

MEMORANDUM

SUBJECT: Key Issues Related to PM_{10-2.5} Speciation Monitoring

FROM: Joann Rice, OAQPS/AQAD/AAMG

TO: PM NAAQS Review Docket (EPA-HQ-OAR-2007-0492)

As part of the recent revision to the Ambient Air Monitoring Regulations (U.S. EPA 2006a), PM_{10-2.5} speciation monitoring is required at National Core (NCore) multi-pollutant monitoring stations by January 1, 2011. PM_{10-2.5} speciation monitoring may also be useful in other locations where characterization of thoracic coarse particle speciation would be of high value. This paper describes the PM_{10-2.5} speciation monitoring requirements specified in the ambient air monitoring rule and provides an overview of the monitoring issues, discussion of the potential use of existing PM_{10-2.5} speciation sampling and analysis techniques in a pilot study to inform the implementation and decision-making process, and related research questions to inform the planning and implementation process. This document also serves as a discussion piece for obtaining feedback and comments on the development and implementation of a long-term PM_{10-2.5} speciation monitoring program.

INTRODUCTION

The EPA issued revisions to the Ambient Air Monitoring Regulations (40 CFR Parts 53 and 58) on October 17, 2006 (U.S. EPA 2006a). The final rule establishes ambient air monitoring requirements for an indicator of thoracic coarse particles (PM_{10-2.5}) to support continued research on particle distribution, sources, and health effects. At the same time, EPA also promulgated a new Federal Reference Method (FRM) for measuring the mass concentration of PM_{10-2.5} in ambient air. Although EPA is not adopting a National Ambient Air Quality Standard (NAAQS) for PM_{10-2.5} at this time, the FRM for PM_{10-2.5} is of value to aid in a variety of research studies and the development of speciation samplers capable of providing improved characterization and understanding of the composition of thoracic coarse particles.

The final monitoring rule contains a requirement for PM_{10-2.5} speciation at NCore multi-pollutant monitoring sites by January 1, 2011, with state monitoring implementation plans due July 1, 2009. As compared to the proposed rule, the final rule increases the number of monitoring sites from ~20 to ~75 and shifts the focus from urban monitoring to both urban and rural monitoring locations. Manually-operated PM_{10-2.5} speciation samplers must operate on at least a 1-in-3 day schedule and be collocated with PM_{2.5} speciation at NCore stations. Since EPA is requiring PM_{10-2.5} speciation monitoring primarily for scientific purposes, it is appropriate to have monitoring at a variety of urban and rural locations to increase the diversity of areas that will have available chemical species data. NCore will have about 75 sites mostly in urban areas, with a subset of about 20 rural sites. For more information on NCore, see: <http://www.epa.gov/ttn/amtic/ncore/index.html>.

The primary objective for PM_{10-2.5} speciation data in the monitoring rule is to support further research in understanding the chemical composition and sources of PM₁₀, PM_{10-2.5}, and PM_{2.5}. In addition, more specific uses for the data can be inferred and include:

- Collection of PM_{10-2.5} composition data to inform health effect studies, both in terms of the relationship between specific PM_{10-2.5} species and health, and between PM emitted from different source types and health.
- Advancement of PM_{10-2.5} speciation monitoring methods in anticipation of wider use under a PM_{10-2.5} NAAQS if one is adopted later.
- Use of PM_{10-2.5} speciation data to promote advancement of source attribution methods.
- Determination of spatial and temporal variations in PM_{10-2.5} concentrations in urban and rural environments.

PM_{10-2.5} SPECIATION MEASUREMENT ISSUES

The Criteria Document (CD), prepared for the previous PM NAAQS review, provides an overview of the current information on coarse particle formation, sources, composition, and mass measurement issues (U.S. EPA 2004). No clear recommendations were given for an approach to collecting PM_{10-2.5} speciation data. It was noted that *“satisfactory techniques are available to separate fine particles from coarse particles and to collect the fine particles on a filter. However, no consensus exists as yet on the best technique for collecting a coarse particle sample for determination of mass and composition. Candidates include multistage impaction, virtual impaction, and difference (subtracting PM_{2.5} mass or composition from PM₁₀ mass or composition).”*

Since the writing of the CD, the EPA Office of Research and Development (ORD) has conducted a multi-site field evaluation of candidate methodologies for PM_{10-2.5} mass (U.S. EPA 2006b). Five PM_{10-2.5} measurement approaches were initially selected for study and included virtual impaction (dichotomous sampling), difference, and continuous methods. In addition to continuous monitoring devices, integrated filter-based monitors were used to collect filters for subsequent speciation analysis. The ORD results from speciation analyses of the filters are pending and when available, can be used to inform this planning process. So far, ORD has found that when reconstructing PM_{10-2.5} mass using the speciation results (sum of species), there is a significant portion (10-50%) of the mass that is unaccounted for or unidentified in some locations. It is important to note that this includes uncertainties associated with the factors used in reconstructing mass (e.g., the factor used in conversion from OC to OM). Although the level of agreement between the reconstructed mass and the measured mass was not always high, linear regression comparisons between constructed mass and measured mass did show high correlation. The PM_{2.5}, PM_{10-2.5} and PM₁₀ mass comparisons of the dichotomous (dichot) sampler with FRMs in Phoenix, AZ showed the dichot to be 10% higher for PM_{2.5}, 7% lower for PM_{10-2.5} and 4% lower for PM₁₀. It was hypothesized that the higher PM_{2.5} dichot mass was due to coarse particle intrusion into the fine mode and significant measurement biases will occur only if the coarse fraction of PM₁₀ appreciably exceeds the PM_{2.5} size fraction, as was seen in Phoenix. Mass comparisons in other locations (Birmingham, AL and Lindon, UT) showed very good agreement ($\pm 4\%$) between the dichots and FRMs for PM_{2.5}, PM_{10-2.5} and PM₁₀. High correlations ($R > 0.986$) were found in all cases, indicating that the response between the dichot and FRM is very consistent from one sampling event to another.

Limited PM_{10-2.5} speciation monitoring studies have been conducted in the U.S. and most of these studies were conducted using the difference method. The uncertainties and inconsistencies between the analytical techniques used in these studies are unknown. PM_{10-2.5} speciation has been studied at both urban locations (Chow et al., 1996; Chow et al., 1993; Sardar et al., 2005, Edgerton et al., 2005) and rural IMPROVE monitoring locations (Eldred et al., 1997; Malm et al., 2007; Lee et al., 2007). Soil components (e.g., Si, Al, Ti, Ca, Fe, K), and organic carbon (OC) were consistently found to be dominant components of PM_{10-2.5} and the significance of nitrate and sulfate found was dependent on the location studied. For coarse mass in rural locations, Malm et al. (2007) found the soil components (61%) and particulate organic carbon mass (24%) to be the major components, with nitrate at 8%, elemental carbon (EC) at 1%, sea salt at only 2%, and sulfate as negligible. Particulate organic carbon mass was defined as OM = OC*1.8. In southeastern urban locations, Edgerton et al., (2005) found similar results to Malm et al. (2007), but also showed a significant portion (26-38%) of the reconstructed PM_{10-2.5} mass to be unidentified when accounting for OM as OC*1.4 and on the order of 16-23% when using OM as OC*2.5. In the San Joaquin Valley, Chow et al., (1996) also found total carbon aerosol (TC); ions (e.g., nitrate, sulfate, sodium, chloride); and soil components to be abundant in the PM₁₀ fraction and in Southern California, Sardar et al., (2005) found the soil components, OC and nitrate to be dominant.

A list of coarse particle constituents was provided in the Criteria Document and includes suspended soil or dust; fly ash; nitrates/chlorides/sulfates; soil components (Si, Al, Ti, Ca, Fe); sea salt; tire/brake/road wear debris; and biological materials. Not all of these components can be measured directly through a filter-based speciation monitoring program (e.g., fly ash, tire/brake/road wear debris); however, some components or species may be represented by components that can be measured with existing techniques used for PM_{2.5} speciation (e.g., sodium and chloride ion for sea salt).

The current PM_{10-2.5} FRM difference method, dichotomous sampler, and current speciation filter-based samplers serve as logical choices for the basis of a PM_{10-2.5} speciation sampler design. A combination of filter types and analytical methods are currently being used in both the PM_{2.5} Chemical Speciation Network (CSN) and IMPROVE monitoring programs to collect components of PM_{2.5}. These existing techniques can also be applied to a PM_{10-2.5} speciation monitoring program, but not without some complication.

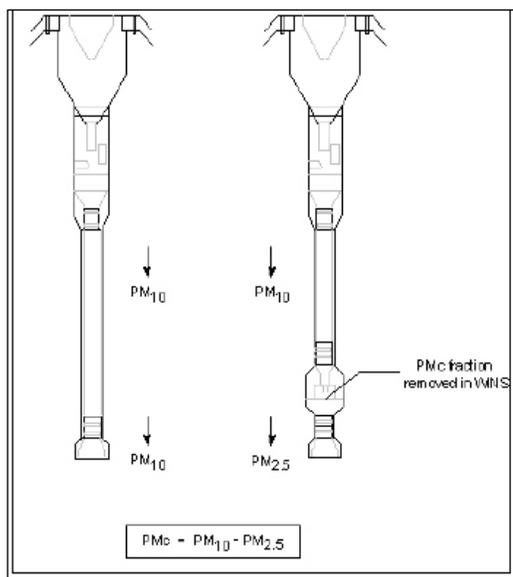
The FRMs for PM_{2.5} and PM₁₀ (low-volume sampling at 16.7 Lpm) provide relatively precise (within $\pm 10\%$) methods for determining the mass on a Teflon filter. However, uncertainties remain about the relationship between the mass and composition of material remaining on the filter as determined by the FRM and the mass and composition of material that existed in the atmosphere. Measurement errors of concern for PM₁₀ sampling include uncertainty in cut point tolerances, particle bounce and re-entrainment, impaction surface overloading, and losses to sampler internal surfaces (U.S.EPA 2004). Another measurement uncertainty for PM_{2.5} sampling is the potential for inclusion of a small fraction of coarse particles in the fine mass fraction under some circumstances.

Modification of the PM_{2.5} speciation sampler inlets to PM₁₀ was suggested by CASAC (EPA-SAB-CASAC-CON-04-005) as an option for PM_{10-2.5} speciation by difference. This may be a viable alternative as long as both speciation samplers have identical flow rates, filter sizes, and filter handling procedures. One limitation of the most widely used PM_{2.5} speciation sampler (MetOne SASS) is the difference in flow rate (6.7 Lpm) from the PM_{2.5} and PM₁₀ FRMs (16.7 Lpm). Differences in flow rates result in differences in filter face velocity and pressure drop across the filters, which may adversely affect the volatile species and subsequent comparison of mass closure or reconstructed mass with the FRM total mass; however, volatility issues are most likely less important for PM_{10-2.5} particles than for PM_{2.5}.

PM_{10-2.5} FRM Difference Method

As is the case with all PM measurement methods, uncertainties exist with the PM_{10-2.5} difference method. These include data loss if either the PM_{2.5} or the PM₁₀ sampler fails; uncertainties in flow rate and filter weights (both before use and after collection and equilibration of particles); and uncertainties due to the loss of semi-volatile components which may occur for each size cut. Allen et al. (1999) have suggested ways to improve coarse particle difference measurements by instituting careful control of sampling aspects (e.g., flow rate control), management of gravimetric analysis issues, and proper implementation of field blanks. The viability of PM_{10-2.5} speciation by a difference method requires further evaluation. However, preliminary regression comparisons for speciation by difference and the dichot method have shown high levels of agreement and high correlation for predominant species. While there is currently no consensus on whether the mixing of PM_{2.5} and PM_{10-2.5} aerosols causes a bias in either measurement, CASAC mentioned the need for sampling separation and collection of filters with only coarse particles to avoid mixing of PM_{2.5} and coarse particles and the potential for subsequent chemical interaction. Allen et al. (1999) also mentions the importance of maintaining filter flow rates greater than 10 Lpm, preferably 16.7 Lpm, to avoid degraded precision. As mentioned above, the most widely used speciation sampler has a flow rate of 6.7 Lpm. per channel. The impact of this low flow rate should be evaluated if the low-flow speciation samplers are used for PM_{10-2.5} by difference.

Figure taken from EPA 2006b



Dichotomous Samplers (Dichots)

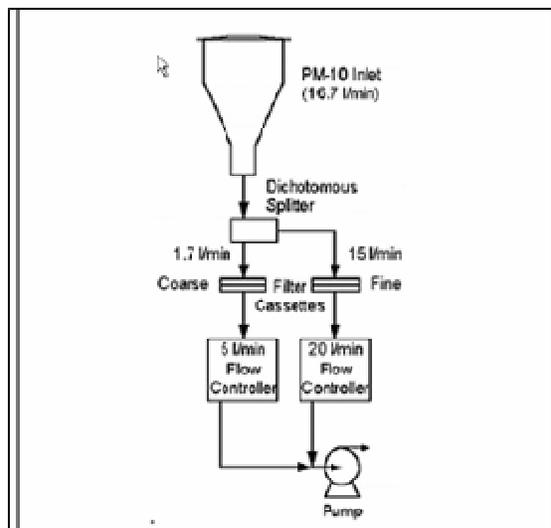
Measurement uncertainties have also been identified with Virtual Impactors in dichotomous samplers. These include fine and coarse particle intrusion; and potential errors in the results from the dichotomous sampler caused by uncertainties in the coarse mass channel enrichment factor which is used to estimate virtual impactor performance (Allen et al., 1999). Improvements have been made to address some of these issues. Current commercial impactors reflect design changes earlier identified to reduce the contamination of coarse particles by fine particles, while maintaining low losses and sharper size cuts. Fine particle intrusion of 10% into the coarse mode is well known (Loo and Cork, 1988) and can be mathematically corrected for. ORD

Figure taken from EPA 2006b

continues to evaluate and characterized virtual impactors. As mentioned previously, results from the multi-site evaluation of PM_{2.5}, PM_{10-2.5} and PM₁₀ mass comparisons of the dichotomous sampler with FRMs showed very good agreement (except in Phoenix) and very good correlations (U.S. EPA 2006b).

PM_{10-2.5} Species or Components

Table 1 provides a list of candidate or potential PM_{10-2.5} species that can be measured with the existing PM_{2.5} speciation methods. The specific species that need to be measured for PM_{10-2.5} must be identified in order to design a monitoring program. For example, ions (e.g.,



nitrate and sulfate) have been identified as only minor components of PM_{10-2.5} in some locations. It is not clear whether the resources to measure ions are needed to support research needs for PM_{10-2.5} speciation. Elemental analysis methods (e.g., X-Ray Fluorescence) can provide sulfur, potassium, chloride, and sodium elements; therefore, it needs to be determined if these elements are sufficient surrogates for the information needed for PM_{10-2.5}. If ions are not needed, then it would eliminate the need to collect an additional filter (nylon) and resources for an additional lab analysis. In addition, the need for elements by XRF versus extractable or water soluble elements by ICP/MS should be determined.

Table 1. List of Candidate PM _{10-2.5} Species			
Species	Filter Type	Denuder	Analysis Method
PM _{10-2.5} Gravimetric Mass	Teflon	None	Filter weighing
Elements: <ul style="list-style-type: none"> • Crustal or soil (Si, Al, Ti, Ca, Fe) • Several other elements currently measured routinely for PM_{2.5}, including: K, Cl, P, Mg, Cr, etc. 	Teflon	None	EDXRF (Energy Dispersive X-Ray Fluorescence) or alternative extraction method
Soluble Ions <ul style="list-style-type: none"> • Nitrate, sulfate, sodium, potassium, chloride, ammonium 	Nylon or Teflon	MgO	Ion Chromatography

Carbon	<ul style="list-style-type: none"> Organic and Elemental Carbon Quartz 	None	Thermal Optical Reflectance (TOR) and transmittance (TOT) by IMPROVE_A
	<ul style="list-style-type: none"> Carbonate Carbon 		Separate acidification and analysis
Biological Material (Bioaerosols)	Teflon or Quartz	None	Scanning Electron Microscopy (SEM) or Total Protein Assay as indicator
Fly ash	Teflon	None	Scanning Electron Microscopy (SEM)

Potential issues with XRF measurement of particles have been identified. XRF is typically done under vacuum to improve performance, enhance detection limits, and reduce contamination of detector sources. Use of XRF under vacuum and the loss of volatile nitrate (as much as 30%) have been demonstrated (U.S. EPA 2001). In the PM_{2.5} speciation program, the effects of vacuum are eliminated by analyzing the filter for mass prior to analysis of elements by XRF. A separate, denuded nylon filter is used for nitrate and other ionic species. Large or coarse particle size effects may also be problematic for XRF. Larger particles (greater than 3 micrometers) may absorb some of the incident and emitted x-rays for light elements such as sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium (Chow 1995). Absorption corrections procedures for particle size effects on XRF results can be applied (Van Dyck et al., 1985) and these factors will have to be optimized for PM_{10-2.5} element analysis by XRF. Another issue to consider is the sensitivity of XRF and the sampling method or sampler chosen.

Alternative techniques like Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). ICP/MS have some advantages (e.g., improved detection limits for many species but lower for some), but also some disadvantages which include increased cost, labor intensive sample preparation, the need for strong acid extraction, incomplete extraction efficiencies, and sample filter destruction (XRF is a non-destructive analysis). If the particle size effects are addressed with XRF and the method sensitivity is adequate for dichotomous sampling, then XRF may be a more appropriate choice for elemental analysis.

PM_{10-2.5} organic and elemental carbon (OC and EC) species can be measured using the same thermal-optical analysis (TOA) method that is used for PM_{2.5} speciation. It is well known that both positive and negative OC sampling artifacts exist (Eatough et al., 1990; Turpin et al., 1994, Mader et al., 2001). Some of the positive artifact can be addressed by the use of backup quartz filter collection and subsequent subtraction. The artifact correction method to be applied to the urban PM_{2.5} CSN is currently being evaluated and developed. Once developed, it will need to be evaluated for use in the PM_{10-2.5} program. Organic vapor denuders are not currently being used for either the PM_{2.5} CSN or IMPROVE programs. Although denuders may be appropriate, they are still not ready for “prime time” and may introduce negative OC artifacts due to the disruption of the gas-particle equilibrium during sampling. Han et al., (2007) mention an interference with metal oxides (e.g., iron oxides) and TOA analysis; whereby certain metal oxides can serve as a

source of O₂ in the helium atmosphere. Since the soil component of PM_{10-2.5} is expected to be significant, any effects of metal oxides on the OC and EC results will need to be explored. Carbonate carbon may also be a significant constituent of PM_{10-2.5} and a separate punch from the quartz filter will have to be analyzed to quantify it.

Biological materials (bioaerosols) are collected with the filter-based particle sampling techniques used for PM_{10-2.5} or PM_{2.5} monitoring and included in the OC measurement, but are not quantified separately from other components. If bioaerosol species (e.g., pollens and molds) need to be qualitatively or quantitatively identified for the PM_{10-2.5} speciation program, an appropriate measurement technique will need to be identified (or developed) and evaluated. Some biological materials can be identified using the scanning electron microscopy (SEM) technique (U.S. EPA 2002). Existing bioaerosol monitoring programs (e.g., BioWatch) collect particles using filters and qualitatively test for biological pathogens (e.g., anthrax). Total protein has been measured from filters with an assay technique and used as an indicator of total biological material (Menetrez et al, 2007). The specific bioaerosol species of interest (or indicator/surrogate species) need to be specified in order to explore appropriate collection and analysis techniques.

Fly ash is also included in the list of PM_{10-2.5} constituents of interest in the CD. Like bioaerosols, fly ash is collected with the filter-based particle sampling techniques used for PM_{10-2.5} or PM_{2.5}, but not quantified separately from other components. If fly ash is needed for the PM_{10-2.5} speciation program, an appropriate measurement technique will need to be identified or developed and evaluated. Some fly ashes can be identified using the SEM analytical technique (U.S. EPA 2002).

NETWORK DESIGN ISSUES

The final monitoring rule contains a requirement for PM_{10-2.5} speciation at NCore multi-pollutant monitoring sites by January 1, 2011. As mentioned previously, this was revised from the proposed rule. The NCore will have about 75 sites mostly in urban areas, with a subset of about 20 rural sites. Spatially, the candidate NCore locations (see map) may not be the best choice for PM_{10-2.5} speciation given that the highest PM_{10-2.5} mass concentrations are in the Southwest and Southern CA (summer peak). The NCore site selection is based on representative monitoring to provide community-wide characterization of exposure and sites leveraged with other measurement systems (e.g., PAMS, NATTS). Since PM_{10-2.5} mass is more likely to be influenced by local sources or wind-blown dust in areas with little vegetation, NCore is not necessarily the optimal design for PM_{10-2.5} speciation. The spatial adequacy and representativeness of the NCore sites for long-term PM_{10-2.5} speciation monitoring will need to be evaluated.



PM_{10-2.5} MONITORING PLAN AND METHOD RESEARCH NEEDS

There are still many unanswered questions regarding PM_{10-2.5} speciation monitoring; however, a few PM_{10-2.5} by difference and dichotomous monitoring sites (3 to 5 locations) should be used for pilot monitoring to answer some of the questions outlined below and to fine tune the final monitoring approach. The CASAC (EPA-SAB-CASAC-CON-04-005) expressed concerns about speciation by difference due to the cumulative effects of the imprecision in both PM_{2.5} and PM₁₀ measurements. White (1998) showed the uncertainty in coarse mass by difference to be about 3 times the uncertainty in the fine measurement. An evaluation of the practicality and validity of PM_{10-2.5} speciation by difference method is needed. The CASAC comments also leaned toward virtual impactation and felt it had significant advantages (e.g., collects the PM_{10-2.5} size fraction directly). For those PM_{10-2.5} species that are in common with the PM_{2.5} speciation program, the existing National Laboratory Contract for PM_{2.5} speciation can be used to analyze the filters. In order to sample for the current suite of species in the PM_{2.5} speciation program (including ions) by difference, identical PM₁₀ versions of the PM_{2.5} speciation sampling devices can be collocated with existing PM_{2.5} samplers. PM₁₀ sharp cut cyclones would need to be commercially available at a flow rate of 6.7 Lpm for the MetOne SASS speciation samplers and the vendor has been contacted about developing and characterizing such cyclones. A PM₁₀ cyclone is already available for the 22 Lpm speciation carbon sampling device. The existing SASS sampler could be retrofitted to have two PM_{2.5} channels with Teflon and nylon filters and two PM₁₀ channels with Teflon and nylon filters if needed. One additional PM₁₀ speciation carbon sampler would need to be collocated with the existing PM_{2.5} sampler for OC/EC aerosol species. If PM_{10-2.5} speciation was based on the dichotomous sampler, it would require three samplers at each location to collect the Teflon, nylon, and quartz filters for speciation if elements, ions, and carbon species are needed.

Some of the questions relevant to PM_{10-2.5} speciation monitoring are outlined below:

- ❖ What are the important PM_{10-2.5} species to measure?
- ❖ Are ions important PM_{10-2.5} species? If so, what ions should be on the target species list?
- ❖ What are the PM_{10-2.5} speciation sampling artifacts that may be encountered and how should they be addressed in the monitoring program? Is speciation by the difference method problematic for PM_{10-2.5} speciation and if so what specific issues make it problematic?
- ❖ The current and most widely used PM_{2.5} speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Lpm which is significantly lower than either the FRM for PM_{10-2.5} mass or the dichotomous sampler (16.7 Lpm). If this sampler was configured to do PM_{10-2.5} by difference, would the 6.7 Lpm flow rate be problematic, especially with our knowledge of concerns about low-flow cut-points and particle intrusion, and the need to compare to what is collected by the PM_{10-2.5} FRM for mass?
- ❖ What analysis methods should be used? What PM_{2.5} speciation analysis methods are appropriate to also use in the PM_{10-2.5} speciation program?
- ❖ Is XRF the most appropriate method for PM_{10-2.5} speciation? Can the complication of particle size and absorption effects in XRF be adequately resolved using absorption correction factors? Does XRF provide adequate sensitivity (detection limits)? If XRF sensitivity is not adequate, should some other more sensitive and potentially more expensive and destructive analytical technique be considered? If an elemental method

that has more sensitivity and applies acid extraction is needed, is the recovery of extractable metals adequate versus total metals by XRF?

- ❖ Are metal oxides a significant source of interference in thermal-optical analysis (TOA) of $PM_{10-2.5}$ for OC and EC given the large expected soil component?
- ❖ If biological particles and fly ash need to be characterized, what specific types of biological materials and fly ashes should be measured? What analysis methods should be used to identify and quantify these species? Is scanning electron microscopy (SEM) on Teflon filters adequate to quantify and identify the biological material present? Is the use of other assay techniques necessary to adequately obtain a quantitative indicator (e.g., total protein) of the total biological material present?
- ❖ When reconstructing $PM_{10-2.5}$ mass using the sum of $PM_{10-2.5}$ species concentrations, a significant portion of unidentified mass has been identified. Are there other $PM_{10-2.5}$ target species or analysis methods that can be used to help identify the source of this mass in order to reduce the amount of unidentified mass and obtain better mass closure?
- ❖ What factors should be considered in the selection of pilot monitoring site locations or areas? One key issue in the proposed PM rule (January 2006) was the need to distinguish urban from rural coarse particles. What pilot site selection criteria would help in selecting urban and rural sites for collecting data to address this issue? What analysis methods or target species are particularly important to inform this issue?
- ❖ Various sampling devices, including dichotomous samplers, MetOne SASS speciation monitors, PM_{10} and $PM_{2.5}$ FRMs are potential sampling devices (with the appropriate filter types) for $PM_{10-2.5}$ speciation. Which of these sampler types should be included or excluded from the pilot network design?

Additional information may be provided to inform some of the questions above when ORD publishes results on $PM_{10-2.5}$ speciation from the multi-city field evaluation. In addition, any pilot monitoring program that is developed and implemented for $PM_{10-2.5}$ speciation may also provide information to resolve some of these issues.

QUALITY ASSURANCE (QA)

The $PM_{10-2.5}$ speciation monitoring program is expected to follow similar requirements as specified for the $PM_{2.5}$ speciation monitoring program, which include collocation for precision estimates and sampler flow-rate audits. $PM_{10-2.5}$ species-specific goals for bias and precision have not been specified. Additional QA procedures and possibly DQOs will need to be developed for $PM_{10-2.5}$ speciation.

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