impacts and visibility-altering properties of airborne PM.

5. to address various scientific issues and their ozone- and PM-related policy implications with this data base.

Study Dates

The measurement program is scheduled for the four week period commencing at 7 am on Wednesday, August 3, and ending 7 am Wednesday September 1, 1999. This is one day earlier than originally planned so as to allow investigators to return home before the labor day weekend. The site will be ready for instrument setup on or about Monday July 19. Systems audits are tentatively yet scheduled for the Friday and Monday preceding the measurements, and during the first week of measurements (Wednesday - Friday July 28-30, Mon Aug 2, Wed Aug 4, Thurs Aug 5). The weekend is not available for audits.

Study Site

Measurements will be made on the grounds of Georgia Power Company at 829 Jefferson Street NW, Atlanta, GA 30318. This site was established for the SEARCH and ARIES programs, and it is being expanded to accommodate the measurements of the Atlanta SuperSite. The SEARCH/ARIES measurements will continue during the August Study. SEARCH is an ongoing, multiyear particle and air quality study with eight paired urban rural sites in southeastern US. The SEARCH Atlanta site is also used for ARIES, which is an ongoing health effects study based on measurements at this site. SEARCH/ARIES are sponsored through EPRI, utility, petroleum and automotive industry concerns. Off-site support facilities will be available through Georgia Tech, as described below.

Organizational Responsibilities

Table 1 lists the individuals with responsibility for various aspects of the Atlanta SuperSite activities.

The Atlanta SuperSite is operated by the Southern Oxidants Study under a Cooperative Agreement between the National Exposure Research Laboratory At Research Triangle Park (NERL-RTP) of the U.S. EPA and the Georgia Institute of Technology. Bill Chameides is SOS' Atlanta SuperSite Project Director and, as such, chairs the Atlanta SuperSite Steering Committee which has responsibility for all decisions relating to the scientific goals of the SuperSite and the methods and approaches to be taken to reach these goals. Members of the Steering Committee include Project Directors/Liaison Officers representing all organizations and agencies supporting the SuperSite Experiment.

The implementation of the overall scientific plan for the **SuperSite is managed by the "Atlanta Supersite Coordination Committee Underpinning Success (ASCC-US).** ASCC-US has responsibility for the logistics and day-to-day operation of the August Field Experiment, as well as the overall synthesis and analysis of the data. ASCC-US is chaired by John Jansen and includes Tina Bahadori, Bill Chameides Elis Cowling, Eric Edgerton, Fred Fehsenfeld, Susanne Hering, C.S. Kiang, Peter McMurry, Jim Meagher, Dennis Mikel, and Paul Solomon

Administration of the Atlanta SuperSite is directed by the SOS Atlanta SuperSite Project Director (Chameides). along with Project Officers in charge of the Jefferson Street Site (Eric Edgerton), the sampling protocol (Susanne Hering), quality assurance (Dennis Mikel), data management (Jim StJohn), and off-site laboratoty facilities (Karsten Baumann).

Table 1. Atlanta SuperSite Organization(*)

A. Steering Committee

W.L. Chameides, Chair	SOS SuperSite Project Director
Tina Bahadori	SEARCH/ARIES Project Officer
Ellis Cowling	SOS Study Director
Fred Fehsenfeld	NOAA Liaison Officer
C.S. Kiang	GaTech Liaison Officer
John Jansen	Southern Company Liaison Officer
Jim Meagher	SOS 1999 Field Marshall
Paul Solomon	EPA Project Director/Liaison Officer

B. Coordination Committee (ASCC-US)

John Jansen, Chair

Tina Bahadori, Bill Chameides Elis Cowling, Eric Edgerton, Fred Fehsenfeld, Susanne Hering, C.S. Kiang, Peter McMurry, Jim Meagher, Dennis Mikel, and Paul Solomon

C. Administration

W.L. Chameides	SuperSite Project Director
Karsten Baumann	Off-site Laboratory Facilties Officer
Eric Edgerton	Jefferson Street Site Director
Susanne Hering	Sampling Protocol Officer
Dennis Mikel	Qaulity Assurance Officer
Jim StJohn	Data Manager

(*) See Appendix A for listing of entire Science Team

Measurements and Participants

Planned measurements are listed in Table 2. These include filter-based techniques for chemical characterization, single particle composition mass spectrometers, automated methods for high-time resolution particle chemistry, and physical characterization of the particles. The methods are supported by various gaseous and meteorological measurements. In Table 1 the measurements are grouped in accordance with type and the measurement schedule described below. The decision to add measurements is at the discretion of the project leadership, and is dependent on available facilities as well as benefit to the program.

Sampling Schedules

There are five sets of sampling schedules, as outlined in Table 3.

Schedule A, "Alternate Day Schedule" is for the EPA speciation samplers and certain other filter collectors. Samples will be collected for a full 24 hours sample starting at 0700 EDT on alternate days, beginning with the first day of the study. This schedule provides for a total of 15 sampling periods, and allows for full 24-hr sample collection with a single, manual sampler. With an August 3 start date, these sampling days correspond to odd numbered calendar dates (3,5,7,9…). On even calendar study dates, the EPA speciation samplers will not be operated. Other investigators are asked to sample for 12 hour periods, or to select an even divisor of 12 hours (such as two 6-hr samples during the daytime 12-hr period).

Schedule B, or "Base Schedule" is a consistent day/night sampling beginning at 0700 and 1900 EDT every day. It will be used by two of the MOUDI impactors (for ions, organic and elemental carbon (OC/EC) and metals), and one of the ARIES/SEARCH particle composition samplers. These samplers will provide a consistent, uninterrupted measurement throughout the study period. If operators need time to change out their samplers, this time should be taken before the end of the sample period. For example the 0700 sample could be stopped at 1830, changed, and the new sample started at 1900.

Schedule C, "Continuous", is for samplers with high time resolution. These investigators are asked to provide their data in a manner that allows for calculation of one-hour averaged concentrations beginning on the hour. For example, acceptable formats would be 1min, 5min, or 10min averaged data starting on the hour.

Schedule M, or "Multiday" provides for collection of large samples as needed for some trace metal and organic speciation analyses. Schedule S is the SEARCH/ARIES and standard monitoring schedule that has 24-hr sample collection beginning at midnight standard time (0100 EDT).

Table 2. List of measurements

Sch[1]	Investigator[2]	Organization		Instrument & Measured Parameters
Integrated Particle Samplers with alternate 24-hr and 12-hr Collection beginning @ 0700 EDT				
A	Baumann	GaTech	1	MCFP: Multichannel denuder filter pack system for PM2.5 mass, ions, trace elements, OC/EC, and gaseous ammonia, nitric acid and sulfur dioxide.
A	Gundel	LBL	2	IOGAPS: integrated gas and particle sampler for organic speciation
			1	Low vol IOGAPS: OC/EC, selected PAH analysis
			1	High flow filter-PUFF for organic speciation method development
A	Tanner	TVA		PC-BOSS sampler
A	Solomon-Eatough	EPA,BYU		PC-BOSS sampler
A	Solomon	EPA	5	5 types of Speciation Samplers: Andersen, Met One, URG, Improve, VAPS
			3	FRM PM2.5 samplers with teflon filters
			1	FRM PM2.5 sampler with quartz filter
			1	Auto Dichotomous sampler with electron microscopy and XRF analysis of fine and coarse PM.
A	Kiang/Bayor	GaTech	1	Personal exposure monitors
A	Koutrakis	Harvard	1	Personal exposure monitors
Integrated Particle Samplers with daily 12-hr Collection beginning @ 0700 EDT				
B	Maring	U Miami	1	MOUDI for ions (RH controlled)
B			1	MOUDI for OC,EC, mass (RH controlled)
B	Edgerton	ARA		PCM particle composition monitor for PM2.5 mass, trace elements, water soluble metals, ions, OC/EC.
On-Line Particle Mass Spectrometry				
C	Middlebrook	NOAA		PALMS: particle mass spectrometer
C	Prather	UC Riverside		ATOFMS: aerosol time of flight mass spectrometer
C	Warsnop	Aerodyne		AMS: aerosol mass spectrometer
C	Wexler	U Delaware		RSMS2: second generation rapid single particle mass spectrometer
Continuous and Semi-Continuous Particle Chemistry				
C	Dasgupta	Texas Tech		Automated IC with water vapor condensation collection system for sulfate and nitrate Automated IC with non-water collection system for sulfate and nitrate
C	Edgerton	ARA		Automated catalytic reduction system for ammonium, nitrate, and sulfate. Commercial (R&P) for OC/EC.
C	Hering	ADI		ICVC: Integrated collection and vaporization cell for automated nitrate, sulfate and particulate carbon
C	Slanina	ECN		SJAC: Steam jet aerosol collector for nitrate, sulfate and ammonium ion
C	Ondov			GFAA for continuous metals
C	Turpin	Rutgers		In situ carbon analyzer for organic and elemental carbon
C	Weber/Lee	GaTech,BLN		CPCIC: CNC-based collection for aerosol ion chromatography

Continuous and Semi-Continuous Particle Mass				
C	Koutrakis	Harvard		CAMMS: pressure drop mass measurement
C	Russell	GaTech		TEOM [3]: tapered element oscillating microbalance for particle mass, with RH control.
C	Solomon	EPA/BYU		RAMS for continuous particle mass
Continuous and Semi-Continuous Particle Physical Characterization				
C	McMurry	U Minn		Double size spectrometry for particle density
C	“	“		DMPS [3]: Particle size distributions 3 nm-3 um
C	Savoie	U Miami		TSI nephelometer for particle light scattering at three wavelengths
Continuous and Semi-Continuous Supporting Measurements				
C	Edgerton	ARA		Met [3]: meteorology station at 10 m for wind speed, wind direction, temperature, barometric pressure, solar radiation and relative humidity.
C	Edgerton	ARA		Criteria and reactive gases [3] (O3, NOx, NO, NO2, SO2, CO, NOy, HNO3, NH3)
C	Baumann	GaTech		Met and criteria gases (T, RH, WS/ WD, global radiation, uv radiation, NO, NOy, O3, CO, SO2.
C	Bergin	GaTech		Aerosol optical depth, spectral radiometer, sun photometers
C	Hardesty	NOAA		LIDAR: boundary layer O3 and aerosol backscatter
C	Dasgupta	Texas Tech		Semi-continuous HCHO and H2O2 (gas)
C	McNider	UAH		Wind profilers for winds aloft
C	Zika	U Miami		On-line GC for volatile organics and oxygenates
Multiday Sample Collectors				
M	Maring	U Miami	1	MOUDI for organic speciation
M	“	“	1	MOUDI for heavy molecular weight compounds
M	Ondov		1	Mega Vol for trace metals
M	Koutrakis	Harvard SPH	1	High volume sampler for sample archiving
Particle and Vapor Collection through SEARCH/ARIES (24-hr beginning at 0100 EDT) [3]				
S	Rasmussen	OGI		Whole air canisters for volatile organic hydrocarbons and oxygenates [3]
S	Burge	Harvard		Burkard Sampler for Pollen and Molds [3]
S	Edgerton	ARA		PM2.5 FRM mass [3] PM10 FRM mass (dichot) [3] PCM particle composition monitor for PM2.5 mass, trace elements, water soluble metals, ions and OC/EC [3]
S	Koutrakis	Harvard		HEADS for gaseous ammonia, particle acidity and sulfate [3]
S	Zielinska	DRI		Particle Organics Collector [3]
Supporting Laboratory Analyses				
	Jahren	GaTech		Isotope analysis of PM2.5 (C13 and N15)
	Bayor	GaTech		Trace element and heavy organics analysis of MOUDI samples

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1 Sch: Schedule code, as given in Table 2.
2 Investigators and Organizations listed in Appendix A.
3 SEARCH/ARIES instrumentation operating under different protocol and Quality Assurance.

Table 3 Sample Schedules

Code	Schedule
A	Alternate Day Schedule: 24 hour sample beginning at 0700 on Aug 3, 5 (odd calendar dates) 12 hour sampling beginning at 0700 on Aug 4, 6.(even calendar dates)
B	Base Schedule: 12-hour sample beginning at 0700 and 1900 every day.
C	Continuous and near-continuous 5 min – 60 min average concentrations, beginning on the hour
M	Multiday Sampling (for large sample collection purposes) beginning at 0700 EDT, at discretion of investigator
S	SEARCH schedule for existing SEARCH sampling program 24 hour samples beginning at midnight standard time.

Study Schedule

Important milestones for the project are listed in Table 4. Please note dates during the study for audits and meetings.

Quality Assurance

All participants are asked to submit a Standard Operating Procedure by May 17, 1999. These should be sent directly to Bill Chameides at Georgia Tech. He will distribute copies to George Momberger, who is preparing the Quality Assurance Plan for the project, and to Dennis Mikel of US EPA Region IV who will handle the field audits.

Field audits will be conducted on weekdays. These will focus on flows, and will be conducted by the EPA Region IV audit team in Athens. Those with particle samplers should be prepared for audits by the week prior to the beginning of the study. The tentative schedule is:

Week of July 19	Audits of continuous gas monitors
Wed-Thurs July 28-29	EPA speciation sampler audits
Fri, July 30	Audits of other particle filter samplers
Monday Aug 2	Audits of continuous monitors
Wed-Thur Aug 4 - 5	Continued audits as needed.

Systems audits, that is an on-site review of the operations of each system, are under discussion. To the extent possible this will be done through Dennis Mikel, but it may not cover all experiments.

Table 4. Study Schedule

Pre-study	
2/7-9/99	Planning Workshop, Atlanta Georgia
Feb-Mar 99	Logistics questionnaire circulated, site plan drafted
5/12	Draft protocol, site layout and occupancy agreement circulated.
5/17	Participants submit Standard Operating Procedures to Bill Chameides
5/30	Site layout finalized and circulated
6/15/99	Protocol completed and submitted
6/25/99	Quality Assurance Plan distributed for comment
7/10/99	Quality Assurance Program Plan completed and submitted

During Study	
7/19	Site ready for setup, audits for gaseous instruments this week
7/27-7/30	Check-in at Headquarters
7/30, 6:30	Social gathering at Headquarters with goodies
8/1, 8 pm	Kick-off Science Team Meeting at Headquarters
7/28-30, 8/2, 8/4, 8/5	On-site audits
8/3, 0700 EDT	**Measurements begin**
8/7, 8/13, 8/19, 8/25, 8/31, 8 pm	Investigator meeting and/or social gathering (at Headquarters unless otherwise designated)
9/1, 0700 EDT	**Measurements end**
9/7	Site demobilization complete

Post-Experiment	
3/1/00	SOS Data Analysis Workshop
3/1/00	Quality Assurance Report completed and submitted
3/15/00	Submission of preliminary data to central website
6/1/00	Submission of Interim Report to U.S. EPA
6/1/00	Joint Health Effects/Atmospheric Sciences Workshop
7/1/00	Submission of Report on Recommended Future Studies To Further Investigate the Link Between PM and Human Health
12/20/00	Special SOS Session at Winter AGU Meeting
01/01/01	Submission of all quality assured data to the NARSTO Archive, and, where appropriate, AIRS.
01/15/01	Submission of papers for peer-review and publication in as Special Issue in a technical journal
02/15/01	Submission of Final & QA Reports on the 1999 SuperSite Experiment

Protocol for Continuous and Near-Continuous Measurements

Most of the continuous, near-continuous and mass spectrometer particle measurements will be housed inside trailers. Each investigator is asked to arrange for their own inlet, which will extend out of a window and above the roof of the trailer. Recommended sample height is 2 m above the roof top. The inlet should have a size cut at 2.5 µm at ambient relative humidity, unless the system otherwise sizes or excludes coarse particles. Cyclones that provide these cutpoints can be obtained from URG, BGI or Met One. Additionally, investigators should avoid inlets of ¼" (6 mm) diameter because these are attractive to nesting insects prevalent to Atlanta this time of year.

The relative humidity for the particle measurements is left to the discretion of the individual investigators, but should be known. The trailer that houses the instrumentation will be air conditioned, but temperatures will be maintained at or above 78 F to avoid water condensation in the sampling lines.

Protocol for Integrated Samplers

Most of the integrated sample collectors will be housed on an outdoor platform, 0.5 m in height. General inlet and sampling considerations for the PM2.5 samplers are the same as for the continuous instruments, as listed in Table 5. Note that all carbon vane pump exhausts must be filtered to avoid contamination.

To assess spatial uniformity over the sampling area, three FRM PM2.5 samplers will be operated, one at each end of the platform and one on top of the platform between the continuous instrumentation shelters. These will be run with Teflon filters and analyzed for mass, metals (by XRF) and possibly ions.

The exact protocol for operations, beyond those indicated above, has not been defined ands is left to the discretion of the PI's. Comprehensive documentation of sampling operating procedures will facilitate post-experiment analysis.

Table 5. Summary of Sampling and Inlet Recommendations

Item	Recommendation
Provision of inlets.	Each investigator is responsible for their own inlet, tubing and hardware.
Inlet Height:	2 m above platform, or 2 m above the top of the trailer.
Inlet Cutpoints:	If needed, particle cutpoints should be at 2.5 µm at ambient RH
Inlet Size:	¼" inlet diameter not recommended because they are attractive to nesting insects.
Relative humidity:	The relative humidity at the point of measurement is at the discretion of each investigator, but should be reported.
Trailer temperature:	Trailers will be kept 78-80 F to avoid water condensation in lines
Pumps:	To be placed outside or underneath the trailer
Pump exhaust:	All carbon vane pump exhausts must be filtered.
NOx monitors:	All NOx monitor exhausts should be scrubbed to remove ozone.
Solvent use:	Solvents, other than water, are strongly discouraged. Notify S. Hering or E. Edgerton of plans to use organic solvents.
Other emissions:	In all cases please avoid contamination at the site

Documentation and Data Exchange

The data will be submitted to James St. John of Georgia Tech. Guidelines regarding data submission will be forthcoming. Expect to report particle composition concentrations (such as sulfate, carbon etc.) in units of $\mu g/m^3$, where the volume is evaluated at ambient conditions. As appropriate, an uncertainty should be assigned to each data value.

Although we have used daylight time in describing the sampling schedules, the data base will employ standard time, consistent with the NARSTO format. To avoid confusion, expect to report your data in standard time. This means that sampling begins at 0600 EST (=0700 EDT).

It is understood that investigators are free to exchange data among themselves, but that no one's data is to be used in a publication without their permission, and without including that person's name on the paper (unless the individual specifically indicates a preference not to be a coauthor)

Communications / Weather Updates

Supersite Web Address: http://www-wlc.eas.gatech.edu/supersite
This address will house updates about the study, weather and air quality forecasts, and major parts of this protocol.

Check-in: When you arrive, please "check-in" with the GaTech staff person at the headquarters at 575 Fourtheenth St NW. This person will have a information sheet with the latest updates regarding audits, and the first Kick-off meeting. They will ask you where you are staying, so that we can compile of list of "how-to-reach" investigators during the study. If you do not already have a key card, this will be handed to you.

July 30 Social: For those on site by Friday, July 30, there will be am evening social gathering. Check in at Headquarters to learn the details!

Kick-off Meeting on Sunday August 1, 8 pm: This will be the first of the Science Team meetings, to keep us posted during the progress of the project. At the first meeting everyone will be asked to complete a field contact list, so that people can be reached if necessary during the study.

Science Team Meetings: Communications will be handled through investigator (Science Team) meetings held at 8 pm every sixth day, beginning with a Kick-off meeting on Sunday August 1. Dates are Aug 1, 7, 13, 19, 25, 31. Location: Headquarters, unless otherwise stated. Investigators are encouraged to share their data through postings on the board as the study progresses.

Weather/AQ Updates: Daily weather and air quality updates and messages will be maintained on a web site, and posted on the bulletin board at headquarters and at the sampling site. Data will be displayed in graphical format and will be accessible via the internet. Weekly briefings will be given at each of the Science Team Meetings. Special requests for meteorological data should be submitted to Jim St. John at (404) 894-1754, or email: stjohn@eas.gatech.edu.

Headquarters Facilities

The Study Headquarters and general meeting space will be located in the building of the Institute for Paper Science and Technology (IPST) located approximately 2.5 miles north of campus, 2.5 miles from Jefferson St. site. There will be desk and meeting space, telephones for local and credit card long distance calls, bulletin board and internet access via an on-site Workstation as well as direct connections using internet-capable laptops. There is ample parking at the front of the building, as well as secure, fenced parking in back. (See attached figures and maps.)

You will need a keycard to gain off-hours access, and for parking. C.S.Kiang will be issuing these, and has e-mailed all of you asking for names, social security nos, hotel where you are staying and duration of stay. The plan is to have the keycards waiting for you at your hotel when you arrive. If it is not there, you will need to get your card from headquarters during regular business hours (9:00 - 5:00, M-F).

The headquarters address, phone and fax numbers are:

575 Fourteenth St. NW, Atlanta GA 30318
Phone: 404 385 0520 (with message service)
Fax: 404 385 0795

Off-Site Laboratory Space

Karsten Baumann has graciously offered to share his laboratory space with study participants. The expectation is to provide space for those who need to coat denuders, clean filter holders and so forth. Karsten's lab is located in the same building as the Study Headquarters. His lab has a fume hood, ultrasonic bath in the fume hood, laminar flow hood, a clean room and a walk-in refrigerator. There is an ample supply of 18.3 MegaOhm distilled water, which has been purified using resin canisters. But space and facilities are not unlimited, so coordination among investigators will be necessary.

Those planning regular use of the laboratory should make arrangements directly with Karsten in advance of the study. He may be reached at 404-385-0583.

Lab address, phone and fax are:
575 Fourteenth St. NW, Room 1374, Atlanta
Phone: 404-385-0438
Fax: 404-385-0795

The emergency lab contact, should all other contacts fail is Karsten's cell phone at 404-401-9222. Karsten's students / assistants in the lab are Danny Dipasquale, Jing Zhao and Wes Younger at 385-0438. They may help with small questions during the study.

Site Layout and Power

Arrangements for site access, logistics and support are being handled by Eric Edgerton of ARA. Access to the site will be through the western gate on Jefferson Street via a unique key code to be given to all study participants by Eric Edgerton. The attached figures show the general layout for the experiment.

New equipment will be accommodated in one of three ways, as shown in Figure A: 1) mounted outdoors on platforms; 2) housed in shelters provided by ARA; and 3) housed in trailers owned by the researchers. Two new shelters (14'x45') will be installed inside the fenced compound and connected by a 5' wide elevated walkway. The walkway will provide access to sampler inlets, which should extend about 2 m above platform level (7-8 m above ground level). Auxiliary power (1500 amps) will be installed at a junction box in the southwest corner of the compound, from which it will be distributed to shelters, platforms and trailers. A restroom facility and a dedicated parking area will be located adjacent to the Jefferson Street entrance.

Four research trailers will be parked to the north, east and south of the fenced compound. The dimensions of these trailers are approximately 40' long by 10' wide by 12' tall. Trailers to the north and south will have roof-mounted equipment extending about 8 m above ground level. Trailers to the south will have sample towers extending about 10 m above ground level (same as existing towers). Two low wooden platforms (5' long x 65' wide) on the north side of the compound will support integrated samplers installed and operated by EPA. Figure B shows space assignments inside the two new shelters. We have attempted to provide the floor space requested by individual PIs; however, working room inside each shelter will be tight. PIs are asked to economize their use of space to the extent possible. Each PI will have one or more 3' wide x 6' long table(s) for installatioin of analyzers, data systems, etc. Sample lines will go through a window and up to their respective inlets along the walkway. Space for storage of pumps, gas cylinders and other material will be available underneath the walkway and below the shelters. Each shelter will have telephone service, chairs and extra tables (space permitting) for sample preparation, etc. Refrigerators (freezers) for food and samples will also be provided. Electrical receptacles will be installed at each station in the voltage/amperage/phase requested by PIs.

Figure C shows platform assignments for the discrete samplers. Each location will have a receptacle and a dedicated 20-amp circuit.

Off-site storage will also be available. ARA will provide a rental truck for transport of material to/from the storage facility during installation and demobilization.

Courtesy Rules

At the site we are the guests of Georgia Power, and we must be careful not to hinder their activities. Courtesy towards our hosts is especially important during setup. First impressions are lasting, and deployment activities tend to be a bit chaotic. Eric Edgerton will be sending an E-mail with the gate access code, and with special precautions to assure that we do not interfere with Georgia Power during setup.

As noted above, access to the site will be through a security gate. Dedicated parking will be located near the gate and approximately 75 meters south of the site. All visitors to the site must use the designated gate and parking area to avoid interference with Georgia Power Company activities. There is limited parking, and carpooling is encourgaged.

Some specifics :
- Carpooling to the site is encouraged.
- Eating will be allowed in the shelters, but eating areas must be kept clean. A designated bin will be provided for food trash, and this will be disposed of each evening.
- There will be no smoking or consumption of alcoholic beverages on site.
- All carbon vane pumps must have exhaust filters. Any pump found to be operating without an exhaust filter will be turned off until a filter is installed.

Shipping Addresses

Shipments to the site should be sent to
Attn: Larry Guest/Eric Edgerton
829 Jefferson Street NW
Atlanta, GA 30318
Tel: 404-506-4483

Please use this address for boxes that will be retrieved immediately, as storage space at Georgia Power is limited.

Mailing Addresses

Personal mail should be sent to the hotel where you are staying. If this is not possible, you may send it in care of Carol Thomas, EAS, GaTech, and it will be held for you at the Headquarters (although this will cause some delay).

Housing

The “official” SuperSite hotel is:
Regency Suites Hotel
975 West Peachtree Street, Atlanta, GA 30309
Telephone 404-876-5003 or 800-642-3629
FAX 404-817-7511

The Regency will hold rooms for us at a rate of $65 per night plus tax, until the cut off date on JUNE 26. The price includes breakfast each day and dinner Monday-Thursday. There is an additional flat parking fee of $30 for the duration of your stay. Each room is equipped with a microwave, refrigerator and coffee maker, and coffee supplies are provided in the rooms each day. The hotel has a 24 hour exercise room and is very secure. It is located next door to the Midtown Marta Station (Atlanta's rapid rail system which runs directly from the airport approximately every 15 minutes at a cost of $1.50 per ride). The hotel also provides local transportation between 7:30 a.m. and 5:30 p.m.

You should make your own reservations directly with the hotel. Please quote group number #1202 SUPERSITE FIELD EXPERIMENT. Please note that after June 26, if there is space available it will be at a rate of $89 per night. If you cancel 24 hours prior to arrival and the hotel is able to resell the room then a refund for the first nights room and tax will be issued.

Directions from the Airport & Public Transportation

The easiest way to the Regency Suites Hotel or Georgia Tech is by the Atlanta rapid rail system, which is called MARTA. MARTA leaves from baggage claim, and stops next to the Regency Suites at the “Midtown Stop”. Cost is $1.50. MARTA operates from 5 am to 1 am Monday - Sat, and until 12:30 am Sundays and Holidays. Departures are every 8-10 min Mon-Fri, 10-15 min weekends and holidays.

If you rent a car at the airport: Travel northbound on I-75/I-85. Take exit #101 for 10th/14th St. Turn right at first traffic light onto 10th St headed east. The Regency Suites will be on the SE corner facing you at the 3rd traffic light. (remember there is a fee for parking at the hotel, see above)

If you are coming southbound on I-75: Take exit #102, 14th/10th St. Stay in left land. Turn left at the second traffic light onto 10th. Go east, bearing to right lane. The Regency Suites will be on the SE corner facing you at the 3rd traffic light.

If you are coming southbound on I-85: Take exit #26, 14th/10th St. Turn left at second traffic light onto 10th ST. Go east to third traffic light. The Regency Suites will be facing you on the SE corner.

Atlanta Contacts

Supply houses

McMaster-Carr, 6100 Fulton Industrial Boulevard, Atlanta, GA 30336-2852
Ph: (404) 346-7000

Matheson Gas, 6874 S. Main St., Morrow, GA 30260
Ph: (770) 961-7891

Grainger, 1721 Marietta Blvd. Atlanta GA 30318
Ph: 404-355-1984

Georgia Valve and Fitting, 3361 W. Hospital Ave, Atlanta, GA 30341
Ph: (404) 458-8045, Fx: (404) 454-7930

Emergency -- Hospitals

Piedmont Hospital (near the Regency Suite Hotel)
1968 Peachtree Road, N.W., Atlanta, GA 30309
24-Emergency (404) 605 3297

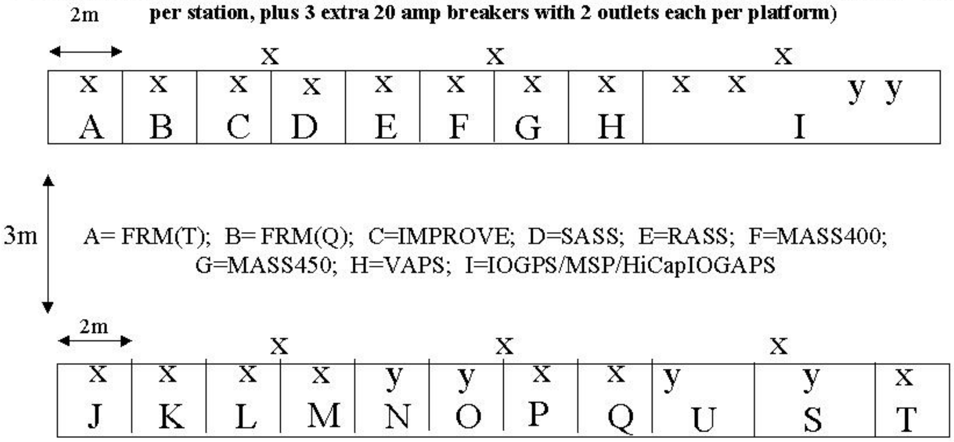
Grady Memorial Hospital (near the Jefferson Site)
80 Butler Street SE, Atlanta, GA
404 616 4307

Emergency Contacts

Bill Chameides: Office: (404) 894-1749, Cell Phone: (404) 229-8346
Eric Edgerton, Office: (919) 402-9381, Home: (919) 490-5171
Lab emergency: Karsten Baumann, Office: 404-385-0583, Cell: 404-401-9222.

Sampling Platform Layout for Aerosol Samplers

(Each platform is 23m long, x 1.6m wide with one 20 amp breaker (x) or 30 amp breaker (y) and 2 outlets per station, plus 3 extra 20 amp breakers with 2 outlets each per platform)

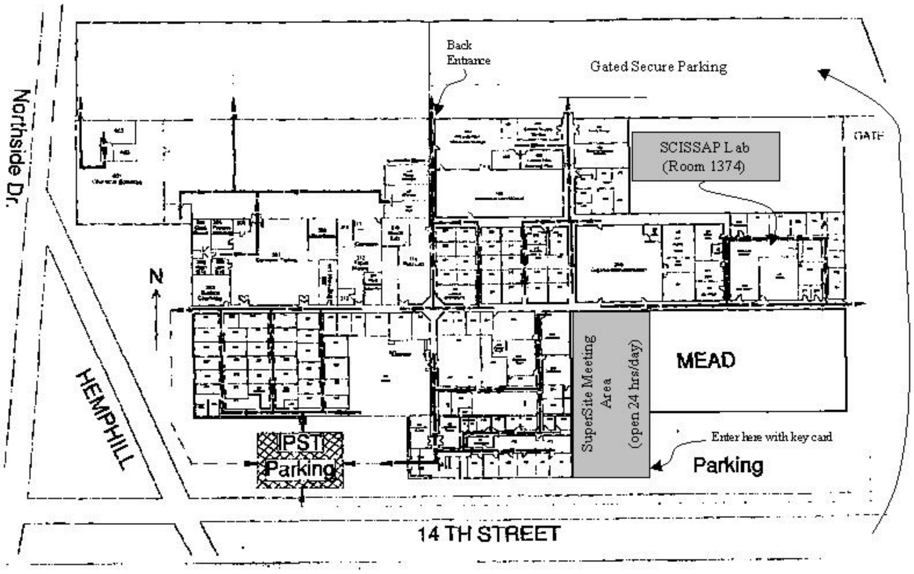


A= FRM(T); B= FRM(Q); C=IMPROVE; D=SASS; E=RASS; F=MASS400; G=MASS450; H=VAPS; I=IOGPS/MSP/HiCapIOGAPS

J=Personal Exposure Monitors ; K=Autodichot; L= ARIES/SEARCH; M = R&P Chem Monitor
N= PC-BOSS(TVA); O=PC-BOSS(BYU); P= RAMS; Q= CAMM; U= unassigned;
S=HVOPS; T= FRM-T1; FRM-T2 located on roof of trailer

1999 Atlanta SuperSite Experiment:Central Facility

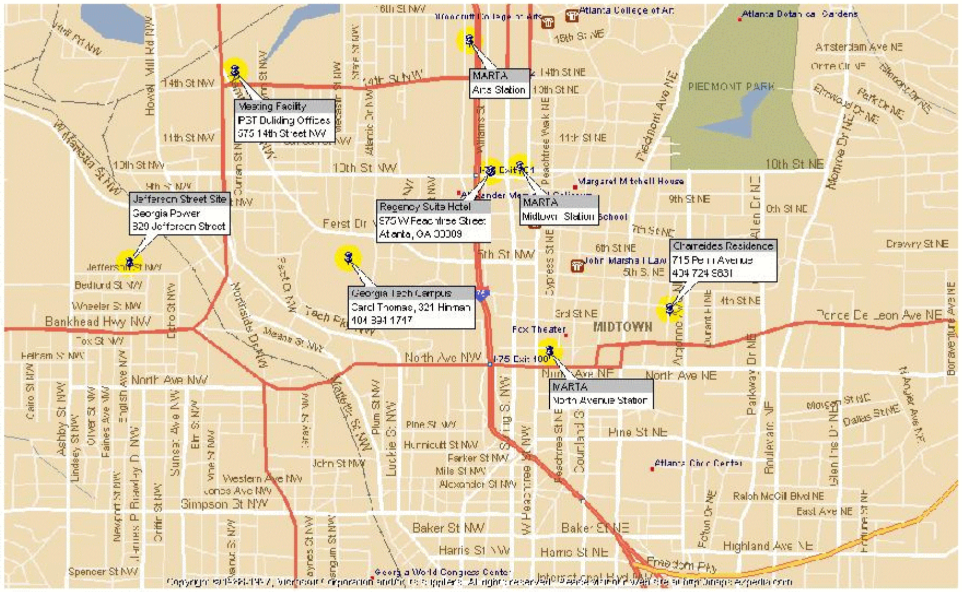
IPST Building Offices, 575 14th Street



To site ←——— ———→ To hotel

1999 Atlanta SuperSite Experiment

Measurement Site, Meeting Facility, Hotel, and environs


Meeting Facility
IPST Building Offices
575 14th Street NW

MARTA
Arts Station

Jefferson Street Site
Georgia Power
820 Jefferson Street

Regency Suite Hotel
975 W Peachtree Street
Atlanta, GA 30309

MARTA
Midtown Station

Chameides Residence
715 Penn Avenue
404 724 9831

Georgia Tech Campus
Carol Thomas, 321 Hinman
404 894 1747

MARTA
North Avenue Station

Appendix A. Study Participants

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FRESNO SUPERSITE INSTALLATION, OPERATION, AND DATA ANALYSIS

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

First Draft

February 22, 1999

SUBMITTED BY:

Energy and Environmental Engineering Center
Desert Research Institute
2215 Raggio Parkway
Reno, NV 89512

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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 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 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 $PM_{2.5}$ 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 PM_{10} mass concentrations and are described as follows (U.S. EPA, 1997):

- Twenty-four-hour average $PM_{2.5}$ not to exceed 65 $\mu g/m^3$ 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 $\mu g/m^3$ concentrations from a single community-representative site or the spatial average of eligible community-representative sites in a monitoring area.
- Twenty-four-hour average PM_{10} not to exceed 150 $\mu g/m^3$ for a three-year average of annual 99th percentiles at any site in a monitoring area.
- Three-year average PM_{10} not to exceed 50 $\mu g/m^3$ for three annual-average concentrations at any site in a monitoring area.

The statistical form of these standards and the community-oriented monitoring sites used for $PM_{2.5}$ and PM_{10} 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 PM_{10} mass concentrations are considered to be indicators of adverse health, and 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.

The U.S. Environmental Protection Agency'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 $PM_{2.5}$/PM_{10} 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). It offers synergistic opportunities to accomplish this as well as methods evaluation and health objectives with the initiation of an EPA Supersite at Fresno. Table 1-1 lists the measurements that will be acquired at the Fresno Supersite with their monitoring periods, frequencies, and averaging times. Uses for the acquired data are also documented in Section 2.

1.2 Fresno First Street Site

The 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 $\mu g/m^3$ 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 $\mu g/m^3$ 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 $\mu g/m^3$ 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 in danger of being exceeded. $PM_{2.5}$ constitutes ~80% of PM_{10} during winter and ~50% of PM_{10} 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 PM_{10} levels.

Table 1-1. Fresno Supersite measurement specifications.[a]

Observable and Method	Operator	Period	Avg Time	Frequency
Gases				
NO/NO_x (TEI 42 Chemiluminescence)	ARB	Always	1-hr	daily
Ozone (API 400 UV Absorption)	ARB	Always	1-hr	daily
Carbon Monoxide (Dasibi 3008 Infrared Absorption)	ARB	Always	1-hr	daily
Non-Methane Hydrocarbons	ARB	Always	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)	ARB	Always	24-hr	6th day
PM_{10} Mass, Sulfate, Nitrate, Chloride, Ammonium Carbon (Hivol SSI w/ quartz filter)	ARB	Always	24-hr	6th day
PM_{10} and $PM_{2.5}$ Mass, Elements (dichotomous sampler with Teflon filter)	ARB	Always	24-hr	6th day
$PM_{2.5}$ mass (Andersen sequential FRM w/ Teflon filter)	ARB	Always	24-hr	daily
Toxic (metals, chromium VI, aldehydes) (Xontec 920)	ARB	Always	24-hr	6th 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)	ARB	Always (starting 6/1/00)	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
$PM_{2.5}$ 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

Table 1-1. (continued)

Continuous Particle Mass and Chemistry				
$PM_{2.5}$ mass (heated TEOM)	DRI/ARB	6/1/99-3/31/01	10-min	daily
PM_{10} mass (heated TEOM)	DRI/ARB	6/1/99-3/31/01	10-min	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	10/1/99-3/31/01	10-min	daily
$PM_{2.5}$ organic and elemental carbon (R&P or Met-1 In Situ Analyzer)	DRI	4/1/99-3/31/01	30-min	daily
Individual particle size and chemistry (UC Riverside Time of Flight spectrometer)	ARB/ UCR	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	Always	24-hr	6th day
Carbonyls (Xontec 925 DNPH sampler)	ARB	Always	24-hr	6th day, summer
Light hydrocarbons (canister & GC/FID)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	5 to 8-hr	daily for Episodes
Heavy hydrocarbons (TENAX & GC/TSD/FID)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	5 to 8-hr	daily for Episodes
Aldehydes (DNPH & HPLC)	CRPAQS	15 Episode Days, 11/15/00-1/31/01	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	5 to 8-hr	daily for Episodes
$PM_{2.5}$ 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 DUSTRACK 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

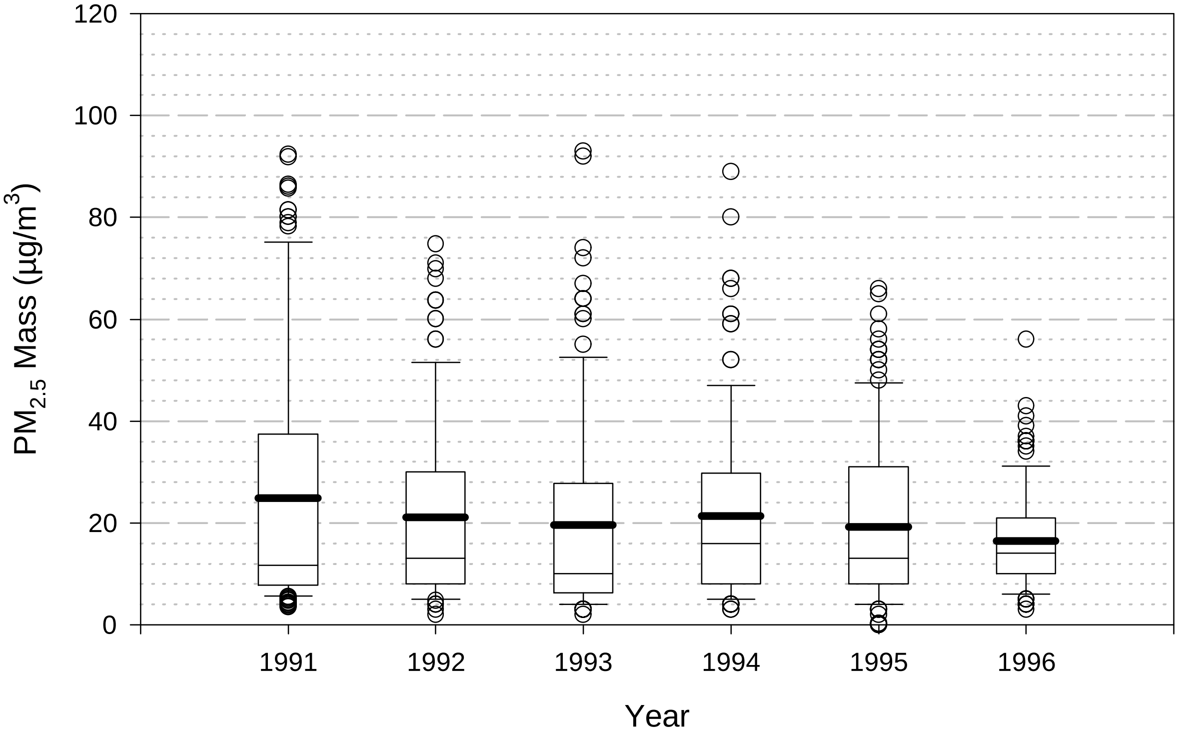
Table 1-1. (continued)

Light Absorption				
Coefficient of Haze (AISI paper tape sampler)	ARB	Always	1-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)	DRI/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
Relative Humidity (High accuracy sensor)	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.

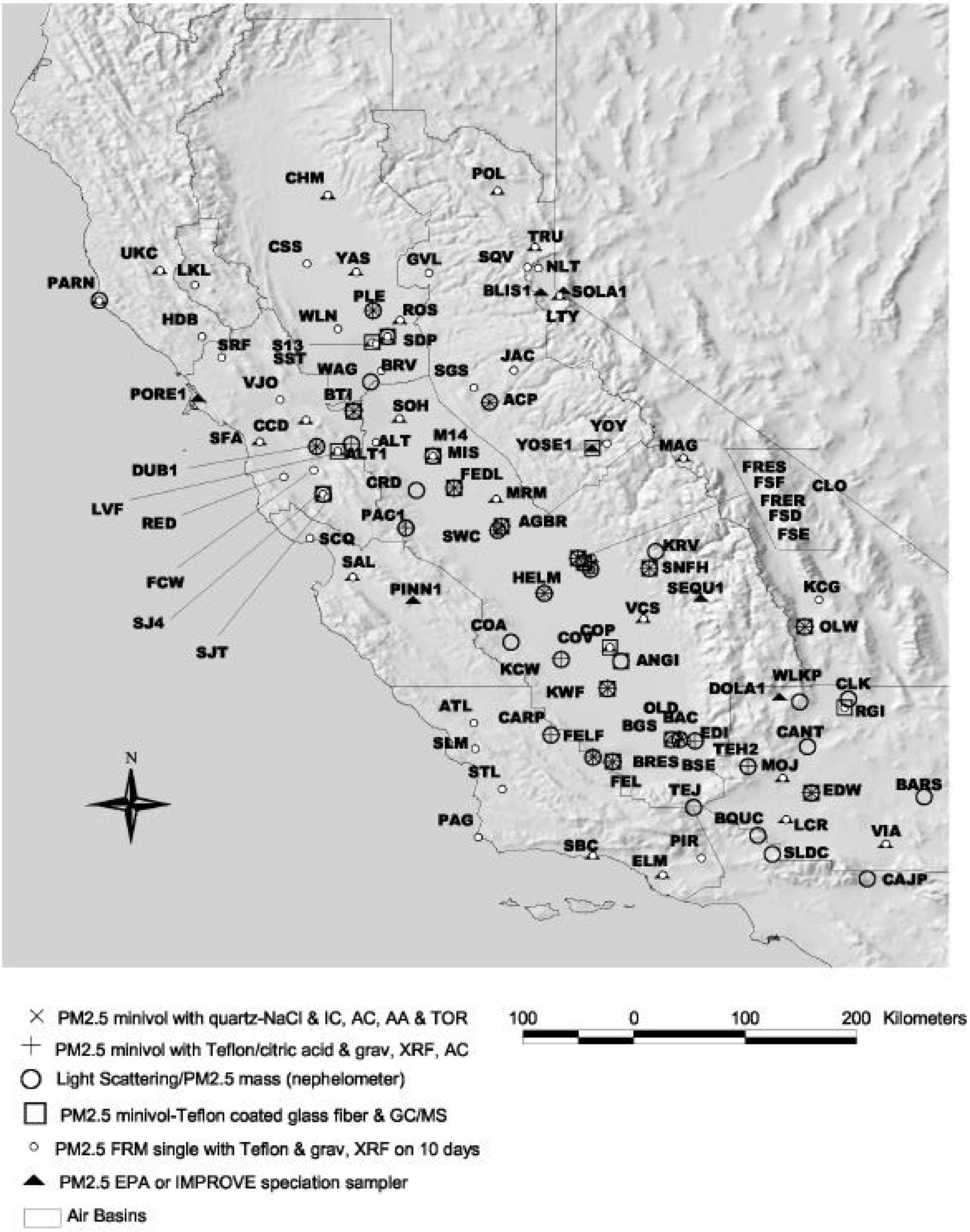
[b] May be integrated with scanning mobility particle sizer (0.005 to 1.0 µm).

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. in Clovis 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. CRPAQS (Watson et al., 1998a) will also operate an extensive network of gas, PM_{10}, 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).



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 and health monitoring.
- 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

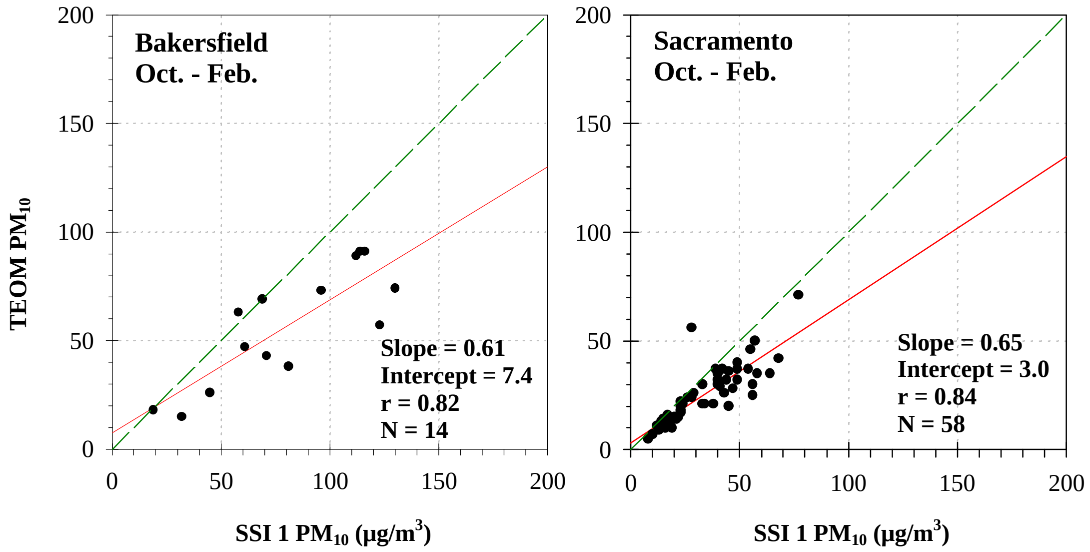
Methods testing and evaluation at the Fresno Supersite is based on evidence that there is a climatology for the validity and comparability of measurements acquired by the same instrument. Meteorological conditions, source contributions, and aerosol chemical composition in central California are known to change substantially over a year and even between different parts of the day (Chow et al., 1992, 1993a, 1994a, 1994b, 1996, 1998). Long-term measurements for a year or more are needed to evaluate the feasibility, practicality, and equivalence of measurements and to 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:

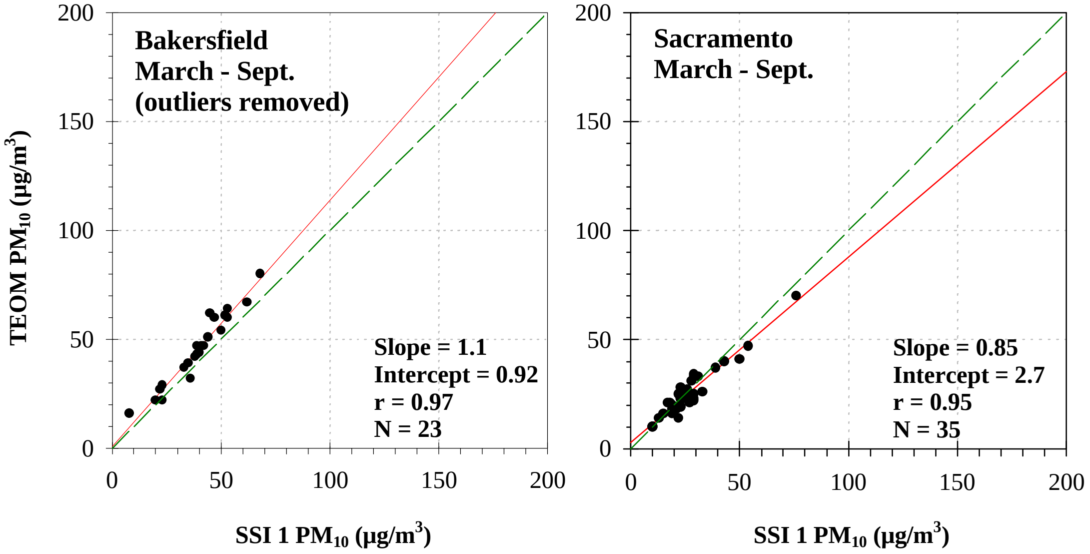
1. Mass and chemical (elements, ions, and carbon) measurements from routine filter samplers with a Teflon filter (from FRM or saturation samplers) represent actual $PM_{2.5}$ mass within the spatial zone of representation of a CORE site.
2. Elemental analysis of Teflon filters under a helium atmosphere does not result in a significant (>10%) loss of volatile nitrate.
3. Carbon gases absorbed on quartz-fiber filters are a small (<15%) fraction of organic carbon measured on these filters.

Figure 1-3. Collocated comparison of 24-hour-averaged TEOM and high-volume SSI PM_{10} 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)



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.

5. Volatilized particulate nitrate is a minor (<10%) part of actual $PM_{2.5}$ during all seasons.

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.

7. $PM_{2.5}$ mass concentrations estimated from particle size, weighted sums of chemical components, light scattering, light absorption, or light extinction are equivalent to those measured with a $PM_{2.5}$ FRM monitor.

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.

2. Nearby emitters represent a small (<15%) fraction of $PM_{2.5}$ measured at a CORE sampling site.

3. The majority of ultrafine particles are from nearby (<500 m), fresh emissions sources.

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.

5. 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.

6. 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.

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.

1.3.3 Health Relationships

Mauderly et al. (1998) identify the following potential indicators for adverse health effects: (1) PM_x 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 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.

The measurements cited in Table 1-1 are sufficient to support health studies related to categories 1, 2, 3, 4, 7, 8, 10, and 11 for more than one year. Although sulfuric and other acids could be quantified, there is sufficient evidence from previous studies to demonstrate that available anions are completely neutralized by ammonia and sodium in central California. Organic composition 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 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 will be 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.

2. Soluble transition metals are a small fraction (<15%) of total metal concentrations in $PM_{2.5}$.

3. Measurements at a CORE sampling site represent the minimum to which people are exposed in their neighborhoods within an urban area.

4. The ammonium nitrate portion of $PM_{2.5}$ shows the same epidemiological relationships to health end-points as $PM_{2.5}$ mass.

5. Ultrafine particle concentration, PM_{10} mass, and coarse particle mass relationships to health indicators are more significant than $PM_{2.5}$ relationships.

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 $PM_{2.5}$/PM_{10} 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.

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 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

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	Radiance 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		

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[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.

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 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 PM_{10} 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.

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.

Unify data from all measurements into formats and units compatible with the CRPAQS data system described by Watson et al. (1998a). Perform Level 1 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.

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.

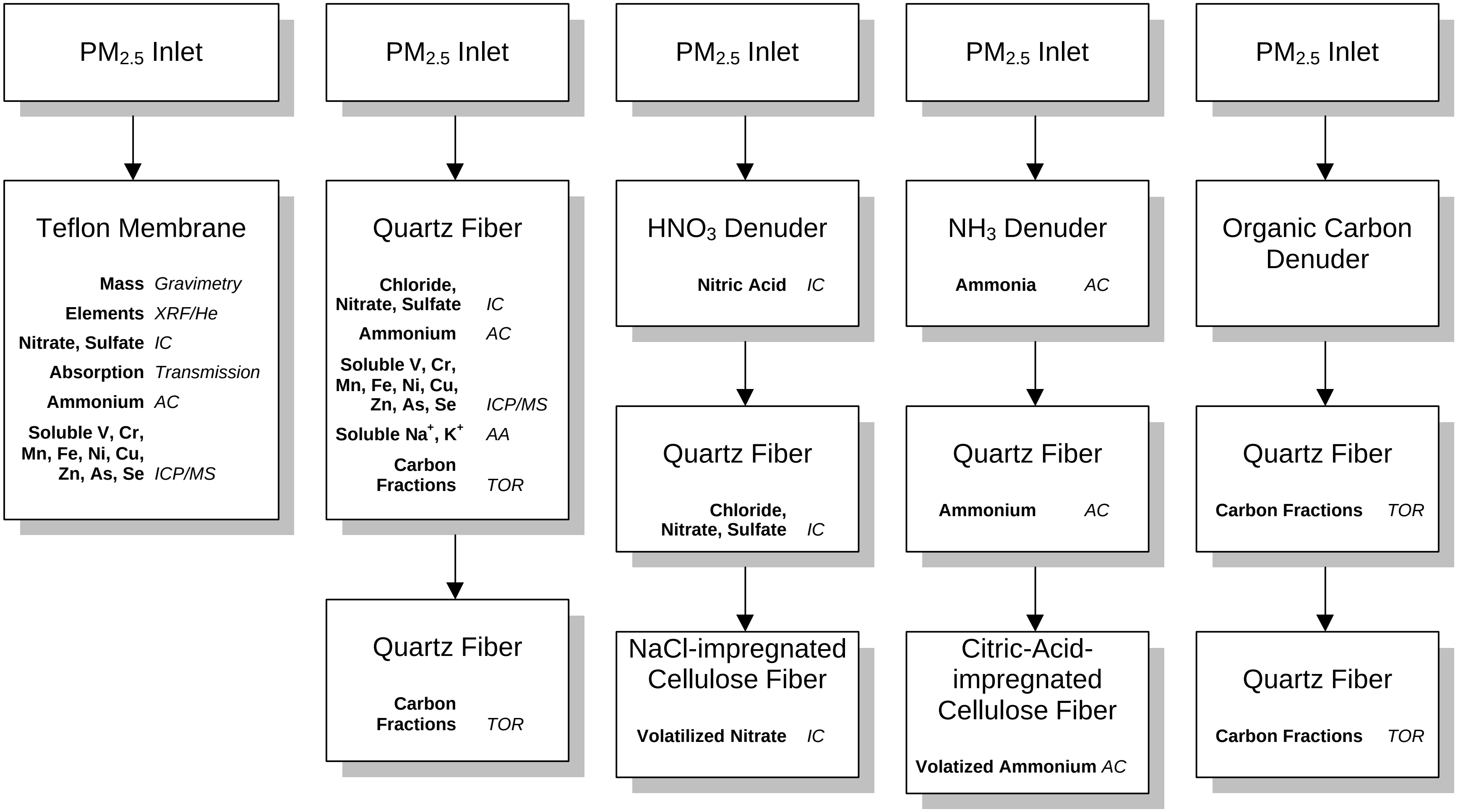
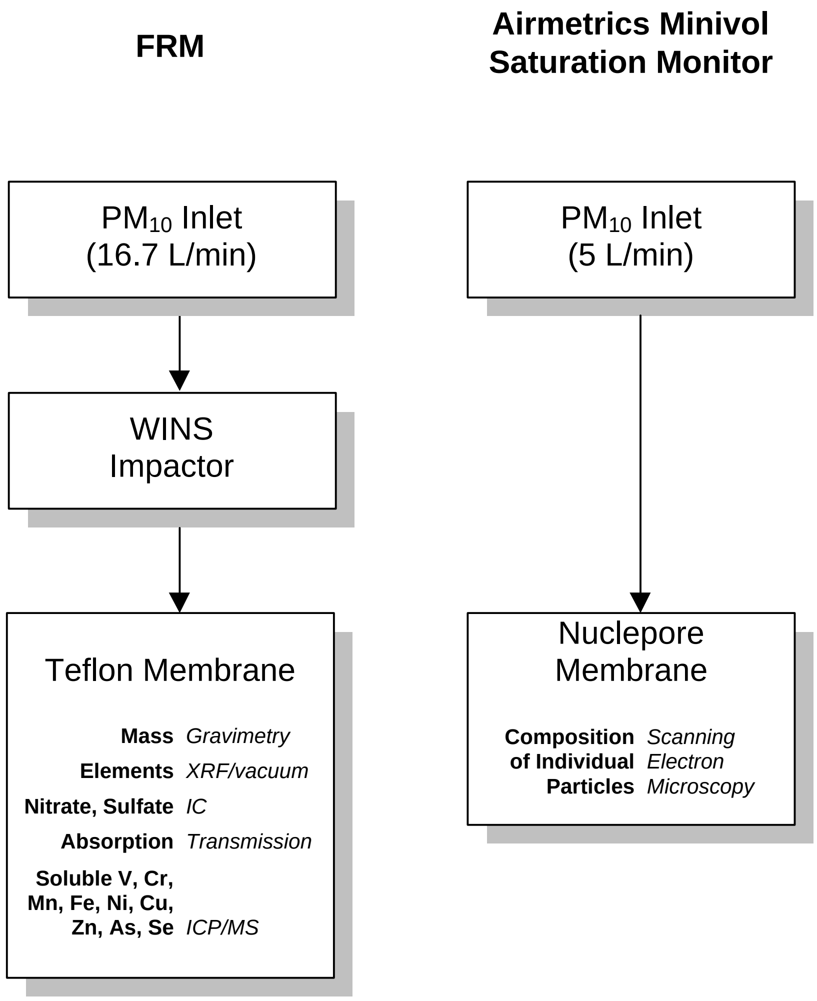


Figure 2-2. Configurations of the $PM_{2.5}$ FRM and saturation monitors.



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. Provide the integrated, Level-2-validated data base to analysts via a Web site interface and on CD-ROM.

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 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 cm^2 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. 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.** 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.** 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.** 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.** Plot nitrate and ammonium concentrations from the denuded front filter nitrate 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.** Plot volatilized nitrate and ammonium concentrations as a function of $PM_{2.5}$ and PM_{10} 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 PM_{10} 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 those measured with a $PM_{2.5}$ FRM sampler.** 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.** 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.** 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.** 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.

- **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.** 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.** 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.** 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.** 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.** 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 $PM_{2.5}$.** 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.** 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 analysis, 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.** Calculate multivariate Poisson regressions between health end-points (derived from concurrent studies described in Section 4) 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.** Calculate multivariate Poisson regressions between health end-points (derived from concurrent studies described in Section 4) 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.

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, 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 bench testing and calibration, procedures development, and data reduction for measurements from the condensation particle counter, the optical particle counter, continuous sulfate and nitrate analyzer, and continuous carbon analyzer.

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 meteorology 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 Kaiser Foundation Research Institute. 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 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 $11.5M California Regional PM_{10}/$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) 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 2-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.

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.

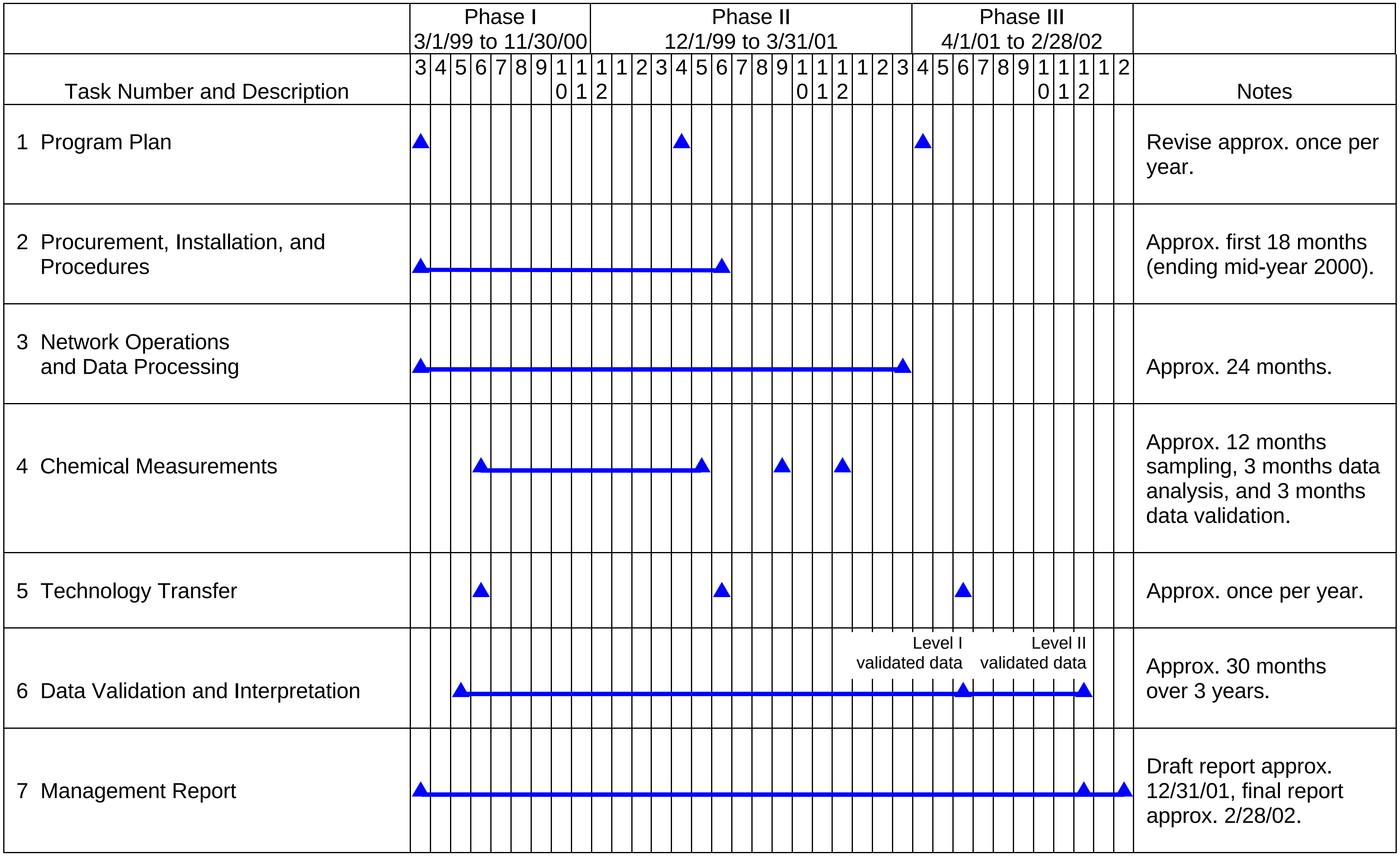
It is anticipated that monitors will be deployed between deployed April 1, 1999, and November 15, 2000. Table 5-1 shows milestones for commencing various measurements. Additional instruments such as a scanning mobility particle sizer (capable of measuring particles in the 0.005 to 1.0 µm size fraction) are currently under investigation and may be added to acquire higher-resolution size distributions of ultrafine (dp<0.01 µm) and fine (dp<1.0 µm) particles. $PM_{2.5}$ 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 $PM_{2.5}$ 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 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 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.

Figure 5-1. Project milestones for Supersite measurements and data analysis.



Task Number and Description	Notes
1 Program Plan	Revise approx. once per year.
2 Procurement, Installation, and Procedures	Approx. first 18 months (ending mid-year 2000).
3 Network Operations and Data Processing	Approx. 24 months.
4 Chemical Measurements	Approx. 12 months sampling, 3 months data analysis, and 3 months data validation.
5 Technology Transfer	Approx. once per year.
6 Data Validation and Interpretation	Approx. 30 months over 3 years.
7 Management Report	Draft report approx. 12/31/01, final report approx. 2/28/02.

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	$PM_{2.5}$ mass	
	Met One PM_{10} Beta Attenuation Monitor	PM_{10} mass	
	R&P 5400 Ambient Carbon Particulate Monitor	Organic and elemental carbon	
	Optec NGN-2 Ambient Temperature Nephelometer	Ambient temperature light scattering	
	Optec NGN-3 Heated $PM_{2.5}$ Nephelometer	Dry particle light scattering	
	Magee Scientific AE14U Aethalometer	Particle light absorption at 880 nm	
	Greentek GT640A or DUSTRAK Ambient Particulate Monitor	Particle light scattering	
	Upgrade Meteorological Sensors (High-Sensitivity Wind Vane, Anemometer, Temperature Sensor, and/or Relative Humidity Sensor)	Wind direction, wind speed, temperature, and relative humidity	
	Data Acquisition System	Continuous 5-min to 1-hr data	
June 1, 1999	Rupprecht & Patashnick 1400A $PM_{2.5}$ Monitor	$PM_{2.5}$ mass	
	Rupprecht & Patashnick 1400A PM_{10} Monitor	PM_{10} mass	
	Radiance M903 Heated Nephelometer	Dry particle light scattering	
	Met One Speciation Monitor (SASS) (one year only)	$PM_{2.5}$ mass, light transmission, elements, ions, and carbon	
	Airmetrics MiniVol Saturation Monitor (one year only – samples for computer-controlled scanning electron microscopy analysis)	Individual particle composition	
	Additional Graseby Andersen Sequential FRM Monitors (one year only)	$PM_{2.5}$ 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	NO_y, HNO_3	
	TEI 17C or API 200 NH_3 Monitor	NH_3	
	Aerosol Dynamics/Rupprecht & Patashnick Ambient Particulate Nitrate Monitor	Nitrate	
	Aerosol Dynamics/Rupprecht & Patashnick Ambient Particulate Sulfate Monitor	Sulfate	
	Aerosol Dynamics Ambient Particulate Carbon Monitor	Carbon	
	TSI 3025A Ultrafine Condensation Particle Counter	Particle number distribution for particles between 0.003 and 0.2 µm diameter	
	Grimm Technologies Optical Particle Counter	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)	$PM_{2.5}$ mass, elements, ions, and carbon	
	Magee Scientific AE30S Multiwavelength Aethalometer	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)	Diurnal (3- to 8-hr, 5 times/day) mass, elements, ions, and carbon	
	MSP100 MOUDI Cascade Impactors (for 15 episode days between 11/15/00 and 1/31/01)	Diurnal (5- to 8-hr, 4 times/day) mass, ions, and carbon size distributions in nine size fractions between 0.054 and 15 µm	
	U.C. Riverside Time-of-Flight Spectrometer (for 15 episode days between 11/15/00 and 1/31/01)	Individual particle size and chemistry	
	CRPAQS Canister Sampler	Light hydrocarbons (C_2 to C_{11})	
	CRPAQS Tenax Sampler	Light hydrocarbons (C_{10} to C_{20})	
	CRPAQS Aldehyde Sampler (for 15 episode days between 11/15/00 and 1/31/01)	Aldehydes	
	CRPAQS Organic Sampler (for 15 episode days between 11/15/00 and 1/31/01)	Particle organic compounds	

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