UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON D.C. 20460

OFFICE OF THE ADMINISTRATOR
SCIENCE ADVISORY BOARD

March 6, 2009

EPA-CASAC-09-006
The Honorable Lisa P. Jackson
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, N.W.
Washington, D.C. 20460

Subject: Consultation on Monitoring Issues Related to the NAAQS for Particulate Matter

Dear Administrator Jackson:

The Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring & Methods Subcommittee (AAMMS) held a public teleconference on February 11, 2009, to consult with staff from EPA's Office of Air and Radiation (OAR) Office of Air Quality Planning and Standards (OAQPS) on issues related to monitoring and speciation sampling for coarse particles ($PM_{10-2.5}$). When EPA issued the final rule to revise both the primary and secondary NAAQS for particulate matter (PM) in October 2006, a new Federal Reference Method (FRM) was also promulgated for measuring the mass concentration of $PM_{10-2.5}$ in ambient air. As part of the revisions to the Ambient Air Monitoring Regulations, $PM_{10-2.5}$ speciation monitoring will be required at National Core (NCore) multi-pollutant monitoring stations by January 1, 2011.

The CASAC uses a consultation as mechanism for technical experts to provide comments to the Agency on the issues under consideration. Several areas of concern have been identified in the written comments provided by the individual Subcommittee members. They include (but are not limited to): the omission of organic compounds; the current lack of consensus on sampling and analytical methods for both $PM_{10-2.5}$ and its speciated components; and the haste with which the Agency is committed to launch the $PM_{10-2.5}$ monitoring network without sufficient time to analyze the data from the pilot study. As this is a consultation, we do not expect a formal response from the Agency. We thank the Agency for the opportunity to provide advice in the NAAQS review process.

Sincerely,

/Signed/

Dr. Armistead (Ted) Russell, Chair
CASAC AAMMS

Enclosures

Enclosure A

U.S. Environmental Protection Agency
Clean Air Scientific Advisory Committee
Ambient Air Monitoring and Methods Subcommittee

CASAC MEMBERS

Dr. Armistead (Ted) Russell (Chair), Professor, Department of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA

Dr. Donna Kenski, Data Analysis Director, Lake Michigan Air Directors Consortium, Rosemont, IL

SUBCOMMITTEE MEMBERS

Mr. George A. Allen, Senior Scientist, Northeast States for Coordinated Air Use Management (NESCAUM), Boston, MA

Dr. Judith Chow, Research Professor, Desert Research Institute, Air Resources Laboratory, University of Nevada, Reno, NV

Mr. Bart Croes, Chief, Research Division, California Air Resources Board, Sacramento, CA

Dr. Kenneth Demerjian, Professor and Director, Atmospheric Sciences Research Center, State University of New York, Albany, NY

Dr. Delbert Eatough, Professor of Chemistry, Department of Chemistry and Biochemistry , Brigham Young University, Provo, UT

Dr. Eric Edgerton, President, Atmospheric Research & Analysis, Inc., Cary, NC

Mr. Henry (Dirk) Felton, Research Scientist, Division of Air Resources, Bureau of Air Quality Surveillance, New York State Department of Environmental Conservation, Albany, NY

Dr. Philip Hopke, Bayard D. Clarkson Distinguished Professor, Department of Chemical Engineering, Clarkson University, Potsdam, NY

Dr. Rudolf Husar, Professor, Mechanical Engineering, Engineering and Applied Science, Washington University, St. Louis, MO

Dr. Kazuhiko Ito, Assistant Professor, Department of Environmental Medicine, School of Medicine, New York University, Tuxedo, NY

2

Dr. Thomas Lumley, Associate Professor, Biostatistics, School of Public Health and Community Medicine, University of Washington, Seattle, WA

Dr. Peter H. McMurry, Professor and Head, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN

Mr. Richard L. Poirot, Environmental Analyst, Air Pollution Control Division, Department of Environmental Conservation, Vermont Agency of Natural Resources, Waterbury, VT

Dr. Kimberly A. Prather,* Professor, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA

Dr. Jay Turner, Visiting Professor, Crocker Nuclear Laboratory, University of California, Davis, CA

Dr. Warren H. White, Research Professor, Crocker Nuclear Laboratory, University of California - Davis, Davis, CA

Dr. Yousheng Zeng, Air Quality Services Director, Providence Engineering & Environmental Group LLC, Baton Rouge, LA

Dr. Barbara Zielinska, Research Professor, Division of Atmospheric Sciences, Desert Research Institute, Reno, NV

SCIENCE ADVISORY BOARD STAFF

Ms. Kyndall Barry, Designated Federal Officer, 1200 Pennsylvania Avenue, N.W. (Mailcode 1400F), Washington, DC, Phone: 202-343-9868, Fax: 202-233-0643, (barry.kyndall@epa.gov)

*Dr. Prather did not participate in this CASAC AAMM Subcommittee activity.

Enclosure B

Comments received:

Mr. George Allen

$PM_{10-2.5}$ Speciation Measurement

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

For all references to Table 1 in my revised comments, I am referring to the simpler version included with the EPA slide presentation, not Table 1 from the white paper. Other species: None that I am aware of; uncertainties in OC (estimated) mass measurements (there are many) may be part of the missing mass puzzle. Methods: ICPMS may be needed to get robust measurements of some of the listed acid/water soluble species at the range of concentrations expected from a dichotomous coarse channel filter. Ions could be done on quartz filter media (after punches are taken for carbon and protein analysis); if this is being considered, I would recommend that for the pilot study ions be done on both the Teflon and quartz filters to evaluate both and to provide a consistency check.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

For PM-coarse, I strongly recommend using only a dichotomous (dichot) sampler (virtual impactor, VI) for coarse PM speciation sampling, since it has multiple advantages over a simple difference method (accuracy and precision, separation of pm-coarse from most of the pm-fine). The "classic" dichot VI combined with the existing low-volume PM10 inlet is a well characterized sampler. It is not an FRM or FEM for PM-coarse since there is no NAAQS for PM-coarse at this time.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

There are the usual fuzzy issues with OC artifacts, both positive and negative; we will probably have to live with these. The issue of how OC blanks will be created, handled, and applied to the data, and how samples are transported and stored (warm or cold) before analysis is important to clearly define. Nitrate in the coarse mode is complex -- there will be a mixture of ammonium nitrate and reaction products of nitric acid with alkaline crustal components. The latter may be more dominant.

Speciation by difference is strongly discouraged. Any species that is primarily in the fine mode,

such as sulfate, will be difficult to measure with useful precision by a difference method that is run routinely in SLT networks. This would be looking at a small difference between two large measurements, and measurement errors and biases get magnified dramatically when this is done. For a more detailed discussion of this topic, see: "Techniques for High-Quality Ambient Coarse Particle Mass Measurements", George A. Allen, Jung-a Annie Oh, and Petros Koutrakis, *Journal of the Air & Waste Management Association*, Volume 49, September 1999, PM-133-141.

While it is possible to generate highly precise PM-coarse mass data by difference under very carefully controlled "research-grade" conditions, routine networks are unlikely to provide this level of precision. Also, although the difference method can work well for PM when great care is taken to insure high precision, it remains unclear if analytical techniques for speciation can be made as precise as mass measurements without excessive cost in a routine network.

4. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

Yes, this is likely to be problematic for many reasons. I do not recommend anything other than a 16.7 Lpm dichotomous sampler for coarse pm speciation.

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

Yes it is, for the "classic" dichot inlet flow of 16.7 Lpm. Note that although the coarse channel flow is only 1.67 Lpm, the coarse channel dichot filter includes (in theory) all the coarse particles present in the 16.7 inlet flow. Thus, the low flow for the coarse channel is not a relevant issue, and the comment on page 8 of EPA's background document for this consultation about adequacy of XRF for dichot samples is not relevant. Another important parameter for evaluation of dichot performance is the filter diameter - it does not have to be 47 mm. The early dichots used 37 mm filters (33 mm exposed area). If enhanced loading is needed on the coarse channel, a 25 mm filter or a mask could be used; the coarse channel flow is low and large particles do not plug pores readily, so pressure drop should be minimal even with a much smaller filter diameter. There are loading-related issues with XRF and coarse particle analysis; self-absorption for large particles is a major issue and gets worse with high loading.

One area that is still of potential concern is loss of particles from the dichot coarse mode filter during shipping. It should be clearly demonstrated that shipping does not cause mass loss; early work by Spengler and Thurston showed shipping loss with a 15 um inlet in the range of 30 to 50% (Spengler and Thurston, *JAPCA* December 1983, **33**:12; and Dzubay and Barbour, *JAPCA* August 1983, **33**:7). Higher losses would be expected from filters with a 15 um inlet cutpoint compared to 10 um. More recent work by Bob Vanderpool (EPA-ORD) did not show this loss using various shipping methods with one exception, where significant losses were observed.

Dichot shipping loss tests done by Environment Canada in 2002 with a PM10 inlet showed losses ranging from 0 to 25 ug on a filter, but the actual filter loading was not reported and it is not clear if the original weighings were done before any shipping of the filters had occurred. My conclusion is that shipping can be an issue for coarse channel dichot filters; an established protocol that has been shown to not lose mass must be used. The Vanderpool work noted above can be used to establish a reasonable shipping protocol.

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

Species priority: I agree with the order as listed in Table 1, with elements first, soluble ions second, then carbon and lastly bioaerosols. One aspect of pm-coarse speciation not on this list is particle surface composition. For coarse mode particles, the surface composition -- not the bulk mass composition -- may be much more relevant for health effects. For example: urban coarse mode particles are black, not earth colored, since they have a coating of soot (and things that absorb on soot...) on the surface (Figure 1 below, from Boston at a location approximately 100 feet above street level, downtown). But by mass, EC would be very low. Thus, simple bulk mass measurements may not be that relevant for health effect studies. Methods for measurement of particle surface composition do exist, but may be expensive compared to traditional bulk chemical analysis.

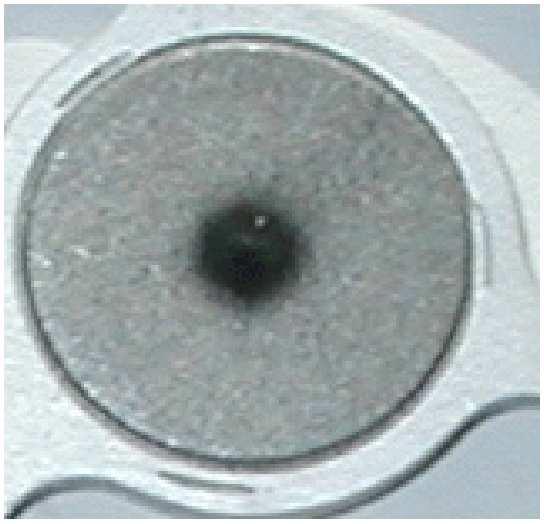


Figure 1. Deposit of particles greater than 2.5 um on an impactor surface in Boston.

Finally, it may not be worth the added analytical expense to fully characterize carbonate carbon with a separate analysis. A TOA analysis time-temperature profile that goes higher than 580C-helium only can give a reasonably useful indication of carbonate carbon. Carbonate comes off as a sharp peak between 700-750 C, during the transition from 615 to 870 C, the highest helium only temperature used in the Sunset Labs laboratory carbon analyzer protocol. With some care, the modest amount of OC that comes off in this last helium only temperature step can be differentiated from carbonate, since the OC usually evolves off more slowly than carbonate. Also, it is important to get carbonate off at this time in the run profile, since otherwise it could be classified as EC; while this is not much of an issue for fine mode pm, it may be a major issue for coarse mode pm.

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

The ions listed are appropriate, with the exception of ammonium. Ammonium ion concentrations will be biased low in areas where nitrate is the major source of ammonium ion, as noted above. I do not consider ammonium ion by itself important enough to justify the extra effort needed to measure it correctly.

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

These species are at the bottom of my priority list. The analysis is expensive, and at least for bioaerosols, there is no way to control them. I wouldn't expect a significant amount of fly ash in the coarse mode at most sites unless they are unusually impacted by a local source.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

This may be a large problem for coarse pm speciation by difference, since PM10 loading will be larger than that on a pm-fine or pm-coarse dichot filter, and different [and imprecise] absorption correction factors would need to be used, resulting in additional coarse-mode by difference errors. Absorption correction factors are more practical for dichot filters. Still, ICPMS should be considered as an alternative analysis technique for acid/water soluble components since it is both more sensitive and does not have any issue with self-absorption.

5. 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 so, how should this interference be addressed?

Probably not. Metal oxides in crustal material can be sources of O2 or catalysts that can move the EC/OC split point in TOA analysis, but this does not necessarily mean the EC/OC split result is wrong -- it is just a limited amount of "pre-oxidation". However, another potential issue with TOA is interference from biogenic coarse mode humic material; it may have some absorption of the ~660 nm wavelength used for pyrolysis correction. If biogenic mass is much greater than EC mass, the interference could be significant.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

If a site's PM10 is nearly all coarse-mode on a mass basis, it still may be useful to do dichot-based pm-coarse speciation. Some species of interest do not contribute much to the total PM mass. Pilot sites should be primarily in areas with large populations, to assist health effect studies. A subset in very large cities should be daily monitoring, since that is needed for health studies to properly account for any lag effect.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

There are issues of large spatial gradients in urban pm-coarse; siting must be urban scale to be useful. It may be appropriate to have a second urban site (traffic oriented?) with at least limited speciation at mid-scale locations near sources of coarse PM. Results from the EPA-funded PM-coarse STAR grant projects on "Sources, Composition, and Health Effects of Coarse Particulate Matter" http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/recipients.display/rfa_id/450/records_per_page/ALL or http://tinyurl.com/d65fcy will (with one exception) not be complete until after January 2011, but perhaps preliminary results from projects under this RFA may be able to inform network design.

Finally, I am concerned about full deployment of this network before an appropriate pilot study period, including analysis of the data and method performance, is completed. Given the present status of the PM-coarse speciation program, I doubt that this can be done in time to have a full network in operation by January 2011. At the least another year, perhaps two years, is needed to prevent a premature deployment. Going forward with full network deployment before we are confident of what we can and should do for PM-coarse methods and species would be a massive waste of limited resources and is to be avoided if at all possible.

Dr. Judith C. Chow

$PM_{10-2.5}$ Speciation Measurement

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

The Revised Table 1 provides a comprehensive list of elements, ions, carbon, and bioaerosol indicators. Additional $PM_{10-2.5}$ species (e.g., filter light transmission [b_{abs}] and organic species) can be measured to assist in health assessment and for source attribution, but these additional marker species will not help to achieve better mass closure. It is not clear how the ORD report (U.S. EPA, 2006) found that 10–50% of the $PM_{10-2.5}$ mass is unaccounted for. The sum of species is not a good indicator for $PM_{10-2.5}$ mass closure calculations, since crustal material accounts for the major portion of $PM_{10-2.5}$. A material balance that commonly groups by source types (e.g., geological material, secondary inorganic aerosols, carbon, salt, and others) may be a better way to evaluate mass closure.

There are two major sources of uncertainties in $PM_{10-2.5}$ mass closure calculations: 1) assumptions about the form of metal oxides present in the atmosphere, and 2) the multiplier used to convert OC to organic mass (OM). Oxides of major crustal components (Pettijohn, 1949) are used in the calculation for geological material. There are two commonly used metal oxide formulas that give similar estimates:

$$\text{Geological Material} = 1.89 \times Al + 2.14 \times Si + 1.4 \times Ca + 1.43 \times Fe \quad (1)$$

$$\text{Geological Material} = 2.2 \times Al + 2.49 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti \quad (2)$$

(Eq. 2 is the IMPROVE formula;Watson, 2002)

Using OM = 1.2 × OC (and Eq. 1; Solomon et al., 1989), Chow et al. (2002a) found that geological material accounted for 72–81% of $PM_{10-2.5}$, with 7–15% organics. The unidentified mass was negligible (<1%) at six urban locations in Mexico City. $PM_{10-2.5}$ mass concentrations were high and variable, ranging from 19 to 56 $\mu g/m^3$. The nature of OM is expected to be different between $PM_{2.5}$ and $PM_{10-2.5}$. A 1.2 multiplier is appropriate for hydrocarbons or freshly emitted vehicle exhaust (composed mainly of H and C atoms), but humic-like substances (HULIS; Kerley and Jarvis, 1997; Schulten and Leinweber, 2000; Thomsen et al., 2002) and bioaerosols (Alexis et al., 2006; Bauer et al., 2008; Heinrich et al., 2003; Lee et al., 2007; Menetrez et al., 2007a) in $PM_{10-2.5}$ probably justify a larger multiplier to account for unmeasured oxygen (O) and nitrogen (N) atoms. Elemental analysis of total H, C, N, O, and sulfur (S) may be applied in the pilot network to estimate OC/OM. These measurements can be compared with solvent extraction or other calculation methods (El Zanan et al., 2005; 2009). Mass closure within ±10–20% is considered sufficient as a quality check.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

Collocated BGI PQ2000 $PM_{2.5}$ and PM_{10} samples have been designated as $PM_{10-2.5}$ FRM (U.S.EPA, 2008). Nevertheless, all filter samplers with well-characterized $PM_{2.5}$ and PM_{10} inlets should be considered. The PM_{10} sampling efficiency (Keywood et al., 1999; Watson et al., 1983; Wedding and Carney, 1983) is most important because the ambient size distribution often peaks near the 10 μm cut-point (Burton and Lundgren, 1987; Lundgren et al., 1984; Lundgren and Burton, 1995). Since PM_{10} and $PM_{10-2.5}$ are highly variable in space and time (Baldauf et al., 2002; Burton et al., 1996; Chow et al., 1981; 1992; 1999; 2000; 2002a), less expensive and portable samplers should be considered (e.g., the BGI OMNI and the Airmetrics MiniVol) to allow more of them to be deployed, especially for short-term studies. These 5 L/min units have well-characterized inlets. These filter samplers can be collocated with $PM_{10-2.5}$ FRM.

To detect short-duration events, optical particle counters (OPCs, e.g., Grimm Dust Monitor, TSI DRX DustTrak II) should also be considered. They can be comparable with filter measurements under certain circumstances (Grimm and Eatough, 2009; Grover et al., 2006; Peters et al., 2006; Teikari et al., 2003). Collocated TEOMs or BAMs with appropriate inlets are also useful for this purpose.

Other low- and medium-volume sampling systems are still in use by different state and local agencies (e.g., Andersen RAAS, URG MASS, R&P2025 Partisol sequential $PM_{2.5}$, and R&P 2300 samplers). Sampling efficiencies should be estimated based on sampling effectiveness curves and anticipated size distributions at potential monitoring locations prior to conducting collocated sampler comparisons. It will be important to verify the homogeneity of $PM_{10-2.5}$ levels across the sampling array (Mathai et al., 1990) using similar instruments for a valid comparison study.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

Carbon gases are adsorbed onto quartz-fiber filters, and this artifact is imperfectly assessed and subtracted using field blanks exposed for the entire sample duration and backup filters (Arp et al., 2007; Chow et al., 2008; McDow, 1986; Noll and Birch, 2008; Watson et al., 2008; 2009). The magnitude of the gaseous organic sampling artifact correction is reduced by using higher sample volumes and lower filter exposed areas so that more carbon is collected per unit of filter area. A better understanding of the adsorbed compounds will be needed to go beyond current $PM_{2.5}$ practices that can also be applied to $PM_{10-2.5}$.

Nitrate is less likely to evaporate from the coarse fraction as it does for $PM_{2.5}$ (Ashbaugh and Eldred, 2004; Chow et al., 2002b; 2005). $PM_{10-2.5}$ nitrate often occurs as non-volatile sodium nitrate (Mamane and Gottlieb, 1992; Mamane and Mehler, 1987; Wu and Okada, 1994). While

there is abundant nitric acid in the atmosphere, it may react with alkaline $PM_{10-2.5}$ (Goodman et al., 2000; Hodzic et al., 2006; Laskin et al., 2005; Ooki and Uematsu, 2005; Umann et al., 2005; Underwood et al., 2001), thereby resulting in a positive nitrate artifact for non-denuded samples at certain locations.

Collocated $PM_{10}/PM_{2.5}$ samplers and virtual impactor (dichotomous) samplers require difference calculations for which the uncertainties of the individual samples should be propagated (Evans and Ryan, 1983; Watson et al., 2001). The propagated uncertainties of differences are about the same for collocated $PM_{10}/PM_{2.5}$ samplers, and may be higher for the dichotomous samplers because the 10 to 1 flow rate ratio between the fine and coarse channels often varies. As pointed out by Allen et al. (1999), variability in $PM_{10-2.5}$ is expected to be higher either by virtual impactor or by the difference method than with an inertial impactor stage. Inertial impactors also have uncertainties due to particle bounce and non-uniform deposits.

Most collocated sampling studies (see Chow, 1995; Chow et al., 2008 for study summaries) have compared $PM_{2.5}$ and PM_{10} separately. PM_{10} comparisons are often poorer than those for $PM_{2.5}$ when: 1) $PM_{10-2.5}$ constitutes a large fraction of the PM_{10}; 2) inlets have different sampling effectiveness curves (even minor ones); and 3) inlet sampling effectiveness changes with inlet loading.

4. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

The MetOne SASS with a flow rate of 6.7 Lpm should be adequate to collect enough $PM_{10-2.5}$ for analysis in urban networks when equipped with a 6.7 Lpm PM_{10} inlet (Kenny et al., 2000; Kenny and Gussman, 2000). The flow rates should be the same through all filters so that filter adsorption and evaporation artifacts would be similar. The URG 3000N sampler used in the current Chemical Speciation Network (CSN) for carbon analysis uses a flow rate of 22.7 Lpm, which is three times higher than the MetOne SASS. The tenfold difference in face velocity (107.2 cm/sec for the URG 3000N versus 9.5 cm/sec for the SASS) and its effect on sampling artifact needs to be further explored. This is more of a $PM_{2.5}$ than a $PM_{10-2.5}$ issue, however. The MetOne SASS filter holder is costly to obtain, process, and ship, and greater operational savings might be obtained by using a simpler sampler pair (e.g., BGI OMNI or PQ2000) that uses the standard Delron FRM filter ring.

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

Yes, the minor flow rate of 1.67 Lpm in the dichotomous sampler is not an issue, since $PM_{10-.2.5}$ is taken from the 16.7 Lpm drawn through the PM_{10} inlet. The dichotomous sampler with either a PM_{15} or PM_{10} initial inlet has been used since the mid to late 1970s. The Harvard Six-City Study used elemental analysis by XRF on dichotomous sampler filters for health assessments

12

(e.g., Ferris, Jr. et al., 1979; Spengler et al., 1983; Spengler and Thurston, 1983; Thurston and Spengler, 1985).

During the early 1980s, dichotomous samplers (Beckman Instruments) were installed in the U.S. EPA's Inhalable Particulate Matter network for $PM_{2.5}$ and PM_{15} at 73 locations (Watson et al., 1981). A subset of samples was submitted to elemental (Al, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Sn, and Pb) and ionic (NO_3^-, $SO_4^=$) speciation. The California Air Resources Board (ARB) also operated dichotomous (Andersen 244) samplers from 1983–2001 at 20 urban sites with elemental analysis for 30 species on both $PM_{2.5}$ and $PM_{10\text{-}2.5}$ samples (Motallebi et al., 2003a; 2003b; 2003c). There are several previous studies using virtual impactors that have involved chemical speciation and used these data for air quality assessment (Dzubay et al., 1977; Dzubay, 1980; Dzubay and Stevens, 1975; John et al., 1988; Li et al., 2001; Lin, 2002; Lin and Tai, 2001; Magliano, 1988; Mamane and Dzubay, 1990; Rashid and Griffiths, 1993; Sprovieri and Pirrone, 2008; Watson et al., 1981; Witz et al., 1982). $PM_{2.5}$ and $PM_{10\text{-}2.5}$ mass and chemical data should be assembled and evaluated to better understand the nature and chemical composition of $PM_{10\text{-}2.5}$.

For very low loading $PM_{10\text{-}2.5}$ samples, the analytical instrument for XRF analysis and extraction volume for ion chromatography (IC) can be optimized to improve the minimum detectable limits (MDLs).

$PM_{10\text{-}2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10\text{-}2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10\text{-}2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

$PM_{10\text{-}2.5}$ is enriched in soil-related elements (e.g., Al, Si, K, Ca, Ti, Mn, and Fe) at inland sites and marine-related elements (e.g., Na and Cl) at coastal sites (e.g., Chow et al., 1994a). Crustal elements, salt (Na and Cl), ions (e.g., NO_3^-) and carbon (e.g., OC and carbonate) are also important $PM_{10\text{-}2.5}$ components to be considered.

Without acidification for carbonate analysis, the presence of carbonate could bias both OC and EC measurements (Chow and Watson, 2002). Cao et al. (2005) found carbonate accounted for 8% of $PM_{2.5}$ mass during Asian dust storms, and ~5% between storms in Xian, China. Although $PM_{2.5}$ carbonate may be negligible at non-urban IMPROVE sites (Chow and Watson, 2002), its abundances may be important in $PM_{10\text{-}2.5}$ at some locations and it should be measured, especially for Asian dust intrusions (VanCuren, 2003; VanCuren and Cahill, 2002).

Decomposition temperatures for various forms of carbonate vary according to the chemical and crystalline forms of the carbonate, catalytic influences of other materials, particle size, rate of heating, and the atmosphere surrounding the material being heated (Webb and Krüger, 1970). Figure A, adapted from Webb and Krüger (1970), shows differential thermal analysis (DTA) curves for various forms of carbonate. Different heating rates, shown in Figure B, also result in variations of DTA curves for magnesian limestone. Murray et al. (1951) found that the presence of salt altered the decomposition temperature of the first dolomite peak by -235 to 40 °C, as

shown in Table A.

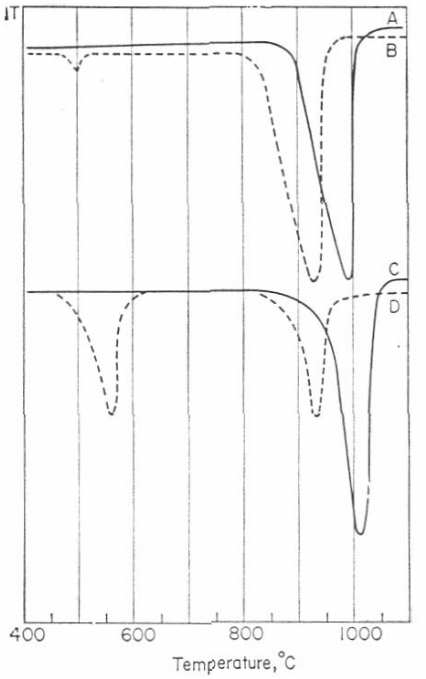


Figure A. Differential Thermal Analyses (DTA) curves for: A) typical calcite (Faust, 1950); B) aragonite (Faust, 1950); C) natural calcite; D) sample giving curve C, calcined, hydrated, and partially recarbonated (from Webb and Krüger, 1970).

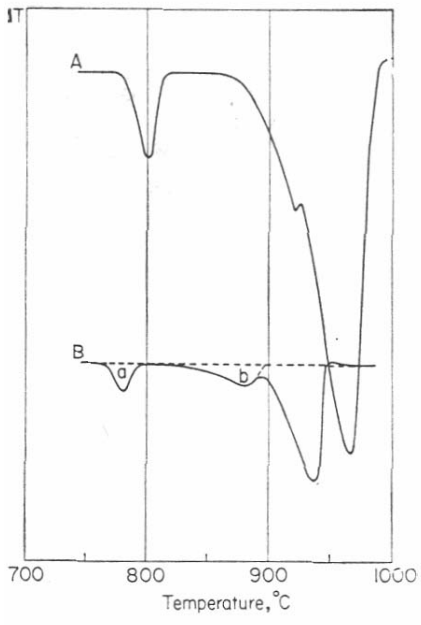


Figure B. Differential Thermal Analyses (DTA) curves for magnesian limestone at a heating rate of: A) 15 °/min; and B) 5 °/min (from Webb and Krüger, 1970).

14

Table A. Effects of salts on the "characteristic" temperature of the first dolomite peak (Murray et al., 1951, from Webb and Krüger, 1970).

Compound added	"Characteristic" temperature °C	Change in "characteristic" temperature deg
$Al_2(SO_4)_3$	775	+40
$(NH_4)_2SO_4$	750	+15
Water	750	+15
$(NH_4)_2SO_3$	745	+10
Untreated dolomite	735	—
$(NH_4)_2HPO_4$	725	−10
$MgSO_4$	710	−25
Na_2SO_4	655	−80
$BaCl_2$	630	−105
$AlCl_3$	565	−170
NaCl	560	−175
KCl	560	−175
$MgCl_2$	535	−200
NH_4Cl	520	−215
$CaCl_2$	515	−220
	515	−220
Na_3PO_4	510	−225
NaF	500	−235

Organic carbon in urban and rural PM_{10} road dusts and agricultural soils ranges from 3–20% (Chow et al., 2003). There is growing evidence that coarse particle organic markers differ from those for $PM_{2.5}$ and can be used to identify and quantify source contributions (Boon et al., 1998; Labban et al., 2006; Omar et al., 2002; Rogge et al., 2006; Rogge et al., 2007; Simoneit et al., 2004; Song et al., 1999). Analyses for organic species (e.g., polycyclic aromatic hydrocarbons [PAHs]) should be considered on a subset of samples, possibly by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) where only a small portion of quartz-fiber filters are needed to speciated non-polar organics (e.g., n-alkanes, alkenes, hopanes, steranes, PAHs; Chow et al., 2007; Hays and Lavrich, 2007; Ho et al., 2008; Ho and Yu, 2004; Yang et al., 2005)

Coarse particles, especially minerals, have different light absorption characteristics at different wavelengths that can be used to distinguish among sources (Fialho et al., 2005; Kim et al., 2004). Filter light transmission (or b_{abs}) has been shown to be highly correlated with $PM_{2.5}$ or PM_{10} EC and can serve as a surrogate for PM black carbon (BC). $PM_{10\text{-}2.5}$ b_{abs} measurements at various wavelengths might be considered, especially for locations where only Teflon-membrane filter samples will be collected.

2. In the consideration of potential ion measurements for $PM_{10\text{-}2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10\text{-}2.5}$?

The anions (i.e., Cl^-, NO_3^-, and $SO_4^{=}$) and cations (i.e., Na^+, Ca^{++}, K^+, NH_4^+) listed in the revised Table 1 should all be measured.

Coarse particle NO_3^- (e.g., sodium nitrate [$NaNO_3$]) has been found in the desert southwest and environments with abundant coarse PM (Mamane and Mehler, 1987; Watson et al., 1994). Chemical reactions convert sodium chloride (NaCl) to hydrochloric acid (HCl) and thermally stable $NaNO_3$ (e.g., Ellis et al., 1983; Pilinis and Seinfeld, 1987; Russell and Cass, 1984). These reactions may dominate coarse particle NO_3^- and occur when NaCl from sea salt, road sanding, or dry lake beds is an abundant atmospheric constituent. Since most of the $PM_{10-2.5}$ contains alkaline crustal material, it is not necessary to use preceding acid gas denuders or nylon filters. Water-soluble Ca^{++}, Mg^+, and PO_4^{3-} are also found in coarse particles and may be indicative of sources. Water-soluble Ca^{+2} is formed by the reaction of acid gases with calcium carbonate (Krueger et al., 2004).

Ion analysis is important for $PM_{10-2.5}$, but it is unnecessary to allocate a separate nylon channel for sampling and analysis. If a URG3000N sampler is used for carbon analysis, a 47 mm quartz-fiber filter should be used (with an exposed area of 11.8 cm^2) to allow for both carbon (0.5 cm^2 punch) and ionic (1/2 of the 47 mm quartz-fiber filter) speciation. The current 25 mm filter configuration in the URG 3000N with an exposed area of 3.5 cm^2 is not adequate for both carbon and ion speciation, especially if carbonate or other analyses are considered.

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

Fly ash may be important if the sampling site is located near a coal-fired power plant or if there are fly ash storage piles nearby. Most modern industrial stacks have particle control devices that remove most of the coarse particles, and fugitive emissions are the most probable sources.

Fugitive fly ash can be collected as grab samples, sieved, and resuspended in a laboratory resuspension chamber (Chow et al., 1994b) for both $PM_{2.5}$ and PM_{10} size fractions, and submitted for the same chemical speciation as those for ambient PM. Resuspended fly ash samples may be useful for in vitro analysis in health assessment. Source profiles for fly ash can also be used in receptor modeling to estimate coal-fired power plant source contributions.

Both optical and electron microscopy (SEM) can be applied to filter samples (Casuccio et al., 1983; Edgerton et al., 2009; Gwaze et al., 2007; Kim, 2007; Ott et al., 2008; Watson et al., 2007; Zhao et al., 2006), but hundreds of particles must be classified to obtain quantitative results. Microscopy has the advantage of identifying unknown sources, but automated image recognition methods perform best with low particle densities (i.e., low flow rates of 1-2 Lpm) and a consistent background, such as that provided by flat polycarbonate filters; this implies a separate filter channel for microscopic analysis.

Bioaerosols, including plant pollen and microorganisms (mold and bacteria) have been recognized as potential health hazards (e.g., Heederik, 2003; Schulze et al., 2006; Steerenberg et al., 2003; Targonski et al., 1995), but have not been widely studied (e.g., Heinrich et al., 2003; Menetrez et al., 2000; 2001; 2007b). If standard operating procedures (SOPs) can be established and target species determined, a subset of $PM_{2.5}$ and $PM_{10-2.5}$ samples (e.g., near agricultural fields, livestock, and vacant lands) should be analyzed for fungi, endotoxins, and proteins.

5. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

Yes, corrections have been successfully devised and applied (Adams and Billiet, 1976; Adams and van Grieken, 1975; Berry et al., 1969; Criss, 1976; Dzubay and Nelson, 1975; Hunter and Rhodes, 1972; Jackson and Hampel, 1992; Rhodes and Hunter, 1972; Sewell et al., 1985; Wagman et al., 1978). Some further work is needed to compare the different approaches and evaluate deviations from basic assumptions (e.g., size distributions). The corrections are specific to the XRF configuration, so it would be good to develop a software system that could be used by different analysis laboratories.

Self-absorption is most prominent for Al and Si, which have the least energetic absorption edges and emitted X-rays. Dzubay and Nelson (1975) showed that attenuation changes with 10 and 15 μm particles as shown in Figure C. The derived attenuation factor is shown in Table B (Dzubay and Nelson, 1975) for their XRF set-up.

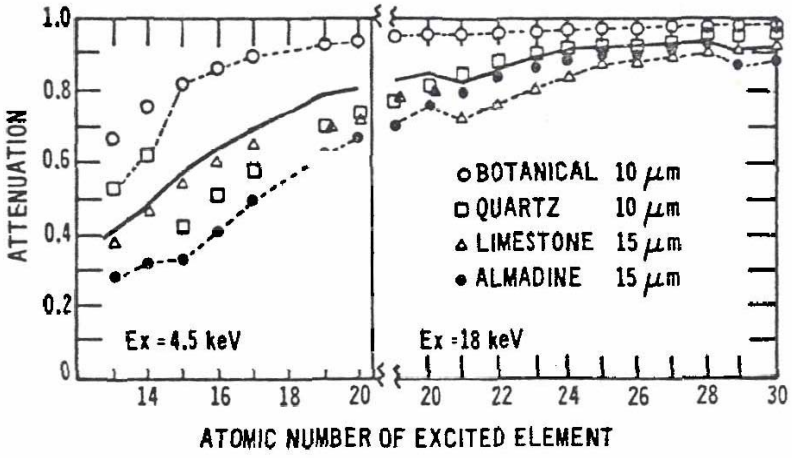


Figure C. Attenuation factors for K_α X-rays of various elements calculated for four different coarse particle compositions (from Dzubay and Nelson, 1975).

17

Table B. Midband attenuation and uncertainty for K_α X-ray fluorescence of various elements in coarse particles deduced from Figure C (from Dzubay and Nelson, 1975).

Element	Attenuation Factor (4.5 KeV excitation)	Element	Attenuation Factor (18 KeV excitation)
Al	0.41 ± 0.12	K	0.83 ± 0.13
Si	0.48 ± 0.15	Ca	0.86 ± 0.10
P	0.58 ± 0.24	Ti	0.87 ± 0.10
S	0.64 ± 0.22	V	0.90 ± 0.08
Cl	0.70 ± 0.20	Cr	0.92 ± 0.07
K	0.78 ± 0.15	Mn	0.93 ± 0.06
	0.81 ± 0.13	Fe	0.94 ± 0.05
		Ni	0.96 ± 0.03
		Cu	0.94 ± 0.06
		Zn	0.95 ± 0.05

ICP-MS presents its own difficulties in that Al, Si, and other elements are closely bound as oxides and need extreme acid digestion to free them for analysis (Anzano and Ruiz-Gil, 2005; Herner et al., 2006; Lu et al., 2003; Margui et al., 2005; Melaku et al., 2005). ICP-MS is not as precise as XRF for some key elements, including Si, P, S, and Cl, although it has lower detection limits for some of the transition metals. ICP-MS should be considered as complementary to, not as a replacement of, XRF.

6. Are metal oxides a significant source of interference in thermal-optical analysis (TOA) of PM10-2.5 for OC and EC given the large expected soil component? If so, how should this interference be addressed?

Metal oxides and catalysts such as NaCl, if present in significant amounts, could be a source of interference in thermal/optical analysis (Chow et al., 2001; 2006; Fung et al., 2004; Han et al., 2007a; 2007b; Lin and Friedlander, 1988a; 1988b; 1988c). Several effects occur: 1) mineral oxides provide oxygen during the inert-atmosphere analysis phased (Fung and Wright, 1990); 2) the color of the minerals interferes with transmittance and reflectance corrections (Fung et al., 2004); and 3) catalysts increase the EC oxidation rate (Lin and Friedlander, 1988a; 1988b). More systematic study is needed to quantify the uncertainties introduced by these effects and to determine thresholds below which they are tolerable.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

Sites with high PM_{10} and low $PM_{2.5}$ (e.g., Las Vegas, NV, during spring; Chow et al., 1999) or

low PM_{10} and high $PM_{2.5}$ (e.g., wintertime in central California; Chow et al., 2005) are good candidates to test the high and low $PM_{10-2.5}$ mass and composition, respectively. The $PM_{2.5}$ Ca from CSN sites can be used to select sites with the potential for high carbonate concentrations. A combination of sites that are influenced by paved and unpaved roads, agricultural activities, storage piles, and bioaerosols are ideal for pilot and long-term monitoring to assess the impacts from specific sources.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

While there is a desire to collocate PM_{10} and $PM_{2.5}$ at sites for source attribution and for assessment of health impacts, this may be an opportunity to modify the NCore sites to accommodate special needs of more source-oriented $PM_{10-2.5}$ sites.

References

Adams, F.C.; van Grieken, R.E. (1975). Absorption correction for x-ray fluorescence analysis of aerosol loaded filters. *Anal. Chem.*, **47:** 1767-1773.

Adams, F.C.; Billiet, J. (1976). Experimental verification of the x-ray absorption correction in aerosol loaded filters. *X-Ray Spectrometry*, **5**(4): 188.

Alexis, N.E.; Lay, J.C.; Zeman, K.; Bennett, W.E.; Peden, D.B.; Soukup, J.M.; Devlin, R.B.; Becker, S. (2006). Biological material on inhaled coarse fraction particulate matter activates airway phagocytes in vivo in healthy volunteers. *Journal of Allergy and Clinical Immunology*, **117**(6): 1396-1403.

Allen, G.A.; Oh, J.A.A.; Koutrakis, P.; Sioutas, C. (1999). Techniques for high-quality ambient coarse particle mass measurements. *J. Air Waste Manage. Assoc.*, **49**(PM): PM133-PM141.

Anzano, J.M.; Ruiz-Gil, M. (2005). Comparison of microwave acid digestion with the wet digestion and ashing methods for the determination of Fe, Mn, and Zn in food samples by flame AAS. *Atomic Spectroscopy*, **26**(1): 28-33.

Arp, H.P.H.; Schwarzenbach, R.P.; Goss, K.U. (2007). Equilibrium sorption of gaseous organic chemicals to fiber filters used for aerosol studies. *Atmos. Environ.*, **41:** 8241-8252.

Ashbaugh, L.L.; Eldred, R.A. (2004). Loss of particle nitrate from teflon sampling filters: Effects on measured gravimetric mass in California and in the IMPROVE Network. *J. Air Waste Manage. Assoc.*, **54**(1): 93-104.

Baldauf, R.W.; Wiener, R.W.; Heist, D.K. (2002). Methodology for siting ambient air monitors at the neighborhood scale. *J. Air Waste Manage. Assoc.*, **52**(12): 1433-1442.

Bauer, H.; Claeys, M.; Vermeylen, R.; Schueller, E.; Weinke, G.; Berger, A.; Puxbaum, H. (2008). Arabitol and mannitol as tracers for the quantification of airborne fungal spores. *Atmos. Environ.*, **42**(3): 588-593.

Berry, P.F.; Furuta, T.; Rhodes, J.R. (1969). Particle size effects in x-ray spectrometry. In *Advances in X-Ray Analysis*, Barrett, C. S., Ed.; Plenum Press: New York, NY, 612-632.

Boon, K.F.; Kiefert, L.; McTainsh, G.H. (1998). Organic matter content of rural dusts in Australia. *Atmos. Environ.*, **32**(16): 2817-2823.

Burton, R.M.; Lundgren, D.A. (1987). Wide-Range Aerosol Classifier - A size selective sampler for large particles. *Aerosol Sci. Technol.*, **6**(3): 289-301.

Burton, R.M.; Suh, H.H.; Koutrakis, P. (1996). Spatial variation in particulate concentrations within metropolitan Philadelphia. *Enivron. Sci. Technol.*, **30**(2): 400-407.

Cao, J.J.; Lee, S.C.; Zhang, X.Y.; Chow, J.C.; An, Z.S.; Ho, K.F.; Watson, J.G.; Fung, K.K.; Wang, Y.Q.; Shen, Z.X. (2005). Characterization of airborne carbonate over a site near Asian dust source regions during spring 2002 and its climatic and environmental significance. *J. Geophys. Res. -Atmospheres*, **110**(D03203): 1-8. doi:10.1029/2004JD005244.

Casuccio, G.S.; Janocko, P.B.; Lee, R.J.; Kelly, J.F.; Dattner, S.L.; Mgebroff, J.S. (1983). The use of computer controlled scanning electron microscopy in environmental studies. *J. Air Poll. Control Assoc.*, **33**(10): 937-943.

Chow, J.C.; Shortell, V.; Collins, J.F.; Watson, J.G.; Pace, T.G.; Burton, R.M. (1981). A neighborhood scale study of inhalable and fine suspended particulate matter source contributions to an industrial area in Philadelphia. Philadelphia, PA.

Chow, J.C.; Liu, C.S.; Cassmassi, J.C.; Watson, J.G.; Lu, Z.; Pritchett, L.C. (1992). A neighborhood-scale study of PM_{10} source contributions in Rubidoux, California. *Atmos. Environ.*, **26A**(4): 693-706.

Chow, J.C.; Fujita, E.M.; Watson, J.G.; Lu, Z.; Lawson, D.R.; Ashbaugh, L.L. (1994a). Evaluation of filter-based aerosol measurements during the 1987 Southern California Air Quality Study. *Environ. Mon. Assess.*, **30**(1): 49-80.

Chow, J.C.; Watson, J.G.; Houck, J.E.; Pritchett, L.C.; Rogers, C.F.; Frazier, C.A.; Egami, R.T.; Ball, B.M. (1994b). A laboratory resuspension chamber to measure fugitive dust size distributions and chemical compositions. *Atmos. Environ.*, **28**(21): 3463-3481.

Chow, J.C. (1995). Critical review: Measurement methods to determine compliance with ambient air quality standards for suspended particles. *J. Air Waste Manage. Assoc.*, **45**(5): 320-382.

Chow, J.C.; Watson, J.G.; Green, M.C.; Lowenthal, D.H.; DuBois, D.W.; Kohl, S.D.; Egami, R.T.; Gillies, J.A.; Rogers, C.F.; Frazier, C.A.; Cates, W. (1999). Middle- and neighborhood-scale variations of PM_{10} source contributions in Las Vegas, Nevada. *J. Air Waste Manage. Assoc.*, **49**(6): 641-654.

Chow, J.C.; Watson, J.G.; Green, M.C.; Lowenthal, D.H.; Bates, B.A.; Oslund, W.; Torres, G.

(2000). Cross-border transport and spatial variability of suspended particles in Mexicali and California's Imperial Valley. *Atmos. Environ.*, **34**(11): 1833-1843.

Chow, J.C.; Watson, J.G.; Crow, D.; Lowenthal, D.H.; Merrifield, T.M. (2001). Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.*, **34**(1): 23-34.

Chow, J.C.; Watson, J.G. (2002). $PM_{2.5}$ carbonate concentrations at regionally representative Interagency Monitoring of Protected Visual Environment sites. *J. Geophys. Res. - Atmospheres*, **107**(D21): ICC 6-1-ICC 6-9. doi: 10.1029/2001JD000574.

Chow, J.C.; Watson, J.G.; Edgerton, S.A.; Vega, E.; Ortiz, E. (2002a). Spatial differences in outdoor PM_{10} mass and aerosol composition in Mexico City. *J. Air Waste Manage. Assoc.*, **52**(4): 423-434.

Chow, J.C.; Watson, J.G.; Edgerton, S.A.; Vega, E. (2002b). Chemical composition of PM_{10} and $PM_{2.5}$ in Mexico City during winter 1997. *Sci. Total Environ.*, **287**(3): 177-201.

Chow, J.C.; Watson, J.G.; Ashbaugh, L.L.; Magliano, K.L. (2003). Similarities and differences in PM_{10} chemical source profiles for geological dust from the San Joaquin Valley, California. *Atmos. Environ.*, **37**(9-10): 1317-1340. doi: 10.1016/S1352-2310(02)01021-X.

Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; Magliano, K.L. (2005). Loss of PM2.5 nitrate from filter samples in central California. *J. Air Waste Manage. Assoc.*, **55**(8): 1158-1168.

Chow, J.C.; Watson, J.G.; Doraiswamy, P.; Chen, L.-W.A.; Sodeman, D.A.; Ho, S.S.H.; Kohl, S.D.; Trimble, D.L.; Voepel, H.; Fung, K.K. (2006). Climate change - Characterization of black carbon and organic carbon air pollution emissions and evaluation of measurement methods. Phase I: Method intercomparison. Volume I: Interim report. Report Number DRI Contract No. 04-307; prepared by Desert Research Institute, Reno, NV, for California Air Resources Board and the California Environmental Protection Agency, Sacramento, CA;

Chow, J.C.; Yu, J.Z.; Watson, J.G.; Ho, S.S.H.; Bohannan, T.L.; Hays, M.D.; Fung, K.K. (2007). The application of thermal methods for determining chemical composition of carbonaceous aerosols: A Review. *Journal of Environmental Science and Health-Part A*, **42**(11): 1521-1541.

Chow, J.C.; Doraiswamy, P.; Watson, J.G.; Chen, L.-W.A.; Ho, S.S.H.; Sodeman, D.A. (2008). Advances in integrated and continuous measurements for particle mass and chemical composition. *J. Air Waste Manage. Assoc.*, **58**(2): 141-163.

Criss, J.W. (1976). Particle size and composition effects in x-ray fluorescence analysis of pollution samples. *Anal. Chem.*, **48**(1): 179-186.

Dzubay, T.G.; Stevens, R.K. (1975). Ambient air analysis with dichotomous sampler and x-ray fluorescence spectrometer. *Enivron. Sci. Technol.*, **9**(7): 663-668.

Dzubay, T.G.; Nelson, R.O. (1975). Self absorption corrections for x-ray fluorescence analysis of aerosols. In *Advances in X-Ray Analysis, Vol. 18*, Pickles, W. L., Barrett, C. S., Newkirk, J. B., Rund, C. O., Eds.; Plenum Publishing Corporation: New York, NY, 619-

21

631.

Dzubay, T.G.; Stevens, R.K.; Peterson, C.M. (1977). Application of the dichotomous sampler to the characterization of ambient aerosols. In *X-ray Fluorescence Analysis of Environmental Samples*, Dzubay, T. G., Ed.; Ann Arbor Science Publishers Inc.: Ann Arbor, MI, 95-105.

Dzubay, T.G. (1980). Chemical element balance method applied to dichotomous sampler data. *Annals of the New York Academy of Sciences*, **338**: 126-144.

Edgerton, E.S.; Casuccio, G.S.; Saylor, R.D.; Lersch, T.L.; Hartsell, B.E.; Jansen, J.J.; Hansen, D.A. (2009). Measurements of OC and EC in Coarse Particulate Matter in the Southeastern United States. *J. Air Waste Manage. Assn.*, **59**: 78-90.

Ellis, E.C.; Farber, R.J.; Eatough, D.J. (1983). Formation of Coarse Particle Secondary Nitrate in the Los Angeles Basin. *Aerosol Sci. Technol.*, **2**: 176.

El Zanan, H.S.; Lowenthal, D.H.; Zielinska, B.; Chow, J.C.; Kumar, N.K. (2005). Determination of the organic aerosol mass to organic carbon ratio in IMPROVE samples. *Chemosphere*, **60**(4): 485-496.

El Zanan, H.S.; Zielinska, B.; Mazzoleni, L.R.; D.A. Hansen (2009). Analytical Determination of the Aerosol Organic Mass-to-Organic Carbon Ratio. *J. Air Waste Manage. Assn.*, **59**: 58-69.

Evans, J.S.; Ryan, P.B. (1983). Statistical uncertainties in aerosol mass concentrations measured by virtual impactors. *Aerosol Sci. Technol.*, **2**: 531-536.

Faust, G.T. (1950). Thermal analysis studies on carbonates I. Aragonite and calcite. *Am. Miner.*, **38**: 207-224.

Ferris, B.G., Jr.; Speizer, F.E.; Spengler, J.D.; Dockery, D.W.; Bishop, Y.M.M.; Wolfson, M.; Humble, C. (1979). Effects of sulfur oxides and respirable particles on human health. *Am. Rev. Respir. Dis.*, **120**: 767-779.

Fialho, P.; Hansen, A.D.A.; Honrath, R.E. (2005). Absorption coefficients by aerosols in remote areas: a new approach to decouple dust and black carbon absorption coefficients using seven-wavelength Aethalometer data. *J. Aerosol Sci.*, **36**(2): 267-282.

Fung, K.K.; Wright, B. (1990). Measurement of formaldehyde and acetaldehyde using 2,4-dinitrophenylhydrazine- impregnated cartridges during the Carbonaceous Species Methods Comparison Study. *Aerosol Sci. Technol.*, **12**: 44-48.

Fung, K.K.; Chow, J.C.; Chen, L.-W.A.; Chang, M.-C.O.; Watson, J.G. (2004). Evaluation of pyrolysis correction by reflectance and transmittance in thermal/optical OC/EC analysis techniques. In *Proceedings, Symposium on Air Quality Methods and Technology*, Air and Waste Management Association: Pittsburgh, PA, 10.4-1-10.4-10.

Goodman, A.L.; Underwood, G.M.; Grassian, V.H. (2000). A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles. *J. Geophys. Res.*,

105(D23): 29053-29064.

Grimm, H.; Eatough, D.J. (2009). Aerosol Measurement: The Use of Optical Light Scattering for the Determination of Particulate Size Distribution, and Particulate Mass, Including the Semi-Volatile Fraction. *J. Air Waste Manage. Assn.*, **59**: 101-107.

Grover, B.D.; Eatough, N.L.; Eatough, D.J.; Chow, J.C.; Watson, J.G.; Ambs, J.L.; Meyer, M.B.; Hopke, P.K.; Al-Horr, R.; Later, D.W.; Wilson, W.E. (2006). Measurements of both non-volatile and semi-volatile fractions of fine particulate matter in Fresno, CA. *Aerosol Sci. Technol.*, **40**: 811-826.

Gwaze, P.; Annegarn, H.J.; Huth, J.; Helas, G. (2007). Comparison of particle sizes determined with impactor, AFM and SEM. *Atmospheric Research*, **86**(2): 93-104.

Han, Y.M.; Cao, J.J.; Chow, J.C.; Watson, J.G.; An, Z.; Jin, Z.D.; Fung, K.K.; Liu, S. (2007a). Evaluation of the thermal/optical reflectance method for discrimination between char- and soot-EC. *Chemosphere*, **69**(4): 569-574.

Han, Y.M.; Cao, J.J.; An, Z.; Chow, J.C.; Watson, J.G.; Jin, Z.D.; Fung, K.K.; Liu, S. (2007b). Evaluation of the thermal/optical reflectance method for quantification of elemental carbon in sediments. *Chemosphere*, **69**(4): 526-533.

Hays, M.D.; Lavrich, R.J. (2007). Developments in direct thermal extraction gas chromatography-mass spectrometry of fine aerosols. *Trac-Trends in Analytical Chemistry*, **26**(2): 88-102.

Heederik, D. (2003). Biological Agents Monitoring and Evaluation of Bioaerosol Exposure. In *International Modern Industrial Hygiene, Vol. 2; Biological Aspects*, Perkins, J. L., Ed.; American Conference of Governmental Industrial Hygiensist: Cincinnati, OH, 293-327.

Heinrich, J.; Pitz, M.; Bischof, W.; Krug, N.; Borm, P.J.A. (2003). Endotoxin in fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particle mass of ambient aerosols. A temporo-spatial analysis. *Atmos. Environ.*, **37**: 3659-3667.

Herner, J.D.; Green, P.G.; Kleeman, M.J. (2006). Measuring the trace elemental composition of size-resolved airborne particles. *Environ. Sci. Technol.*, **40**(6): 1925-1933.

Ho, S.S.H.; Yu, J.Z. (2004). In-injection port thermal desorption and subsequent gas chromatography-mass spectrometric analysis of polycyclic aromatic hydrocarbons and *n*-alkanes in atmospheric aerosol samples. *J. Chromatogr. A*, **1059**(1-2): 121-129.

Ho, S.S.H.; Yu, J.Z.; Chow, J.C.; Zielinska, B.; Watson, J.G.; Sit, E.H.L.; Schauer, J.J. (2008). Evaluation of an in-injection port thermal desorption-gas chromatography/mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples. *Journal of Chromatography A*, **1200**(2): 217-227. doi:10.1016/j.chroma.2008.05.056.

Hodzic, A.; Bessagnet, B.; Vautard, R. (2006). A model evaluation of coarse-mode nitrate heterogeneous formation on dust particles. *Atmos. Environ.*, **40**(22): 4158-4171.

Hunter, C.B.; Rhodes, J.R. (1972). Particle size effects in x-ray emission analysis: Formulae for

continuous size distribution. *X-Ray Spectrometry*, **1**: 107-111.

Jackson, T.L.; Hampel, J. (1992). Size effects in the energy-dispersive x-ray fluorescence (EDXRF) analysis of archaeological obsidian artifacts. 23 March 92 A.D.; Los Angeles, CA.

John, W.; Wall, S.M.; Ondo, J.L. (1988). A new method for nitric acid and nitrate aerosol measurement using the dichotomous sampler. *Atmos. Environ.*, **22**(8): 1627-1635.

Kenny, L.C.; Gussman, R.A. (2000). A direct approach to the design of cyclones for aerosol-monitoring applications. *J. Aerosol Sci.*, **31**(12): 1407-1420.

Kenny, L.C.; Gussman, R.A.; Meyer, M.B. (2000). Development of a sharp-cut cyclone for ambient aerosol monitoring applications. *Aerosol Sci. Technol.*, **32**(4): 338-358.

Kerley, S.J.; Jarvis, S.C. (1997). Variation in ^{15}N natural abundance of soil, humic fractions and plant materials in a disturbed and an undisturbed grassland. *Biology and Fertility of Soils*, **24**(2): 147-152.

Keywood, M.D.; Ayers, G.P.; Gras, J.L.; Gillett, R.W.; Cohen, D. (1999). An evaluation of PM_{10} and $PM_{2.5}$ size selective inlet performance using ambient aerosol. *Aerosol Sci. Technol.*, **30**(4): 401-407.

Kim, K.W.; He, Z.S.; Kim, Y.J. (2004). Physicochemical characteristics and radiative properties of Asian dust particles observed at Kwangju, Korea, during the 2001 ACE-Asia intensive observation period. *J. Geophys. Res. -Atmospheres*, **109**(D19).

Kim, K.W. (2007). Physico-chemical characteristics of visibility impairment by airborne pollen in an urban area. *Atmos. Environ.*, **41**(17): 3565-3576.

Krueger, B.J.; Grassian, V.H.; Cowin, J.P.; Laskin, A. (2004). Heterogeneous chemistry of individual mineral dust particles from different dust source regions: the importance of particle mineralogy. *Atmos. Environ.*, **38**(36): 6253-6261.

Labban, R.; Veranth, J.M.; Watson, J.G.; Chow, J.C. (2006). Feasibility of soil dust source apportionment by the pyrolysis-gas chromatography/mass spectrometry method. *J. Air Waste Manage. Assoc.*, **56**(9): 1230-1242.

Laskin, A.; Wietsma, T.W.; Krueger, B.J.; Grassian, V.H. (2005). Heterogeneous chemistry of individual mineral dust particles with nitric acid: A combined CCSEM/EDX, ESEM, and ICP-MS study. *J. Geophys. Res. -Atmospheres*, **110**(D10): D10208. doi:10.1029/2004JD005206.

Lee, A.K.Y.; Lau, A.P.S.; Cheng, J.Y.W.; Fang, M.; Chan, C.K. (2007). Source identification analysis for the airborne bacteria and fungi using a biomarker approach. *Atmos. Environ.*, **41**(13): 2831-2843.

Li, W.-W.; Orquiz, R.; Garcia, J.H.; Espino, T.T.; Pingitore, N.E.; Gardea-Torresdey, J.; Chow, J.C.; Watson, J.G. (2001). Analysis of temporal and spatial dichotomous PM air samples in the El Paso-Cd. Juarez air quality basin. *J. Air Waste Manage. Assoc.*, **51**(11): 1551-1560.

Lin, C.; Friedlander, S.K. (1988a). Soot oxidation in fibrous filters. 1. Deposit structure and reaction mechanisms. *Langmuir*, **4**(4): 891-898.

Lin, C.; Friedlander, S.K. (1988b). Soot oxidation in fibrous filters. 2. Effects of temperature, oxygen partial pressure, and sodium additives. *Langmuir*, **4**(4): 898-903.

Lin, C.I.; Friedlander, S.K. (1988c). A note on the use of glass fiber filters in the thermal analysis of carbon containing aerosols. *Atmos. Environ.*, **22**(3): 605-607.

Lin, J.J.; Tai, H.S. (2001). Concentrations and distributions of carbonaceous species in ambient particles in Kaohsiung City, Taiwan. *Atmos. Environ.*, **35**(15): 2627-2636.

Lin, J.J. (2002). Characterization of water-soluble ion species in urban ambient particles. *Environ. Int.*, **28**(1-2): 55-61.

Lu, A.; Zhang, S.; Shan, X.; Wang, S.; Wang, Z. (2003). Application of microwave extraction for the evaluation of bioavailability of rare earth elements in soils. *Chemosphere*, **53**(9): 1067-1075.

Lundgren, D.A.; Hausknecht, B.J.; Burton, R.M. (1984). Large particle size distribution in 5 United States cities and the effect on a new ambient particulate matter standard (PM_{10}). *Aerosol Sci. Technol.*, **3**(4): 467-473.

Lundgren, D.A.; Burton, R.M. (1995). Effect of particle size distribution on the cut point between fine and coarse ambient mass fractions. *Inhal. Toxicol.*, **7**(1): 131-148.

Magliano, K.L. (1988). Level 1 PM_{10} assessment in a California air basin. In *Transactions, PM_{10}: Implementation of Standards*, Mathai, C. V., Stonefield, D. H., Eds.; Air Pollution Control Association: Pittsburgh, PA, 508-517.

Mamane, Y.; Mehler, M. (1987). On the nature of nitrate particles in a coastal urban area. *Atmos. Environ.*, **21**(9): 1989-1994.

Mamane, Y.; Dzubay, T.G. (1990). Dichotomous samplers modified for use with electron microscopy. *Aerosol Sci. Technol.*, **13**: 241-248.

Mamane, Y.; Gottlieb, J. (1992). Nitrate formation on sea-salt and mineral particles - A single particle approach. *Atmos. Environ.*, **26A**(9): 1763-1769.

Margui, E.; Queralt, I.; Carvalho, M.L.; Hidalgo, M. (2005). Comparison of EDXRF and ICP-OES after microwave digestion for element determination in plant specimens from an abandoned mining area. *Anal. Chim. Acta.*, **549**(1-2): 197-204.

Mathai, C.V.; Watson, J.G.; Rogers, C.F.; Chow, J.C.; Tombach, I.H.; Zwicker, J.O.; Cahill, T.A.; Feeney, P.J.; Eldred, R.A.; Pitchford, M.L.; Mueller, P.K. (1990). Intercomparison of ambient aerosol samplers used in western visibility and air quality studies. *Enivron. Sci. Technol.*, **24**(7): 1090-1099.

McDow, S.R. (1986). The effects of sampling procedures on organic aerosol measurement. Oregon Graduate Center.

Melaku, S.; Dams, R.; Moens, L. (2005). Determination of trace elements in agricultural soil samples by inductively coupled plasma-mass spectrometry: Microwave acid digestion

versus aqua regia extraction. *Anal. Chim. Acta.*, **543**(1-2): 117-123.

Menetrez, M.Y.; Foarde, K.K.; Ensor, D.S. (2000). Fine Biological PM: Understanding Size Fration Transport and Exposure Potential (Extended Abstract). In *The Air & Waste Management Association Specialty Conference, PM2000: Particulate Matter and Health - The Scientific Basis for Regulatory Decision-making*, Proceedings of the The Air & Waste Management Association Specialty Conference, PM2000: Particulate Matter and Health - The Scientific Basis for Regulatory Decision-making.

Menetrez, M.Y.; Foarde, K.K.; Ensor, D.S. (2001). An analytical method for the measurement of nonviable bioaerosols. *J. Air Waste Manage. Assoc.*, **51**(10): 1436-1442.

Menetrez, M.Y.; Foarde, K.K.; Dean, T.R.; Betancourt, D.A.; Moore, S.A. (2007a). An evaluation of the protein mass of particulate matter. *Atmos. Environ.*, **41**: 8264-8274.

Menetrez, M.Y.; Foarde, K.K.; Esch, R.K.; Dean, T.R.; Betancourt, D.A.; Moore, S.A.; Svendsen, E.R.; Yeatts, K. (2007b). *Aerosol Sci.Technol.* **41**(9): 884-893.

Motallebi, N.; Taylor, C.A.; Croes, B.E. (2003a). Particulate matter in California: Part 2 - Spatial, temporal, and compositional patterns of $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10}. *J. Air Waste Manage. Assoc.*, **53**(12): 1517-1530.

Motallebi, N.; Taylor, C.A.; Turkiewicz, K.; Croes, B.E. (2003b). Particulate matter in California: Part 1 - Intercomparison of several $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} monitoring networks. *J. Air Waste Manage. Assoc.*, **53**(12): 1509-1516.

Motallebi, N.; Tran, H.; Larsen, L.C.; Croes, B.E. (2003c). Day-of-week patterns of particulate matter and its chemical components at selected sites in California. *J. Air Waste Manage. Assoc.*, **53**(7): 876-888.

Murray, J.A.; Fischer, H.C.; Shade, R.W. (1951). Report on fundamental research fellowship at the Massachusetts Institute of Technology 1950-51. *Proceedings, National Lime Association*, **49**95-116.

Noll, J.; Birch, M.E. (2008). Effects of sampling artifacts on occupational samples of diesel particulate matter. *Environ. Sci. Technol.*, **42**(14): 5223-5228.

Omar, N.Y.M.J.; Abas, M.R.B.; Ketuly, K.A.; Tahir, N.M. (2002). Concentrations of PAHs in atmospheric particles (PM_{10}) and roadside soil particles collected in Kuala Lumpur, Malaysia. *Atmos. Environ.*, **36**(2): 247-254.

Ooki, A.; Uematsu, M. (2005). Chemical interactions between mineral dust particles and acid gases during Asian dust events. *J. Geophys. Res. -Atmospheres*, **110**(D3): ISI:000226901400002.

Ott, D.K.; Cyrs, W.; Peters, T.A. (2008). Passive measurement of coarse particulate matter, $PM_{10-2.5}$. *J. Aerosol Sci.*, **39**(2): 156-167.

Peters, T.M.; Ott, D.; O'Shaughnessy, P.T. (2006). Comparison of the Grimm 1.108 and 1.109 portable aerosol spectrometer to the TSI 3321 aerodynamic particle sizer for dry particles. *Ann. Occup. Hyg.*, **50**(8): 843-850.

Pettijohn, F.J. (1949). *Sedimentary Rocks, Second Edition*. Harper & Brothers: New York, NY.

Pilinis, C.; Seinfeld, J.H. (1987). Continued development of a general equilibrium model for inorganic multicomponent atmospheric aerosols. *Atmos. Environ.*, **21**(11): 2453-2466.

Rashid, M.; Griffiths, R.F. (1993). Ambient K, S, and Si in fine and coarse aerosols of Kuala Lumpur, Malaysia. *J. Aerosol Sci.*, **24**(1): S5-S6.

Rhodes, J.R.; Hunter, C.B. (1972). Particle size effects in X-ray emission analysis: simplified formulae for certain practical cases. *X-Ray Spectrometry*, **1**(3): 113-117.

Rogge, W.F.; Medeiros, P.M.; Simoneit, B.R.T. (2006). Organic marker compounds for surface soil and fugitive dust from open lot dairies and cattle feedlots. *Atmos. Environ.*, **40**(1): 27-49.

Rogge, W.F.; Medeiros, P.M.; Simoneit, B.R.T. (2007). Organic marker compounds in surface soils of crop fields from the San Joaquin Valley fugitive dust characterization study. *Atmos. Environ.*, **41**: 8183-8204.

Russell, A.G.; Cass, G.R. (1984). Acquisition of regional air quality model validation data for nitrate, sulfate, ammonium ion and their precursors. *Atmos. Environ.*, **18**(9): 1815-1827.

Schulten, H.R.; Leinweber, P. (2000). New insights into organic-mineral particles: composition, properties and models of molecular structure. *Biology and Fertility of Soils*, **30**(5-6): 399-432.

Schulze, A.; van Strien, R.; Ehrenstein, V.; Schierl, R.; Kuchenhoff, H.; Radon, K. (2006). Ambient Endotoxin Level in an Area with Intensive Livestock Production. *Ann Agric Environ Med*, **13**: 87-91.

Sewell, D.A.; Love, G.; Scott, V.D. (1985). Universal correction procedure for electron-probe microanalysis: II. The absorption correction. *J. Phys. D. App. Phys.*, **18**: 1245-1267.

Simoneit, B.R.T.; Elias, V.O.; Kobayashi, M.; Kawamura, K.; Rushdi, A.I.; Medeiros, P.M.; Rogge, W.F.; Didyk, B.M. (2004). Sugars - Dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. *Environ. Sci. Technol.*, **38**(22): 5939-5949. ISI:000225272100018.

Solomon, P.A.; Fall, T.; Salmon, L.G.; Cass, G.R.; Gray, H.A.; Davidson, A. (1989). Chemical characteristics of PM_{10} aerosols collected in the Los Angeles area. *J. Air Poll. Control Assoc.*, **39**(2): 154-163.

Song, X.H.; Hopke, P.K.; Bruns, M.A.; Graham, K.; Scow, K. (1999). Pattern recognition of soil samples based on the microbial fatty acid contents. *Environ. Sci. Technol.*, **33**(20): 3524-3530.

Spengler, J.D.; Thurston, G.D. (1983). Mass and elemental composition of fine and coarse particles in six U.S. cities. *JAPCA*, **33**(12): 1162-1171.

Spengler, J.D.; Duffy, C.P.; Letz, R.; Tibbitts, T.W.; Ferris, B.G., Jr. (1983). Nitrogen dioxide inside and outside 137 homes and implications for ambient air quality standards and health effects research. *Enivron. Sci. Technol.*, **17**(3): 164-168.

27

Sprovieri, F.; Pirrone, N. (2008). Particle size distributions and elemental composition of atmospheric particulate matter in southern Italy. *J. Air Waste Manage. Assoc.*, **58**(6): 797-805.

Steerenberg, P.A.; Bischoff, E.W.M.A.; de Klerk, A.; Verlaan, A.P.J.; Jongbloets, L.M.N.; van Loveren, H.; Opperhuizen, A.; Zomer, G.; Heisterkamp, S.H.; Hady, M.; Spieksma, F.T.M.; Fischer, P.H.; Dormans, J.A.M.A.; van Amsterdam, J.G.C. (2003). Acute effect of air pollution on respiratory complaints, exhaled NO and biomarkers in nasal lavages of allergic children during the pollen season. *Int. Arch. Allergy Immunol.*, **131**(2): 127-137.

Targonski, P.; Persky, V.; Rameskirshan, V. (1995). Effect of Environmental Molds on Risk of Death from Asthma During the Pollen Season. *J. Allerg. Clin. Immunol.*, **95**: 955-961.

Teikari, M.; Linnainmaa, M.; Laitinen, J.; Kalliokoski, P.; Vincent, J.; Tiita, P.; Raunemaa, T. (2003). Laboratory and field testing of particle size-selective sampling methods for mineral dusts. *AIHA Journal*, **64**(3): 312-318.

Thomsen, M.; Lassen, P.; Dobel, S.; Hansen, P.E.; Carlsen, L.; Mogensen, B.B. (2002). Characterization of humic materials of different origin: A multivariate approach for quantifying the latent properties of dissolved organic matter. *Chemosphere*, **49**(10): 1327-1337. doi:10.1016/S0045-6535(02)00335-1.

Thurston, G.D.; Spengler, J.D. (1985). A multivariate assessment of meteorological influences on inhalable particle source impacts. *Journal of Climatology and Applied Meterology*, **24**: 1245-1256.

U.S. EPA (2006). Multi-Site Evaluations of Candidate Methodologies for Determining Coarse Particulate Matter ($PM_{10-2.5}$): August 2005 Updated Report Regarding Second-Generation and New $PM_{10-2.5}$ Samplers. Report Number EPA-600/R-06/093; prepared by U.S. EPA, Research Triangle Park, NC,

U.S.EPA (2008). Method 5 - Particulate Matter (PM). prepared by U.S. Environmental Protection Agency, Research Triangle Park, NC, http://www.epa.gov/ttn/emc/methods/method5.html

Umann, B.; Arnold, F.; Schaal, C.; Hanke, M.; Uecker, J.; Aufmhoff, H.; Balkanski, Y.; van Dingenen, R. (2005). Interaction of mineral dust with gas phase nitric acid and sulfur dioxide during the MINATROC II field campaign: First estimate of the uptake coefficient gamma(HNO3) from atmospheric data. *J. Geophys. Res. -Atmospheres*, **110**(D22): ISI:000233936200002.

Underwood, G.M.; Song, C.H.; Phadnis, M.; Carmichael, G.R.; Grassian, V.H. (2001). Heterogeneous reactions of NO_2 and HNO_3 on oxides and mineral dust: A combined laboratory and modeling study. *J. Geophys. Res.*, **106**(D16): 18055-18066.

VanCuren, R.A.; Cahill, T.A. (2002). Asian aerosols in North America: Frequency and concentration of fine dust. *J. Geophys. Res.*, **197**(D24): AAC 19-1-AAC 19-16. doi:10.1029/2002JD002204.

VanCuren, R.A. (2003). Asian aerosols in North America: Extracting the chemical composition and mass concentration of the Asian continental aerosol plume from long-term aerosol

records in the western United States. *J. Geophys. Res.*, **108**(D20): ACH 1-1-ACH 1-16. doi:10.1029/2003JD003459.

Wagman, J.; Miller, J.L.; Griffin, R.J. (1978). Verification of a particle size correction method for x-ray fluorescence spectrometric analysis of environmental samples. *Anal. Chem.*, **50**(1): 37-39.

Watson, J.G.; Chow, J.C.; Shah, J.J. (1981). Analysis of inhalable and fine particulate matter measurements. Report Number EPA-450/4-81-035; prepared by U.S. Environmental Protection Agency, Research Triangle Park, NC,

Watson, J.G.; Chow, J.C.; Shah, J.J.; Pace, T.G. (1983). The effect of sampling inlets on the PM_{10} and PM_{15} to TSP concentration ratios. *J. Air Poll. Control Assoc.*, **33**(2): 114-119.

Watson, J.G.; Chow, J.C.; Lurmann, F.W.; Musarra, S. (1994). Ammonium nitrate, nitric acid, and ammonia equilibrium in wintertime Phoenix, Arizona. *J. Air Waste Manage. Assoc.*, **44**(4): 405-412.

Watson, J.G.; Turpin, B.J.; Chow, J.C. (2001). The measurement process: Precision, accuracy, and validity. In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants, Ninth Edition*, 9th; Cohen, B. S., McCammon, C. S. J., Eds.; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 201-216.

Watson, J.G. (2002). Visibility: Science and regulation. *J. Air Waste Manage. Assoc.*, **52**(6): 628-713.

Watson, J.G.; Chow, J.C.; Chen, L.-W.A.; Kohl, S.D. (2007). Non-destructive XRF and SEM analyses on beta attenuation filters for elemental concentrations at the Craig Road monitor. prepared by Desert Research Institute, Reno, NV, for Clark County Department of Air Quality and Environmental Management, Las Vegas, NV;

Watson, J.G.; Chow, J.C.; Chen, L.-W.A.; Kohl, S.D.; Tropp, R.J.; Trimble, D.L.; Chancellor, S.; Sodeman, D.A.; Ho, S.S.H. (2008). Assessment of carbon sampling artifacts in the IMPROVE, STN/CSN, and SEARCH networks. prepared by Desert Research Institute, Reno, NV.
http://www.epa.gov/air/airtrends/specialstudies/20080822_sampling_artifact_rev.pdf

Watson, J.G.; Chow, J.C.; Chen, L.W.A. (2009). Methods to assess carbonaceous aerosol sampling artifacts for IMPROVE and other long-term networks. *J. Air Waste Manage. Assoc.*, accepted.

Webb, T.L.; Krüger, J.E. (1970). Carbonates. In *Differential Thermal Analysis Vol. 1 - Fundamental Aspects*, MacKenzie, R. C., Ed.; Academic Press: London, 303-341.

Wedding, J.B.; Carney, T.C. (1983). A quantitative technique for determining the impact of non-ideal ambient sampler inlets on the collected mass. *Atmos. Environ.*, **17**: 873-882.

Witz, S.; Smith, T.B.; Shu, M.; Moore, A.B. (1982). A comparison of mass, lead, sulfate and nitrate concentrations in a field study using dichotomous, size-selective and standard Hi-Vol samplers. *J. Air Poll. Control Assoc.*, **32**(3): 276-278.

Wu, P.M.; Okada, K. (1994). Nature of coarse nitrate particles in the atmosphere - A single

particle approach. *Atmos. Environ.*, **28**(12): 2053-2060.

Yang, H.; Yu, J.Z.; Ho, S.S.H.; Xu, J.H.; Wu, W.S.; Wan, C.H.; Wang, X.D.; Wang, X.R.; Wang, L.S. (2005). The chemical composition of inorganic and carbonaceous materials in $PM_{2.5}$ in Nanjing, China. *Atmos. Environ.*, **39**(20): 3735-3749.

Zhao, Y.C.; Zhang, J.Y.; Sun, J.M.; Bai, X.F.; Zheng, C.G. (2006). Mineralogy, chemical composition, and microstructure of ferrospheres in fly ashes from coal combustion. *Energy & Fuels*, **20**(4): 1490-1497.

30

Mr. Bart Croes

These comments also reflect input from California Air Resources Board (ARB) staff responsible for implementing U.S. EPA monitoring requirements and using the data in source apportionment and health studies.

$PM_{10-2.5}$ Speciation Measurement

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

Not that I am aware.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

A dichotomous sampler would be a superior choice. While California has dismantled its 20-site network that operated from 1983 to 2001 (due to resource constraints once the $PM_{2.5}$ FRM network was deployed), the data are in reasonable agreement for $PM_{2.5}$ and PM_{10} (Motallebi, et al., 2003a) which has allowed us to determine long-term PM trends (Motallebi, et al., 2003b) and perform particle pollution assessments in areas of California that exceed state and federal ambient air quality standards (Motallebi, 1999; Motallebi and Dolislager, 1999; Motallebi, et al., 2003bc).

I understand the concerns expressed by Delbert Eatough and Peter McMurry, but PM-coarse speciation by difference should also be considered. The approach is to continue use of the MetOne SASS sampler with a 2.5-μm cut point for ions and metals, add a 10-μm cut point for ions and metals, and calculate PM-coarse species by difference. Even though the flow is lower (6.7 Lpm) we have found in the California network that we always have sufficient material for accurate analyses (few species < LOD), although that may not be the case for other parts of the country. This approach is economical because the standard SASS has three flow controlled channels and two orifice channels. To implement this proposal would be to upgrade one orifice channel to active flow control.

Total, organic and elemental carbon is sampled by the URG 3000N for $PM_{2.5}$. To implement the carbon speciation by difference would require a second URG with a 10-μm cut point.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

31

Any potential artifacts would be consistent with the $PM_{2.5}$ speciation program per the difference approach described above.

4. The current and most widely used PM2.5 speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (Lpm) which is significantly lower than either the FRM for PM10-2.5 mass or the dichotomous sampler (16.7 Lpm). If this sampler was configured for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

In California, it has not been problematic with the PM2.5 speciation program except with elemental carbon, which has been switched to the URG 3000N sampler. We've found measured SASS mass compares well with measured FRM mass.

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

Yes, California has an extensive dataset that confirms there is sufficient mass for trace metal speciation (Motallebi, et al., 2003a).

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important PM10-2.5 species or components missing from this list? Are there important analysis methods missing from this list?

Even though it's not explicitly mentioned, I assume sulfur will be included in the elemental analyses (at minimum it provides a cross check of sulfate ion by IC).

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

Nitrate and ammonium are always important. At least in Los Angeles, coarse particle nitrate appears to be significant, but it is usually in the form of sodium nitrate.

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

I defer to others.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

I defer to others, but we understand these correction factors to be theoretical and crude and that there is no consensus on their use. In California, we do not use any correction factors for $PM_{2.5}$ elemental analyses. We understand that at most these correction factors would be no greater than 10%, and possibly inconsequential.

5. 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 so, how should this interference be addressed?

I defer to others.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

Sites with high PM_{10} and low $PM_{2.5}$ suggest areas dominated by wind blown dust. If the source is obvious for a particular site, I question the value (and diversion of resources) for investigating an air quality issue that may already be well understood. Because of higher deposition rates for coarse particles, a $PM_{10-2.5}$ monitoring site is representative of sources relatively nearby, so it should be obvious if a single source (e.g., windblown dust, coal pile, tire and brake wear) is predominant.

The pilot monitoring study should include a southern California site that is high in both PM_{10} and $PM_{2.5}$ with potential for significant coarse particle contributions from sources other than wind-blown dust, such as coarse particle nitrate. Other sites for pilot studies and long-term monitoring can be selected based on an analysis of existing PM_{10} and $PM_{2.5}$ network data to identify areas (using the difference method) that are high in both $PM_{10-2.5}$ and $PM_{2.5}$.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

The Health Effects Institute or other representations of the air pollution epidemiology community should be consulted as to where year-round PM-coarse measurements would be useful for epidemiologic cohort studies. Otherwise, I agree with USEPA staff that the candidate NCore site may not be the best choice for $PM_{10-2.5}$ speciation since the highest concentrations of $PM_{2.5}$ and $PM_{10-2.5}$ are usually not collocated. A study by ARB staff (VanCuren, 1999) concludes

that, in winter, most coarse (PM10-2.5) particles collected are less than 2 hours old, and even on days that are not truly "stagnant," samplers are very strongly influenced by their immediate surroundings (distances less than 10 km), and only weakly influenced by regional emissions. The implications for interpretation of sample analyses are as follows: (1) Typical PM sampling networks are unlikely to represent regional conditions; (2) Similarity of samples in time and space between widely separated samplers probably arises from sampling analogous local environments rather than a uniformly mixed regional air mass; (3) Even weak sources near a sampler will prevent regionally representative samples, so that "background" specification in models can be strongly skewed by misapplication of sampler data; (4) Source-receptor relationships within a single modeling grid cell can cause measured and modeled source impacts at a sampler to diverge by orders of magnitude, even for grid cells as small as 1 km; and (5) Differential deposition of coarse and fine particles will skew source apportionment by chemical tracers unless the tracers and the source emissions have the same size distribution.

VanCuren, T. (1999) Spatial Factors Influencing Winter Primary Particle Sampling and Interpretation. *J. Air Waste Manage. Assoc.*, **49:** PM-3-15.

Motallebi, N. (1999) Wintertime $PM_{2.5}$ and PM_{10} Source Apportionment at Sacramento, California. *J. Air Waste Manage. Assoc.*, **49:** PM-25-34.

Motallebi, N. and L. J. Dolislager (1999) Characterization of Particulate Matter in California. *J. Air Waste Manage. Assoc.*, **49:** PM-45-56.

Motallebi, N., C. A. Taylor, Jr., K. Turkiewicz, and B. E. Croes (2003a) Particulate matter in California: Part 1 – Intercomparison of several $PM_{2.5}$, PM_{10-25}, and PM_{10} monitoring networks. *J. Air Waste Manage. Assoc.*, **53:** 1509-1516.

Motallebi, N., C. A. Taylor, Jr., and B. E. Croes (2003b) Particulate matter in California: Part 2 – Spatial, temporal, and compositional patterns of $PM_{2.5}$, PM_{10-25}, and PM_{10}. *J. Air Waste Manage. Assoc.*, **53:** 1517-1530.

Motallebi, N., H. Tran, B. E. Croes, and L. C. Larsen (2003c) Day-of-week patterns of PM and its chemical components at selected sites in California. *J. Air Waste Manage. Assoc.*, **53:** 867-888.

Dr. Kenneth Demerjian

$PM_{10-2.5}$ Speciation Measurement

1. *Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?*

See items 2 and 3 below.

2. *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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?*

Run two (2) EC – OC semi-continuous (hourly average) measurements outfitted with PM_{10} and $PM_{2.5}$ inlets respectively. Although this measurement is not totally free of artifacts, volatilization losses of OC should be significantly less than those resulting from 24-hr average sampling.

3. *What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?*

Evaluate OC artifacts by comparing the 24-hr OC filter based measurements with the integrated semi-continuous measurements recommended in (2.) above.

4. *The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?*

The lower flow will likely impact the precision and accuracy of the MetOne SASS as compared to $PM_{10-2.5}$, but why speculate, perform the field test experiments!

5. *Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?*

Survey the concentration ranges from existing CSN measurement networks and calculate the expected reductions resulting from flow differences in the dichotomous sampler. If the range in chemical speciation concentrations estimated for these adjusted flows remain within the detection limits of the analytical methods, case closed. If not, you will need to consider other options.

35

$PM_{10-2.5}$ Species or Components

1. *Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?*

The compiled list is reasonable for the majority of contributing sources to $PM_{10-2.5}$. There is always the possibility of a unique PM coarse source whose chemical composition is not on this list and would require the application of species specific analytical technique.

2. *In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?*

The measurement of nitrate and ammonium ions is important and the measurement technique requires the application of appropriate denuders.

3. *The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?*

SEM analyses are very labor intensive and not very quantitative. I would suggest a plot study should be carried out to demonstrate its potential utility in this application.

4. *Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?*

Absorption correction factors are likely to be variable and only reproducible in controlled environments. Consider the application of ICP/MS analytical technique.

5. *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 so, how should this interference be addressed?*

This is an interesting research question that requires an investment of resources to study the phenomena in the laboratory and the field.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation?

Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

The majority (if not all) of urban NCore monitoring sites are not deployed in locations to adequately sample $PM_{10-2.5}$ exposures. The likely source regions impacting $PM_{10-2.5}$ exposures in urban areas are traffic related and associated with populations situate within 500m of major highways.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

The design criteria for locating urban NCore level 2 monitoring sites must consider measurements in neighborhoods in proximity (e.g. within 500m) of significant traffic sources (major highways). Estimates of population with 500m of major roadways within metropolitan areas is one metric for determining the distribution of traffic impacted vs. central urban monitors to be deployed. One in three urban monitors deployed to characterize exposures within traffic impacted neighborhoods would be a reasonable starting point.

37

Dr. Delbert J. Eatough

I. General comments:

The speciation of coarse particles being undertaken by EPA as part of the revisions to the Ambient Air Monitoring Regulations in connection with the EPA final rule to revise the NAAQS for PM is a new undertaking for the agency. EPA is to be commended for the commitment to speciation of the $PM_{10-2.5}$ (coarse) particle fraction of PM_{10}, even though a NAAQS for coarse particles has not been set by the agency. I encourage the agency to not be limited to the thinking of the past 30+ years with respect to monitoring and speciation of fine particles. The speciation program for fine particles has been necessarily tied to the $PM_{2.5}$ sampling FRM because of the requirement to understand the speciation of $PM_{2.5}$ as traditionally sampled by conventional filter pack techniques, the basis of the standard. This has lead to a disparity between our understanding of sampling of fine particles, the optimization of the understanding of components of fine particles which are not well sampled by the FRM and any subsequent improvement in our understanding of the etiology of health effects related to fine particles to the extent that the mass and composition have been inaccurately measured by these techniques. A coarse particle standard does not yet exist. The health effects which may be associated with exposure to coarse particles are not currently well understood. Therefore, I recommend that EPA include important aspects of improved PM monitoring methods in the coarse particle speciation program to allow for a better tie of all components to any observed health effects exacerbated by exposure to coarse particles.

While many components of coarse particles will be unaffected by the sampling protocols used, this is not true for all components. The components listed on slide 9 in the presentation by Joann Rice represents the current focus of EPA in this sampling effort. Most of the components listed in that slide will not be significantly affect by the sampling methods used. However, this is not true for Ammonium and nitrate ions, nor for the semi-volatile fraction of organic C. Both are components which need to be well understood. Inattention to sampling artifacts in the program will bias the results towards those components which are not affected by the sampling method. There are at least two areas where the sampling methods used will significantly affect the obtained outcome.

In the review of these two areas in the material to follow, I have focused mainly on our past work. I have done this because of the short time available to provide comments and because this work is pertinent to the charge questions asked by EPA. However, it should be recognized that the effects noted below have been observed by several investigators.

II. Alteration of the Mass and Chemical Composition of Coarse Particles During Sampling by Mixing Both Fine and Coarse Particles Together.

The origins of fine and coarse particles in the atmosphere are very different, and as a result their compositions are very different (U.S. EPA 2004). Fine particles are dominated by primary and secondary material associated with anthropogenic emissions. Ammonium sulfate, ammonium nitrate, organic material and elemental carbon are major components of these fine particles. If the aerosol is acidic, the concentrations of ammonium nitrate are low. In contrast, coarse particles are dominated by crustal material, some biogenic material and materials formed from abrasive action, e.g. tire debris, etc. Sulfate concentrations are generally very low. Nitrate can be present in these fine particles, but is generally there are a result of the conversion of sea salt to sodium nitrate by the reaction with nitric acid (e.g., Ellis et al., 1983).

$$NaCl(s) + HNO_3(g) \rightarrow NaNO_3(s) + HCl(g)$$

When fine and coarse particles are collected together reactions can occur in the collected mixture because of the introduction of dissimilar compositions. The best documented of these changes is the loss of coarse particulate nitrate by reaction with acidic salts in the fine particles when the two size fractions are mixed on the filter (e.g., Eatough and Ellis, 1983),

$$NaNO_3(s) + HN_4HSO_4(s) \rightarrow NaHN_4SO_4(s) + HNO_3(g)$$

and similar reactions. In addition, changes in coarse particulate organic material can be expected to occur from reaction with fine particulate reactive species. The presence of these artifacts, some of which are certainly presently unknown, suggests that coarse particulate mass and composition is best determined if the fine and coarse particles are collected and analyzed separately. This argues for the use of a dicot sampler or similar device. The EPA heard several strong pleas fore use of dichot samplers and the avoidance of FM integrated PM_{10} filter collected sample (for use in a differential speciation calculation) in the coarse particle speciation network. I add my strong vote to those views for the additional reasons listed here and in Section III.

III. Alteration of the Mass and Chemical Composition of Coarse Particles During Sampling by the Loss of Semi-volatile Material During Sampling.

Exposure to fine particulate matter ($PM_{2.5}$, particles with an aerodynamic diameter less than 2.5 μm) has been implicated as a contributor to adverse human health effects including increases in cardiovascular and pulmonary disease which leads to elevated human mortality and morbidity (Pope and Dockery, 2007). The role coarse particulate matter ($PM_{10-2.5}$) may play in exacerbating health problems is not as well understood. $PM_{2.5}$ in the atmosphere is not composed of a single pollutant but consists of both stable and semi-volatile species. Stable species in the atmosphere include trace metals (including toxic, crustal, and transition metals), black carbon (BC), and sulfate. Semi-volatile material (SVM) exists in dynamic equilibrium between the gas and particle phase and includes ammonium nitrate (Finlayson-Pitts and Pitts, 2004) and low molecular weight organic species (e.g., SVM that exists in the atmosphere in the

39

particle phase can be lost from particles during sampling making it difficult to measure, Eatough et al., 2003). The composition of coarse particles may also include these semi-volatile components, however this semi-volatile material is less well understood in coarse particles.

Several integrated samplers have been developed which accurately determine both nonvolatile material (NVM) and SVM concentrations (Eatough et al., 2003). These techniques could be applied to the chemical characterization of coarse particles. Although these samplers can accurately speciate $PM_{2.5}$, including SVM, there are several drawbacks to their use. Integrated samplers are very labor and cost intensive. Collection of filter media and in-lab analysis are time consuming and cost intensive, resulting in data interpretation weeks and months from the time of collection. The potential for sample contamination is increased with collection, transport, and laboratory analysis. Furthermore, 1-h time resolved data is usually not possible with integrated samplers which inhibit the ability to temporally resolve short term changes in pollution levels that often occur in urban environments.

To overcome these problems, the development of real-time or near real-time instruments has been attempted. One of the widely used semi-continuous $PM_{2.5}$ measurement techniques is the Tapered-Element Oscillating Microbalance (TEOM, Patashnick et al., 1991) developed by Rupprecht & Patashnick Co., Inc. The TEOM does not accurately determine total $PM_{2.5}$ mass because the particle collection filter is heated to 30-50°C to remove particle bound water, which also results in loss of SVM. The Rupprecht & Patashnick Filter Dynamic Measuring System (FDMS, Meyer et al., 2002), and GRIMM monitors (Grimm and Eatough, 2009) have been developed to measure total $PM_{2.5}$ mass, including SVM. The GRIMM monitor will measure both $PM_{2.5}$ and $PM_{10\text{-}2.5}$. A dicot based FDMS has now been released by Thermo, and is in use at some state monitoring sites, which will also measure both $PM_{2.5}$ and $PM_{10\text{-}2.5.}$ Real-time instruments have several advantages including, reliability, cost effectiveness, ease of sampling and reduction in labor requirements. One prominent advantage of real-time instruments is the ability to temporally resolve short term episodes of $PM_{2.5}$ that occur in urban environments that may be relevant to human health effects. One-hour averaged semi-continuous data has also been shown to increase the performance (i.e., reduce uncertainty) of source apportionment techniques to determine sources, both primary and secondary, of urban PM (Grover and Eatough, 2008; Eatough et al., 2008a).

Both the FDMS TEOM and GRIMM Technologies Inc. (Model 1.180) optical particle monitor have Nafion dryers at the inlet to remove particulate water. $PM_{2.5}$ measurements with these two instruments were compared during the winter of 2007 in Lindon, Utah. The excellent agreement between these two instruments (Figure 1, from Hansen et al., 2009) suggest that both measure particulate SVM in a similar manner.

40

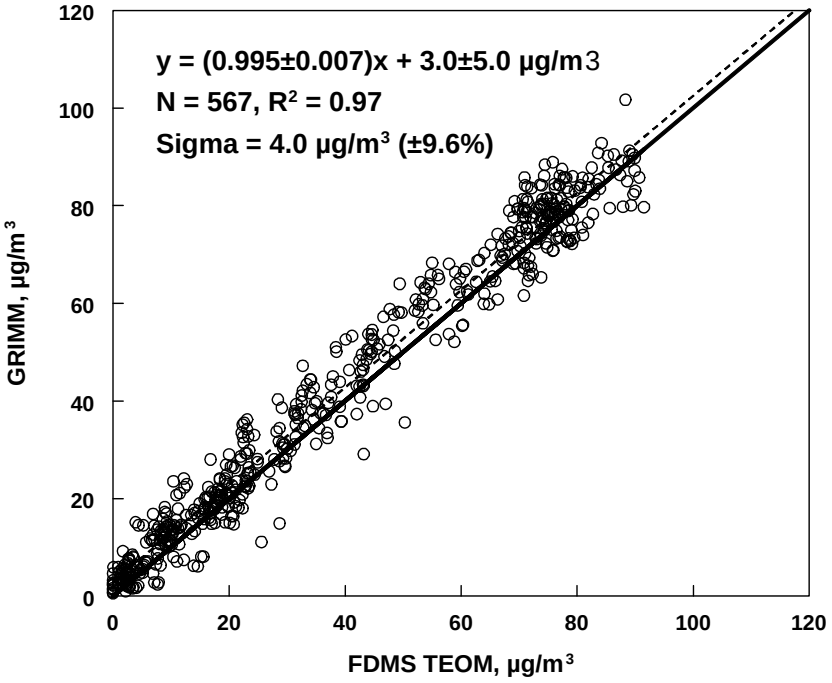


Figure 1. Comparison of $PM_{2.5}$ hourly average mass measurements by an FDMS-TEOM and a GRIMM monitor for the 19 January through 16 February 2007 study at Lindon, Utah. The linear regression fit to the results are given in the Figure

Mass balance studies between 1-h measurements of $PM_{2.5}$ mass with an R&P FDMS TEOM and 1-h measurement of fine particulate components, including the semi-volatile nitrate and organic material in Riverside, California have also shown excellent agreement (Figure 2, from Grover et al., 2008b), indicating the semi-volatile material is well measured by the FDMS TEOM. In This study, the SVM averaged 36% of the total $PM_{2.5}$ mass.

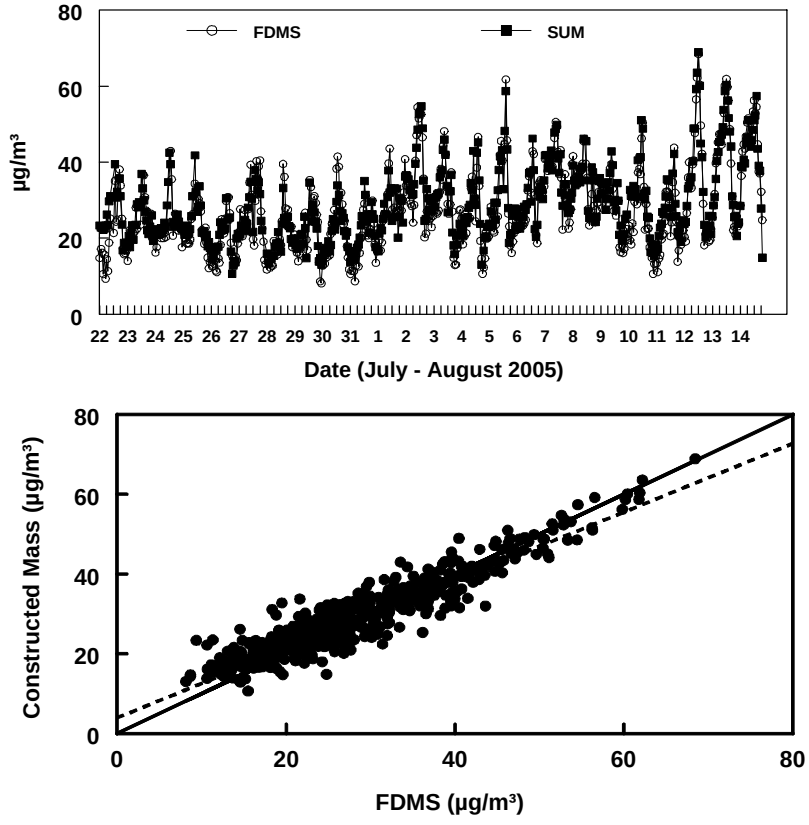


Figure 2. Semi-continuous constructed mass (y axis in both plots) vs. FDMS measured mass. Constructed mass is the sum of all the major components of the aerosol including; NVOM, SVOM, EC, NH_4NO_3 and ammonium sulfate.

The above referenced studies indicate that $PM_{2.5}$ mass and components, including the semi-volatile material can be reliably determined with technology currently available commercially. The ability of the GRIMM monitor to measure the coarse particle fraction and the recent introduction of the dicot FDMS TEOM should allow similar comparisons to be made for $PM_{10-2.5}$.

A measure of the amount of semi-volatile material in both fine and coarse particles can also be using the conventional TEOM (30 or 50 EC), coupled with FDMS TEOM and GRIMM monitor data. This is illustrated by results obtained during the study in Lindon (Hansen et al., 2009). Concentrations of $PM_{2.5}$ mass were made with a conventional TEOM, and FDMS TEOM and the GRIMM monitor. PM_{10} was measured with a conventional TEOM and the GRIMM monitor. The conventional TEOM does not measure the semi-volatile material. The differences between the conventional TEOM and either the FDMS TEOM or GRIMM monitor give the total semi-volatile material in the particles (Grover et al., 2008b). The calculated $PM_{2.5}$ and PM_{10} SVM concentrations obtained from the FDMS TEOM, GRIMM and conventional TEOM monitor data are compared in Figure 3 (from Hansen et al., 2009). Included in Figure 3 are error bars indicated the estimated uncertainty in the comparison. As indicated, the data tend to scatter around the slope equals one line, however, some of the points show a bias towards higher SVM concentrations for the PM_{10}. This indicates the presence of semi-volatile material in the coarse fraction, small, but statistically significant. The SVM material will be composed of semi-volatile ammonium nitrate and organic material. These secondary components would be expected to be concentrated in the fine particles. Thus the results shown in Figure 3 are consistent with these expectations based on atmospheric formation processes. However, a small, but significant amount of semi-volatile material is present in the coarse particles. Chemical analysis of 24-h integrated filter samples confirmed that little nitrate was present in the coarse particles, suggesting the coarse particulate semi-volatile material is organic.

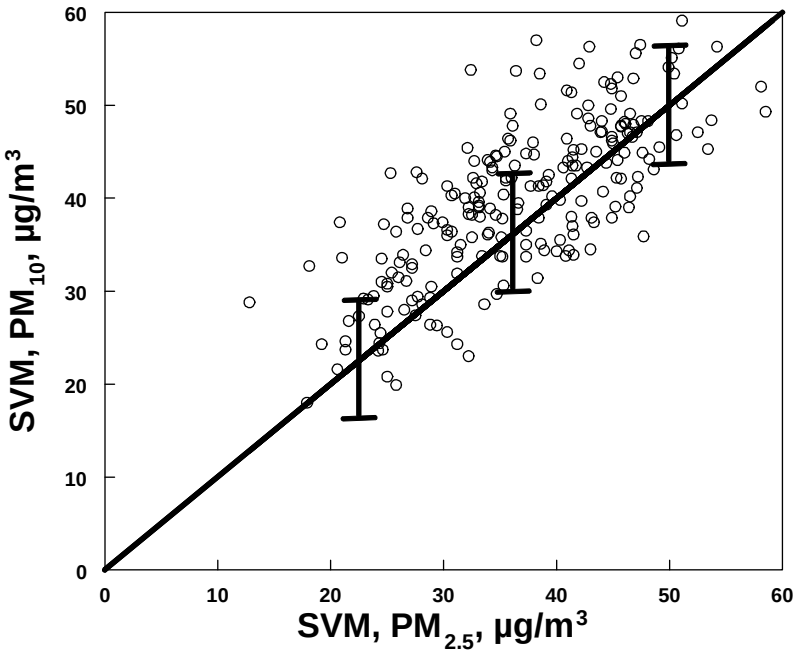


Figure 3. Comparison of the calculated concentrations of $PM_{2.5}$ and PM_{10} semi-volatile material at Lindon UT, see text.

Comparisons such as those shown here should be obtained in the EPA coarse speciation monitoring program to determine if semi-volatile material is important in coarse particles in a variety of urban areas. This will in turn, indicate if conventional filter pack sampling can be expected to give an accurate picture of total coarse particle mass and composition. If significant semi-volatile material is identified in an Urban environment then semi-continuous monitors which will measure the expected semi-volatile components (e.g. ion chromatographic monitors such as the URG AIM and carbon analyzers such as the Sunset Dual Oven monitor which determine both nonvolatile and semi-volatile carbonaceous material) can help elucidate the sources of the semi-volatile material. This will help to close a hole in the chemical speciation of coarse particles from the start which has never been adequately addressed in fine particle research in past EPA monitoring programs.

$PM_{10-2.5}$ Speciation Measurement

1. Table 1provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

Because of the probable alteration of $PM_{10-2.5}$ composition and mass when fine and coarse particles are mixed during sampling (see above discussion), all analyses should be done on a $PM_{10-2.5}$ discrete sample and not inferred by a PM_{10} - $PM_{2.5}$ difference measurement, i.e. a dicot (or equivalent) sampler should be used.

A significant problem with the protocols given in Table 1 is that they provide for the determination of species retained on a filter in an integrated sample only. As I have outlined above, EPA should take advantage of the requirement to characterize coarse particles for better health effect assessment by insuring that semi-volatile particulate matter which is not retained in the particles is quantified. This could first involve the semi-continuous determination of total semi-volatile material by comparison of $PM_{10-2.5}$ mass using a conventional TEOM to measure nonvolatile and either a FDMS TEOM or a GRIMM monitor to measure total mass. The difference between the two is a measure of semi-volatile mass. These measurements should all be made on a $PM_{10-2.5}$ basis and not inferred from difference measurements. The 24-h average of the 1-h conventional TEOM data would be compared to the 24-h integrated filter measured mass. If these comparison indicates significant semi-volatile material is present in an air shed, then the composition of the semi-volatile material could be determined using monitors such as the URG AIM (for nitrate) of the Sunset Dual Oven monitor (for semi-volatile organic material). For the reasons outlined above, it is important that all these measurements be done on a $PM_{10-2.5}$ collected sample and not determined by difference.

Fly Ash. We have done extensive work on the analysis of fly ash in collect PM (e.g. Eatough et al., 2000). SEM analysis is only practicable on Polycarbonate filters. If the data are intended to be use in source apportionment, a PM_{10} sample should be analyzed. We found it best to pre-treat the sample with an acid wash and firing before analysis to optimize detection of insoluble fly ash particles.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

For reason outlined in #1 and discussed in more detail above, chemical speciation should only be done on a dichotomous sampler (or equivalent device to provide a discrete $PM_{10-2.5}$ sample). This would rule out the use of PM_{10} FRM samplers.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

Speciation by the difference method is problematical. Details on artifacts and the approach which should be taken in speciation are discussed in detail above.

4. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

It has been my experience, based on extensive work with diffusion denuder samplers, that in a 24-h sample the results obtained are largely independent of flow rate. This is because the kinetics for changes which occur during sampling are generally of the order of 10s of minutes or shorter. However, a difference method suffers the problems discussed above at any flow rate.

5. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

Since the total mass collected in the minor flow is a function of the inlet flow and not the minor flow, I would not think this would be a problem.

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

If your goal is characterization for source apportionment and health effect etiology applications, none of the components should be eliminated. The importance of quantifying semi-volatile material in coarse particles has been discussed in the previous section and in the introductory material.

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

Nitrate is expected to be present mainly as the sodium salt. But knowing both nitrate and ammonium ion would be valuable. If, as we suspect, ammonium nitrate is negligible in most Urban areas in coarse particles, it would not seem worth the effort to use a denuder in integrated sampling, **if** you also include monitoring for semi-volatile material with conventional TEOM and either FDMS TEOM or GRIMM monitors as outlined above. This would highlight the possible presence of ammonium nitrate and followup with an AIMS would verify the ammonium nitrate presence. If however, you do not monitor for semi-volatile species, then using a denuder system for the coarse particle collection is advised. Do you have any data on the transfer of coarse particles through an annular denuder?

3. *The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?*

I have commented on fly ash above. I am not familiar with monitoring for biological materials.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

I will leave this to those who know.

5. 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 so, how should this interference be addressed?

This is certainly a potential interference but I do not know to what extent. Those knowledge in this area did not seem to think this would be a large problem.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

This question seems to imply the use of difference methods. I have outlined why this is not a good idea above.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

I think the routine inclusion of monitoring for semi-volatile species using the sem-continuous mass monitors I have mentioned above would be a valuable addition. This would proved input on both $PM_{10-2.5}$ mass and components as well as give diurnal data which would be very helpful in understanding the effects of changing meteorology, emissions and atmospheric chemistry on the observed concentrations and composition.

References

Eatough, D.J.; Grover, B.D.; Woolwine, W.R.; Eatough, N.L.;Long, R.; Farber, R. (2008) Source Apportionment of 1-hr Semi-Continuous Data During the 2005 Study of Organic Aerosols in Riverside (SOAR) Using Positive Matrix Factorization, *Atmos. Environ.* **42**, 2706-2719.

Eatough, D.J.; Long, R.W.; Modey, W.K. and Eatough, N.L. Semi-Volatile Secondary Organic Aerosol in Urban Atmospheres: Meeting a Measurement Challenge (2003) *Atmos. Environ.* **37**, 1277-1292.

Eatough D.J.; Farber R.J. and Watson J.G. (2000) Second Generation Chemical Mass Balance Source Apportionment of Sulfur Oxides and sulfate at the Grand Canyon during the Project MOHAVE Summer Intensive, *J. Air & Waste Management Association* **50**, 759-774.

Eatough D.J. and Ellis E.C. (1983) A Comparison of High and Low Volume Particulate Matter Nitrate Concentrations in the Los Angeles Basin, *Aerosol Science and Technology*, **2**, 177.

Ellis E.C.; Farber R.J. and Eatough D.J. (1983) Formation of Coarse Particle Secondary Nitrate in the Los Angeles Basin, *Aerosol Science and Technology*, **2,** 176.

Finalyson-Pitts B.J.; Pitts, J.N. *Chemistry Of The Upper And Lower Atmosphere: Theory, Experiments and Applications*; Elsevier, 2004.

Grimm, H. and Eatough, D.J. (2009) Aerosol Measurement: The Use of Optical Light Scattering for the Determination of Particulate Size Distribution, and Particulate Mass, Including the Semi-Volatile Fraction; *J. Air Waste Manage. Assoc.* **59,** 101-107.

Grover, B.D. and Eatough, D.J. (2008a) Source Apportionment of One-Hour Semi-Continuous Data using Positive Matrix Factorization with Total Mass (Nonvolatile plus Semi-Volatile) Measured by the R&P FDMS Monitor; *Aerosol Sci. Technol.* **42**, 28-39.

Grover, B.D.; Eatough N.L.; Woolwine, W.R.; Cannon, J.P.; Eatough, D.J.; Long, R.W. (2008b) Semi-continuous Mass Closure of the Major Components of Fine Particulate Matter in

Riverside, CA; *Atmos. Environ*. **42**, 250-260.

Hansen, J.; Woolwine, W.R. III; Bates, B.L, Clark, J.M.; Kuprov, R.Y.; Mukherjee, P.; Murray, J.A.; Simmons, M.A.; Waite, M.F.; Eatough, N.L.; Eatough, D.J.; Long R. and Grover B.D. (2009) Semi-Continuous $PM_{2.5}$ and PM_{10} Mass and Composition Measurements in Lindon, Utah During Winter, 2007. *J. Air Waste Manage. Assoc.*, in press.

Meyer, M.B.; Patashnick, H.; Ambs, J.L. (2002) Ongoing Development of a Continuous Reference Standard Particulate Matter Mass Monitor for Ambient Air; paper presented at the Symposium on Air Quality Measurement Methods and Technology, San Francisco, CA, November.

Patashnick, H.; Rupprecht, E.G. Continuous PM_{10} Measurements Using the Tapered Element Oscillating Microbalance; *J. of Air & Waste Manage. Assoc.* **41**, 1079-1083.

Pope, C.A. III; Dockery, D.W. Health Effects of Fine Particulate Air Pollution: Lines that Connect; *J. Air & Waste Manage. Assoc.* **2007**, *57*, 709-742.

U.S. EPA (2004) Air Quality Criteria for Particulate Matter. Report No. EPA/600/P-99/002aF, Environmental Protection Agency, Research Triangle Park, NC.

Mr. Dirk Felton

$PM_{10-2.5}$ Speciation Measurement

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

The conversion to OM from OC is contributing to the unidentified mass issue. The EPA should endeavor to reduce this uncertainty by performing detailed OC component and molecular marker analysis on some of the filter samples.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

The SASS PM-10 inlet is not yet viable and the SASS may not have enough sample volume for some PMc components in some areas of the country. There are many existing Cascade Impactor designs and it is possible that one of those could be modified to make it appropriate for collection of some of the components of interest for the PMc pilot. Other technologies also not on this list include continuous instruments and particle mass spectrometry. Again these latter two new technologies would have to be modified with suitable inlets and they are not user friendly but they have the potential of producing the best results.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

The difference method is likely to suffer the most in areas with high nitrate and high OC. The problem is that component conversion and volatilization are likely to occur preferentially for one component size fraction (PM-10, PM-2.5) or the other depending on the source. This will make the bias between the size fractions component specific.

The Dicot method also has the disadvantage of requiring an adjustment for fine particle intrusion. This adjustment to Dicot mass concentration is less attractive for component analysis because it is not known if the correction or the presence of fine particles on the coarse mode filter will preferentially affect one component over another.

4. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

In Queens, NY, typical 16.7 L/min FRM filter loadings are 260 ug for PM-2.5 and 480 ug for PM-10. It is expected that a 6.7 L/min sampler would have loadings of 104 ug and 192 ug respectively. These lower loadings certainly increase the significance of the precision of the weighing procedure and the magnitude of the filter blanks which are permitted to be as high as 30 ug.

During the recent FEM equivalency evaluations performed by ThermoFisher Scientific, Franklin, MA, the vendor was required to run filter based low volume FRM PM-2.5 and PM-10 samplers in triplicate. The average standard deviation of the three calculated PMc values over 44 sampling days was 0.8 ug/m3. If we assume that the 6.7 L/min sampler performs as well as a carefully operated FRM during an equivalency test, which should be considered a best case, 0.8 ug would indicate a standard deviation of about 20 ug of filter loading on the 6.7 L/min sampler. That makes the precision of the method an issue since the expected PMc by difference is only 88 ug for the 6.7 L/min sampler.

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

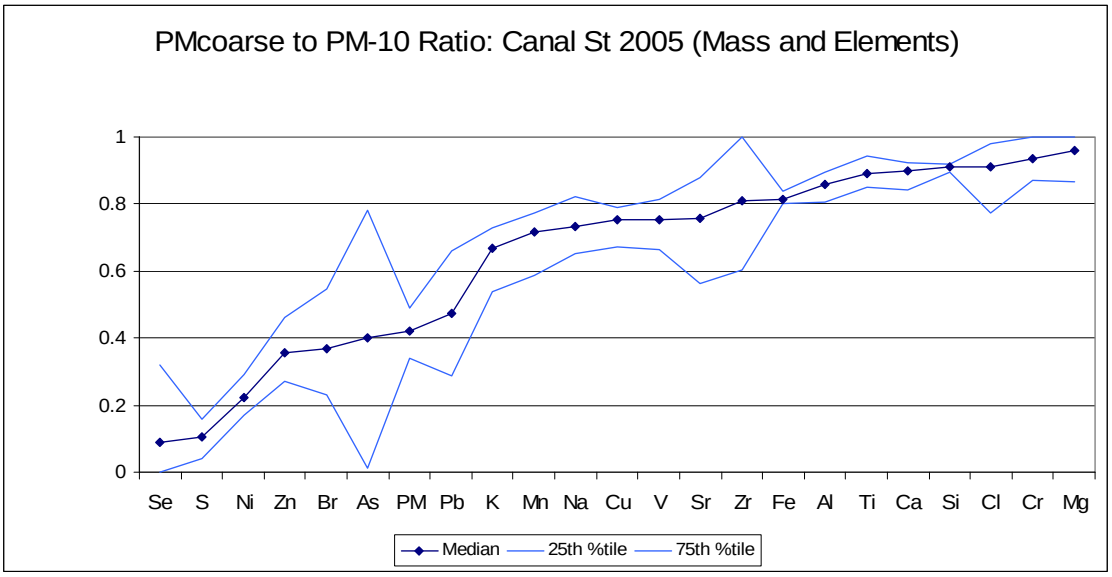
During the Thermo Fischer Scientific FEM evaluation in Queens NY last summer, the correlation between the virtual impactor Coarse mode data and PMc by filter difference was not as good as the correlation with the fine mode. This is not too surprising considering the low PMc concentrations and the issue of large particle retention on filters prior to gravimetric analysis. The amount of mass should be sufficient for most analysis but the precision of the PMc mass measurements by Dicot will not be as good as that for PMc by difference.

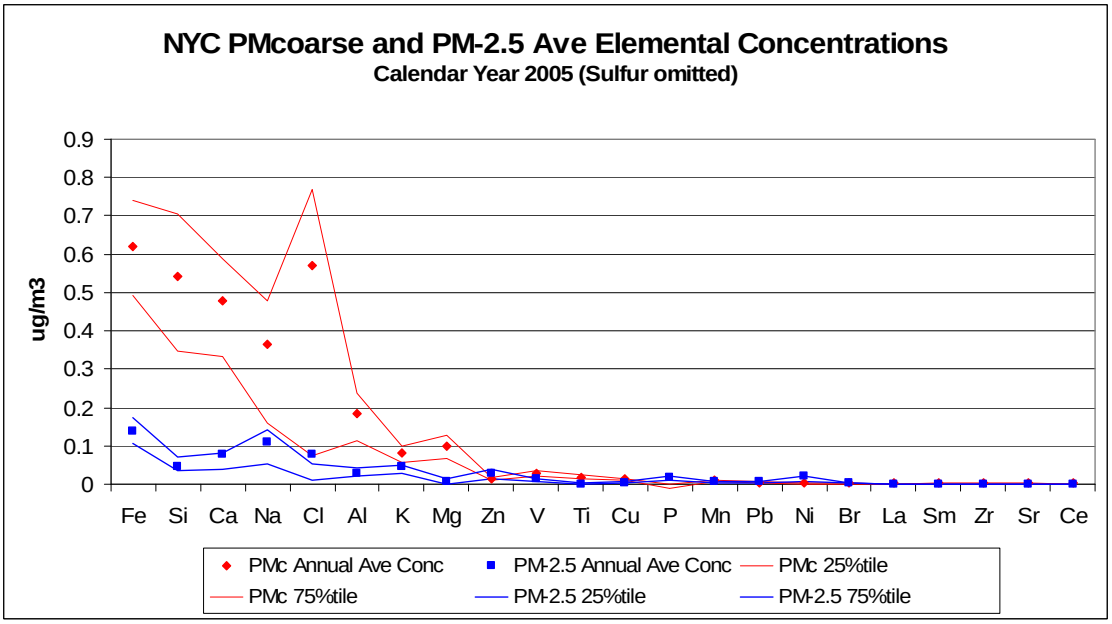
$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

The first question will have a different answer depending on the end use of the data. The PMc component mix will vary greatly by location, season and proximity to sources. In the northeast, the concentrations of elements in PMc tend to be around 30% of the PMc mass. Again from a northeast perspective, the only element missing from Table 1 is Vanadium which can have significant PMc concentrations in some areas. The New York State Department of Environmental Conservation (NYSDEC) undertook a pilot study for PMc speciation by difference. Low volume PM-2.5 and PM-10 FRM samplers were installed in New York City and in Niagara Falls. The samplers were operated on a 1/6 day schedule for a year and the filters were weighed and analyzed by XRF. The results demonstrated that some species such as Pb were found nearly equally in the fine and coarse mode. Arsenic was unique in that it appears to have a distinct source in both fine and coarse modes.

The concentrations of the elemental data for all but about 10 elements were very low in the coarse mode.





Carbon is probably the most important overall group of PM components. It includes many compounds that are not uniquely identified and are likely to be correlated with health effects. The poor understanding of OC's conversion to organic mass is also not well understood which makes it difficult to accurately characterize OC PMc. Continuous carbon monitoring is the most cost effective means of obtaining daily datasets. The Sunset Labs instrument is available as a prototype in a configuration for PM-10. The pilot should establish a few sites in different parts of the country with hourly OC/ECcoarse by difference. The EPA should also attempt to include the volatile portion of all of the components collected in the pilot.

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

Soluble ions are less important for eastern sites. The ion concentrations from Table 1, except for Nitrate, can be estimated from the elemental data. This will not be the case for the west where ammonium nitrate is very important and cannot be estimated from other measurements. A denuder should be employed and the sampler should be modified to keep the sample cool after and during the sampling event if possible.

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

As with all PMc data, the relative importance of one component over another is dependent on location and sources. In and around industrial areas and large, older urban areas such as cities in the midwest and northeast, fly ash and oil soot are found in significant concentrations in the air. Often the majority of these particles are larger than 10 microns and are likely to be excluded in PMc measurements. Since these particles may be correlated with health effects, the pilot monitoring program should consider evaluating concentration differences in results between samples collected with PMc samplers and samplers with low volume TSP inlets such as the URG-2000-30DG.

Teflon filters are suitable for SEM work but are not ideal. Their depth structure prevents reliable quantitation because it tends to hide the smaller particles.

Biological materials such as mold spores, insect parts and moth scales will partially be collected with PMc samplers. It certainly is plausible that mold spores could have a correlation with health effects but it is unlikely that generalized assay tests would sufficiently identify specific components of PM that probably affect only a limited portion of the population.

Pollen for the most part is too large to be included in PMc measurements. Specialized samplers such as the Burkhard spore trap and Rotorod sampler are used for Pollen sampling and counting.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

The XRF analysis for the more heavily loaded PM-10 filters is modified by extending the count time for the detector. Extending the count time may or may not eliminate the uncertainty associated with an increase in X-Ray absorption. The EPA should sponsor experimentation by loading filters with different component mixes of PMc and then compare the XRF results with ICPMS digestive analysis.

5. 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 so, how should this interference be addressed?

The IMPROVE program should have some insight into this.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

The best site is the one that has significant concentrations of the PMc component that has the greatest correlation with health effects. To that end, the pilot should be designed to provide survey information covering the entire range of component mix and concentration ranges. This is the most effective way to determine the importance of specific components of PMc for the design of a future more relevant PMc network. NCore sites are situated to represent large spatial scales and generally will tend to have relatively low contributions from known sources of larger particles.

There are no standards for components of PMc or for mass of PMc so the pilot as well as the initial longer term deployment should be designed to help ascertain the highest concentrations of PMc components likely to be associated with health effects. This strategy will accelerate the linking of health effects and individual PMc component concentrations

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

It is appropriate to tailor the PMc speciation program to the species that are prevalent and likely to be related to health effects in specific regions of the country. In northeastern cities for instance, PMc OC/EC are likely to be much more important than PMc elements. In western cities, soil and nitrate are likely to more relevant. Once health effect correlations are found in areas with high concentrations of specific components of PMc, the network can be modified to include that component in sampling efforts in the rest of the network.

Health researchers are continually stressing a preference for daily data due to lag structure in health effects studies and the PMc pilot should be designed to the extent possible to provide daily or continuous data.

Dr. Philip Hopke

$PM_{10-2.5}$ Speciation Measurement

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

Part of the issue here is what sampling method is to be used. Is there really sufficient precision to be able to use the difference method which unfortunately is still being put forth as the standard approach? I suggest that the key is less on the analytical method as on the sampling approach.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

I strongly recommend against using the difference method. There is the potential for substantial interactions between the fine and coarse particles on the PM10 filter. For example, fine NH4NO3 can dissociate to produce HNO3 that would react with alkaline coarse particles. This could produce an overestimate of coarse NO3.

Dichotomous samplers complicate the analyses by putting about 10% of the fine particle mass onto the coarse particle filter.

It probably makes more sense to develop an impactor system to collect specific coarse particle samples where there would be little supercoarse or fine particle contamination. Such an impactor would have two stages. The first would have as sharp as possible PM10 cut and the second would have a sharp PM2.5 cut. The PM2.5 stage would be the one to be analyzed. However, since this approach was not adopted when the idea of coarse particles was first considered (such that it would now be available), it makes sense to go with the dichot.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

See above.

One question is whether low volume systems provide sufficiently large samples for all of the analyses envisioned. Clarkson is involved in an EPA CRADA to test a high volume (400 LPM) dichotomous sampler that would provide greater mass for chemical characterization. However, it is still a virtual impaction system that would still intermix some fine particles into the coarse particle sample.

4. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

This is why they should develop a reasonable flow, simple impactor system to collect PM10-2.5. It should be relatively easy to design and build such a system. It should have been done rather than spending all of the money that has been spent on trying to justify the inherently flawed difference method and the problematic dichotomous sampler.

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

Probably not. However, it is possible to build high flow dichots that would provide sufficiently large samples to ensure good analytical precision. I have provided a presentation outlining such a system that is ready for testing.

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

We know a lot less about the coarse fraction and what are critical species particularly for primary biological species that are going to be more prevalent in coarse fraction samples compared to fine particle samples. Protein alone is highly unlikely to provide a reliable estimate of total biological particulate mass.

Are there sufficient resources available to perform CCSEM on enough filters for enough particles to provide statistically valid numbers of particles to adequate quantify the particle types. Are they envisioning automated analysis of the data? Will they collect secondary electron images as well as backscatter images and x-ray spectra? One can envision automated image analysis software that could sort the particles into various major categories, but there is no discussion of how the analyses are to be conducted. Manual SEM and review of images will not be sufficient to provide support to a national network of samplers.

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

Nitrate is important for the coarse sample as well as fine although the coarse particle nitrate is generally present because of the reaction of gaseous HNO3 with the alkaline coarse particles. This problem also supports the need for using devices that separate coarse and fine fractions and not using the difference method.

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

See answer to 1 above. Normally Teflon is not an ideal surface for CCSEM. It can be adequate for manual SEM analysis, but it is not possible to have enough people on enough microscopes to do enough particles on enough filters to be meaningful. Much of the biological species would be more carbohydrates than protein so it is not clear that a total protein assay would suffice to provide an index of total biological material. It may be more useful to look at specific species such as endotoxin or specific aeroallergens. There are now easy to use kits at reasonable prices to perform ELIZA analyses. It is likely that additional species tests could be developed for other identified allergens.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

Again, this depends critically on what is collected. If you are still using the difference method, then it makes the XRF analysis much more difficult than if there is a narrower range of particle sizes in just a coarse particle sample. Also the differences in composition from location to location also need to be considered as it is the combination of particle composition and size that affect the penetrability of the fluoresced x-ray.

5. 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 so, how should this interference be addressed?

I am not sure that we really know enough to be able to develop quantitative relationships between transition metal oxides and changes in relative OC/EC values. There is evidence for influence but not clear relationships and it certainly will also depend on the nature of the carbonaceous material as well as the nature of the oxides.

Network Design

1. *Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?*

Are we picking sites based on a criterion like this rather than on a good exposure science basis? Do we want PM coarse samples for the sake of having a clean sample or are we sampling because there are exposure, source identification, or transport issue to be solved? This question is very strange. Without a clear set of objectives for what we are planning to use the data for, it is impossible to judge the value of the sites available.

2. *If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?*

Of course. At this point, when we have very limited knowledge of PM coarse, we are clearly going to make judgment calls that subsequent data will almost certainly tell us that some of our choices were wrong. We must always maintain flexibility in the network design. That was part of the NCore philosophy.

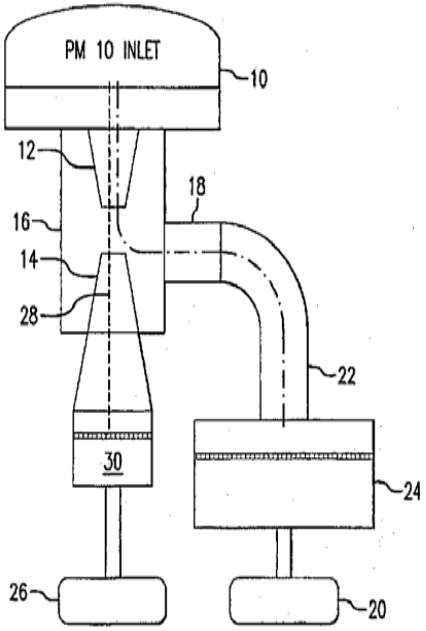
Multi-Filter Coarse Particle Chemical Speciation Sampler Using Virtual

Objective:

Develop a Coarse Particle Chemical Speciation Sampler to Obtain Filter Samplers Similar to the Current Fine Particle Chemical Speciation Sampler Used In EPA's Fine Particle Monitoring Network with the Goal of Obtaining a Nearly Complete Mass Balance on the Collected Coarse PM

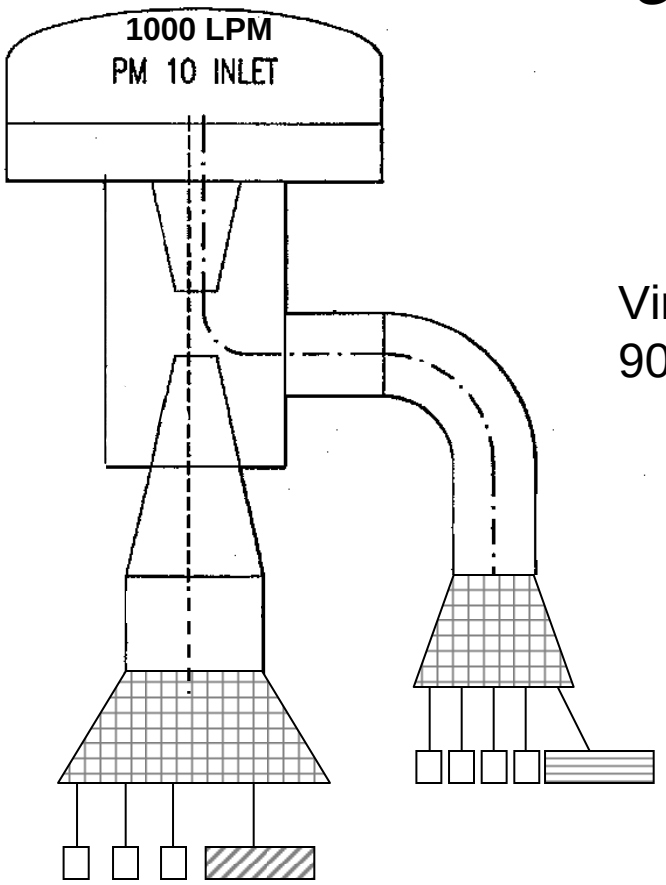
Design

- **Premise**
  - Need to Separate Fine and Coarse Particles for All the Usual Reason
    - Better Understand Health Effects of PMc vs PMf
    - Source Apportionment
    - Not Mixing Fine and Coarse Chemistry (fine acidic, coarse basic)
  - Obtain Separation with a Virtual Impactor
  - Design Around the Current PMc and PMf FRM Flow Rates (16.7 LPM), Option for 6.7 LPM to Match the Current MetOne PMf Speciation Sampler
  - Include Design Flexibility for Additional Measurements
- Flexibility
  - Allows Multiple Filters, Denuders, Back Up Filters as Needed to Minimize Interferences
  - Bypass Allows for Large Samples to Be Collected for Toxicological Testing, Organic Speciation, Trace and Ultra-Trace Metals Speciation, Including Valance States
  - Virtual Impactor Can Have 5% Coarse, 95% Fine to Minimize Gas Phase Artifacts on Coarse Filter*



Existing Commercial High Volume Fine and Coarse Sampler Based on Virtual Impaction

Modified Sampler for PMc Chemical Speciation General Schematic



Virtual Impactor
90% Fine, 10% Coarse*

Fine Particles

Coarse Particles

Design and Evaluation by Clarkson University and U.S. EPS Underway Currently.

Commercialization by Greentech Environmental. Available Prototype for OAQPS Testing, May 15, 2009

Flow Splitters
16.7 LPM, 47 mm Filters
49.1 LPM, 90 mm Filter bypass flow
833 LPM, 203 mnm X 250 mm Filter bypass flow

Dr. Rudolf Husar

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

No

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

Nitrate is important

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

Not familiar with bio aerosol sampling issues

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

Saturation is real. Keep deposition density low?

5. 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 so, how should this interference be addressed?

I am not familiar with oxides-OC/EC interference.

Dr. Donna Kenski

The questions on $PM_{10-2.5}$ speciation measurement and on $PM_{10-2.5}$ species or components are outside my areas of expertise and I respectfully defer to the distinguished panel members' opinions on these subjects. With regard to network design, I've answered the charge questions below, but I feel compelled to note that, given the current lack of consensus on how best to sample for both $PM_{10-2.5}$ mass and its speciated components, it seems much too premature to consider rolling out a network of 75 monitors by 2011, just 2 years from now. This is potentially a huge commitment of dollars and state resources that, once launched, will be very difficult to steer in a different direction if future developments warrant. The purpose of this pilot network is for research into coarse particle concentration distributions, sources, and health effects, which is commendable. But we need to allow enough time for the pilot results to be analyzed and filtered through the scientific community before launching a long-term network. A reasonable pilot network would be more like 5 or 10 sites where intensive sampling can take place (maybe even every day instead of every third day at some sites), characteristics of multiple monitors can be intercompared, and options for speciation of those multiple monitors can be explored and vetted until the research community has more collective confidence in the best way to move forward.

If the purpose of speciation is to perform source apportionment, I agree with several panel members who have noted that the bulk components (OC, EC, ions, metals) will not be sufficient to separate some important sources of $PM_{10-2.5.}$ It is possible that organic carbon speciation would help resolve some of these sources. While this is unlikely to be feasible as part of the routine network, it should have a place in the pilot network since it would shed some light on whether source apportionment with the bulk species is able to resolve carbon sources satisfactorily. This should include source sampling for the $PM_{10-2.5}$ fraction as well, although that's not necessarily a network function. Continuous sampling for $PM_{10-2.5}$ mass and components (at least EC/OC) would certainly be helpful as well.

Network design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

One should aim for a selection of sites that represent varying ratios of PM_{10}:$PM_{2.5}$, as well as varying geographic distribution because the composition of both particle size fractions will vary geographically as well. It will be important to include both coastal and inland sites, urban and rural (not just pristine wilderness areas but agricultural areas also), and various meteorological regimes. It seems like most of the NCore sites as currently proposed are generally population-oriented PM2.5 sites. Sites that reflect maximum and representative $PM_{10-2.5}$ exposures will not necessarily coincide with those PM2.5 sites, so the pilot program should have the flexibility to monitor at locations outside the NCore network. Based on data collected in the next few years, informed decisions could then be made about long-term sites.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

Of course changes to the network should be continually under consideration; hopefully that's an important objective of a pilot network. Learn what works and what doesn't and adjust accordingly. As noted above, it seems much too soon to contemplate 75 speciation sites. I strongly encourage EPA to move ahead slowly and evaluate the pilot study data thoroughly before expanding the network beyond a handful of research sites. The resources spent on monitor and method intercomparisons will be a much better investment of our scarce monitoring dollars than a hasty move to monitor at all 75 NCore sites. Let the research community evaluate these results, come to agreement on speciation sampling and analysis protocols, then move forward with a broader network that's truly science-based.

Dr. Thomas Lumley

$PM_{10-2.5}$ Species or Components

1. *Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?*

Distinguishing burning biomass (wood or grass) from other carbon sources with levoglucosan may be useful and relatively inexpensive.

2. *In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?*

Not my field.

3. *The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?*

In areas where wood is used for heating, wood smoke is important to distinguish as there are straightforward ways to reduce emission. Specific allergenic pollen sources may be important when studying health effects of the coarse fraction.

4. *Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?*

Not my field

5. *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 so, how should this interference be addressed?*

Not my field

Network Design

1. *Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?*

Speciation will be relatively straightforward, especially by the difference method, in sites with high PM10 and low PM2.5. The sources and species contributing to the coarse fraction may well be different in sites with high PM10 and low PM2.5. If so, it would be important to also carry out speciation at other sites. It is entirely conceivable that most of the health impact of coarse PM occurs at sites with moderate coarse:fine ratios rather than at sites with high peak concentrations of wind-blown soil. The sites should be chosen to capture the range of types of coarse PM exposure in the population.

2. *If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?*

It would be useful to add sites whose coarse-fraction composition is likely to be different from those already in the network, especially if large numbers of people may be exposed. While it is true that local sources have a larger contribution to coarse PM than fine PM, some of the highest levels of soil-based coarse PM will affect fairly large areas (not necessarily at the same time). Expanding the network is most useful when it captures qualitatively under-represented types of coarse PM. More monitoring in populated areas California and the Southwest is likely to be useful for understanding the health effects of coarse PM. Monitoring in areas with low population density may be informative about sources but is unlikely to be useful for studying health effects.

Dr. Peter H. McMurry

$PM_{10-2.5}$ Speciation Measurement

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

Biological material is a poorly understood category of particulate matter that is likely to be significant. Matthias-Maser and coworkers {, 2000 #11407} reported that during a complete year of sampling in the Lake Baikal region, "20% of the number concentration and almost 30% of the volume concentration were biological, with no seasonal variation." While the carbon content of biological material ought to be detected by OC/EC analyses, it is important to identify the extent to which bioaerosols contribute to particulate mass if this is indeed such a major source. Fuzzi et al. {, 1997 #6836} reported that "the concentration of airborne bacteria and yeasts is enriched in foggy conditions up to two orders of magnitude compared to clear air conditions, while concentration of moulds is not influenced by the presence of fog," suggesting that fog droplets act as culture media for biological particles. Mohler et al. {, 2007 #21265} report that biological particles may play an important role in cloud formation. Given the potential significance of biological particles in coarse particles, an effort should be made to quantify their contribution to mass. I am not sufficiently knowledgeable to provide useful input regarding suitable analytical methods.

I agree with the concern expressed by several Committee members that OM/OC may be quite different for particles of biological origin, secondary OC, and primary. An effort must be mede to determine those ratios for biological particles.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

I would not favor the use of indirect methods such as the GRIMM optical detector. The correlations between GRIMM mass and gravimetric mass shown by Delbert Eatough in his remarks are extremely impressive. However, assumptions about shape, density, and refractive index must be made to convert optical signals to mass. In my experience, those aerosol properties vary with sampling time and location and will inevitably introduce uncertainties.

I agree with Delbert Eatough's comments that chemical interactions between fine and coarse particles could affect speciation measurements. This argues against using the PM10-2.5 FRM as the speciation sampler. However, it is also true that if a perfect sampler were used to obtain samples for speciation analysis, then it might not be possible to reconcile measured (FRM) mass and reconstructed mass. On the other hand, speciation measurements done on FRM samples could, in principle, produce mass closure. Is "truth" or "agreement" better? I am inclined to agree with Prof. Eatough: If a dichotomous sampler produces results that are more nearly "true,"

then it would be a preferable sampler.

During our conference call Warren White pointed out another reason to inertially separate coarse and fine particles before collection. In previous meetings of this Committee, the point was made that coarse urban particles may contribute more to adverse health outcomes than coarse nonurban particles. This could be because urban coarse particles serve as carriers for toxic compounds picked up by exposure to the urban environment. If those toxic compounds were also present in fine particles at comparable or higher concentrations, then measurements by difference would lead to substantial uncertainties.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

Volatilization and chemical reactions due to interactions of basic and acidic particles; inaccurate determination of the fraction of collected mass that is water.

4. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

I defer.

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

If the sampling rate into the dichot is 16.7 lpm, then the sampling rate for coarse particles would be the same as for the FRM. The dichot would offer the advantage that coarse and fine particles are not combined to the same extent as occurs on the FRM.

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

I feel that highlighting coarse particles of biological origin is appropriate. I am not an expert on biological particles or on ways to detect them. Eric Edgerton has worked on this topic and made some interesting recommendations for chemical assays that might provide further information on biological particles.

The document also suggested that SEM might be used for biological particles. Indeed, visual observations can provide useful insights into possible origins of particles. However, I am not familiar with automated SEM techniques that have proven reliable for providing the type of

quantitative information that might be expected for a monitoring network. I feel that limited use of SEM in research by knowledgeable persons should be encouraged. Sampling times and samplers should be optimized for this purpose. It seems unlikely that heavily loaded PM10 samples would be optimal for SEM analysis.

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

George Allen's admonition that coarse particles are different from fine particles is important. As Bart Croes points out, nitrates (especially sodium nitrate) can be a significant coarse particle component, especially near the coast. Judy Chow's point that magnesium can be a useful tracer for agricultural activities is also persuasive.

3. *The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?*

I do not see a clear reason for separating out fly ash as a source category. My other thoughts pertinent to this question are given above.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

I defer.

5. 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 so, how should this interference be addressed?

I defer.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

Other committee members provided insightful responses to this question.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

I defer.

Mr. Richard L. Poirot

PM10-2.5 Speciation Measurement

1. Table 1 provides a list of proposed PM10-2.5 species and analysis methods. Are there additional PM10-2.5 target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

Generally the list of proposed species seems OK, although if the difference method is being considered for sampling, this list may require more samplers than is feasible. It may not make sense to more or less duplicate the PM2.5 speciation analysis. Possibly it will be more efficient to include some relatively basic "screening" sampling at most coarse speciation sites , with more detailed analyses at selected sites and/or based on the screening analysis. I wonder how much useful information will really be provided by repeating the same TOR & TOT analyses (with the exact same thermal cut-points) for OC & EC? Some molecular level carbon analysis could be revealing at a few sites. A measurement of light absorption from Teflon dichot filters might be a useful, low cost addition to consider. Possibly the ion analysis may not require nylon filters or denuders, as we really don't expect much coarse ammonium nitrate, nor are there really any very satisfactory ways to quantify ambient ammonium concentrations. I don't know much about sampling for biological materials, but think there must be other useful options beyond SEM and Protein Assay. I'm not sure that SEM on Polycarbonate filters for fly ash can really be justified, except at sites where a substantial fly ash contribution is otherwise indicated. Possibly also some sort of toxicity testing might be conducted on (seasonally composited, coarse-only) samples to get a sense of which sites/seasons have the most harmful coarse particle mixtures. Then chemical &/or biological analyses could be focused to the samples of interest.

Regarding mass balance issues, I think (assuming crustal oxides are appropriately estimated) that a large and likely variable fraction unmeasured of non-carbon organic matter could be a significant contributor to mass. For example the C:mass ratios for carbohydrates & cellulose are 2.4 & 2.5, and carbonate – likely to be present in many coarse samples – has a C:mass ratio of 4. Rather than adding additional species in ambient sampling, it might be more efficient to analyze known quantities of different source material by comparable methods to get a better sense of how the easily measured species relate to the masses.

2. Various sampling devices, including dichotomous samplers, MetOne SASS speciation monitors, PM10 and PM2.5 FRMs are potential sampling devices (with the appropriate filter types) for PM10-2.5 speciation. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

I think a sampler such as the one Phil Hopke suggests, that allows for both size-separated particles on multiple filter types, and also has the option to collect relatively large sample sizes to support other more detailed analyses could be useful to test in the pilot study. It could also be useful to evaluate different analyses on different filter media. For example, how does nitrate on coarse dichot quartz and Teflon compare with nitrate on (denuded) dichot Nylon? It would also

be useful to evaluate any continuous speciation instruments, such as the paired PM10 and PM2.5 Sunset Labs carbon analyzers – vs filter samples. While there are so many benefits to the use of dichotomous samplers, one possible disadvantage is that the exposed coarse Teflon filters – without the sticky fines – may not "travel well". Aside from just comparing samplers & filters, it might be useful to look specifically for potential sample loss from coarse dichot filters with rough handling, and to develiop best practices to minimize such losses (if any).

3. What are the PM10-2.5 speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for PM10-2.5 speciation and if so what specific issues make it problematic?

As indicated above, we really don't expect much coarse ammonium nitrate or ammonium sulfate and so Nylon filters and denuders may not be needed (nor would ammonium measurements like reflect ambient concentrations). Coarse nitrate might be measured directly from Quartz or Teflon dichot filters. Loss of some chloride is likely from samples with sea salt or road salt. OC artifacts are likely to be proportionately less than for fine particle sampling, but a careful effort should be made to quantify OC blank concentrations.

Speciation by difference should work reasonably well for any species with relatively high concentrations in the coarse mode, and poorly for any species with relatively high concentrations in the fine mode.

4. The current and most widely used PM2.5 speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (Lpm) which is significantly lower than either the FRM for PM10-2.5 mass or the dichotomous sampler (16.7 Lpm). If this sampler was configured for PM10-2.5 by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the PM10-2.5 FRM?

This may be a concern, but I defer to others for an answer. One potential "advantage" for coarse speciation is that we are not starting out with a strong advance signal that the mass of coarse particles is a good health indicator. Achieving a mass balance is less important than understanding where the various components of coarse particles come from and which are most injurious to health (or welfare).

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

I don't think this should be an issue, except for analyses such as molecular carbon compounds or specific biological components which may require very large sample sizes.

PM10-2.5 Species or Components

1. Table 1 provides a list of proposed PM10-2.5 species and analysis methods. Among these species, which are most important? Are there important PM10-2.5 species or components missing from this list? Are there important analysis methods missing from this list?

See answers to Q 1 under Speciation Measurement Issues. My preference for a minimum Coarse speciation measurement (for the most sites) would be a dichot with XRF and optical absorption on a Teflon coarse filter. My next addition would be a dichot with quartz filters for carbon and ion analysis. Paired (difference method) or virtual impaction (coarse only) mass and OC/EC by continuous methods may also be a valuable complement to provide better time series information. Toxicity assays and/or molecular carbon analyses might be considered on seasonally-composited samples at some sites.

Specific sampling and/or analyses for pollen – or pollen components (often fragmented into or aerodynamically acting like particles smaller than 10 microns) may be useful at some sites or seasons. Possibly, sampling for biological analyses may require other methods (see #3 below) for which absolute particle size cut is less critical than ability to culture or bioassay, and reasonable assumptions can be made about the domination of coarse mode formation or suspension mechanisms.

2. In the consideration of potential ion measurements for PM10-2.5 species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in PM10-2.5?

See previous answers. I don't see why there should be much coarse ammonium nitrate in the ambient air, and I expect coarse nitrate compounds (NaNO3, CaNO3, etc.) to be less volatile – and therefore likely not needing denuders or Nylon filters. But do the necessary experiments to confirm or disprove this in the pilot network.

3. The 2004 CD included a list of important PM10-2.5 components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

As previously indicated, I'm not sure fly ash SEM is generally warranted unless otherwise indicated. For more input on appropriate routine and/or at least occasionally feasible biological (sampling and) analyses, you may want to consult beyond this subcommittee. See for example Dale Griffin's (USGS) paper on: Atmospheric Movement of Microorganisms in Clouds of Desert Dust and Implications for Human Health, Clinical Microbiology Reviews, July 2007, p. 459-477, Vol. 20, No. 3, http://cmr.asm.org/cgi/content/full/20/3/459?view=long&pmid=17630335

In the arid Southwest some specific analyses for Coccidioides fungi could be revealing. See for example Mark Bultman's (USGS) poster at:
http://www.fws.gov/southwest/Climatechange/poster%20pdfs/ValleyFeverPoster_Bultman.pdf

As indicated above alternative sample collection may be warranted for certain kinds of biological analysis.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

Not my area of expertise. I would imagine that reasonable correction factors can be developed.

5. Are metal oxides a significant source of interference in thermal-optical analysis (TOA) of PM10-2.5 for OC and EC given the large expected soil component? If so, how should this interference be addressed?

Not my area of expertise. I would imagine that reasonable correction factors can be developed.

Network Design

1. Are sites with high PM10 and low PM2.5 good candidate sites for PM10-2.5 speciation? Given that there will be some urban and rural NCore monitoring sites with PM10-2.5 speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

Sites with high coarse to fine ratios are likely to be dominated by crustal material, and will not be ideal places to evaluate strengths and weaknesses of different sampling and size-separation techniques. However, I think a few such sites should probably be included in both the pilot and longer-term networks and specifically include sites heavily influenced by: windblown dust, agricultural activities, mining activities and industrial process emissions. In the pilot study, it would also be useful to challenge the size separation methods by including sites with relatively high fine to coarse ratios. It would also be desirable to include sites intended to collect and characterize urban roadway emissions, in both arid and humid regions. Some effort might also be made in the pilot study toward understanding spatial variability and the differences in coarse concentration and composition that might be expected at NCore locations compared to locations closer to sources. A few rural coastal sites on the West Coast in the far Southeast – such as the Redwood, Point Reyes, Everglades or Virgin Island National Park IMPROVE sites – might be useful to best characterize the size distributions, chemical and biological content of Asian and African dust.

2. If there is an opportunity to modify the NCore PM10-2.5 speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

Given the many questions & issues raised in the EPA staff memo and by the members of this review committee regarding sampling and analytical methods, analytes and site characteristics, it may not be possible or desirable to roll out a network of (identical) coarse speciation samplers at all 75 NCore locations by 1/1/11. I think the NCore concept was intended to be flexible, and that pending analysis of existing dichot data (for example from long-term California and Canadian studies), additional results from the current EPA (Bob Vanderpool) coarse particle monitoring sites, the planned pilot coarse speciation network, and other developments, it may be logical to consider changes to the proposed NCore coarse particle speciation network.

Possibly, many of the NCore sites which are otherwise very well suited for assessment of multiple pollutant exposures may not be ideally sited for measuring coarse particle concentrations, compositions and representative exposures. I think it would be useful to

intentionally locate some coarse speciation sites in source-oriented locations, as indicated above. Along similar lines, it might make sense to plan for occasional "event analysis" of samples from many sites on days when certain source influences are otherwise evident – for example wild fires or prescribed agricultural burns, "local dust storms" from different regions, Asian or African dust storms, agricultural tilling, pollen or insect events, etc. Seasonal compositing of samples may also be a useful technique to allow more sophisticated measurements such as for molecular carbon compounds, which require large sample sizes or are too costly for routine application.

I think an important complement to a coarse speciation network, and something that would enhance the value of existing fine speciation monitoring sites as well, would be to conduct an emissions characterization program in which source emissions are characterized by exactly the same sampling and analytical methods that are applied for ambient sampling (including both fine and coarse fractions which together provide better detail on sources). This might include a mix of direct emission sampling (with dilution / settling chambers) and "source oriented sampling – such as near roadway, etc.

If a relatively large number of ambient monitoring sites is considered important, it might be useful to consider a "nested" network, with many sites initially taking a "minimal" set of measurements (for example 1 in 3 day dichots with Teflon filters and XRF and optical absorption analysis – or possibly a second dichot with quartz filters for carbon and ion analysis). Additional samplers, higher sample frequencies, continuous analyzers, and/or additional analyses might be added at smaller numbers of sites or to provide more detail at times and places where the initial measurements show interesting results. As suggested above, it might be informative to conduct some screening toxicity tests on seasonally composited samples to determine locations where more detailed chemical or biological sampling and analyses are most warranted. Although there was never sufficient funding provided to support NCore "Level 1 sites", the concept is a good one and it might be especially applicable for coarse particle speciation monitoring, as it seems likely there will be a lingering need to develop and evaluate new sampling and analytical methods (at a few sites) even while less intensive "routine" coarse species monitoring is conducted at larger numbers of Level 2 sites.

Dr. Jay R. Turner

Implementation of a monitoring network for coarse particle ($PM_{10-2.5}$, called PMc in my comments) speciation will have many benefits including, but not limited to, information about emission sources and their relative contributions to burdens observed at the monitoring sites. The Agency is urged to make steady progress on the development and deployment of this network, but should also conduct the necessary pilot studies and ancillary evaluations (e.g. optimization of analytical methods) to ensure the network, when fully deployed, is robust in terms of sampling methodology and monitor siting. It might be necessary to make revisions to the pilot study design based on preliminary findings from the pilot network towards optimizing the measurement strategy. In my opinion, optimization of sampling hardware and monitor siting guidance (based on early results from the pilot network) should take precedence over meeting the January 1, 2011, date for full deployment of the PMc network at NCore sites. If the deployment date is delayed, the Agency should provide an explanation of the reason(s) for the delay, the remaining work to be done, and the revised timeline for network deployment.

$PM_{10-2.5}$ Speciation Measurement

1. Table 1provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?

The species and analysis methods in Table 1 (amended from the white paper, and referring to the Agency presentation at the February 9 teleconference) meet two objectives – identifying the major chemical components needed to reconstruct PMc mass (as stated in the charge question) and providing additional information about emission sources and their relative contributions. Priority should be given to the analyses needed for mass balance closure and this subset of the list should contain the conventional analyses for gravimetric mass, water soluble ions, XRF elements, and carbon by thermal-optical analysis. Carbonate carbon will influence the OM/OC ratio but is expected to be important for only a limited number of environments. Thus, the carbonate carbon analysis is recommended for the pilot network but if it is expensive then it might be possible to include it at only a subset of sites in the full network. The protein analysis is also recommended for the pilot network with an evaluation of whether these data bring sufficient added value to be performed for the full network.

2. 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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

All of these samplers have advantages and disadvantages as has been discussed in previous deliberations of this subcommittee. Paired PM_{10} and $PM_{2.5}$ FRMs might be most challenged at sites with relatively high $PM_{2.5}$ /PM_{10} ratios because the measurements uncertainties propagate for these independent measurements. This does not necessarily preclude the use of paired PM_{10}

and $PM_{2.5}$ FRMs, but their suitability should be evaluated within the context of the DQOs and MQOs. For example, if source apportionment is an objective then the error structure in the data would be an important consideration. (We have a small data set of XRF elements for filter samples collected in St. Louis using paired $PM_{2.5}$ and PM_{10} Harvard Impactors that can be shared with the Agency; it can be used to demonstrate limitations of the differencing method; there are additional data set, including sets collected by the Agency, which can be used to probe this issue). At this time, I give priority to dichotomous samplers. Historically, one concern has been the potential for losses from the coarse particle filters during handling and shipping since the fine particles present in a conventional PM_{10} sample act as "glue". I recall the Agency examined this issue in their recent PMc characterization field campaign. If it is deemed an issue there might be simple ways to stabilize the deposit on the filters prior to shipping. Samplers with multiple sampling channels, such as used in the CSN network, are preferred because they allow the collection of particles on different filter media using a single sampler. However, the use of parallel samplers (a one sampler-one substrate approach), such as used in the IMPROVE network, has proven to be robust. In either case, the design should be sufficiently flexible to permit the use of upstream sample conditioning such as denuders. For mass balance closure, the low flow rate of the MetOne SASS speciation monitor should not be a major issue since the focus will be on the major chemical constituents. However, there could be issues with detection limits for the trace elements that are often important for emission source identification, especially if paired with XRF instead of ICP-MS.

3. What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?

It will be helpful to understand how the virtual impactor cutpoint curve compares to the $PM_{2.5}$ FRM cutpoint curve. The $PM_{2.5}$ FRM impactor has been characterized in detail, and we know that the cutpoint curve is relatively broad (by design). The dichotomous sampler (or any other sampler being deployed) should also have a well-characterized cutpoint with this information ideally available when interpreting data from the pilot network, The white paper addresses potential artifact issues concerning carbon and nitrate; perhaps the nitrate is less of an issue if the counterion is not ammonium but rather sodium or potassium but it is not clear to me we can generalize our understanding of the chemical form of coarse PM nitrate based on the data collected to date. It would be ideal to evaluate the importance of denuders as part of the pilot network measurements.

4. The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?

The low flow rate for the MetOne SASS might indeed be an issue for trace elements if XRF is the de facto analytical method, further compounded if using the difference method. The low flow rate might be less of a concern if ICP-MS or a similar high-sensitivity method is used, but in this case there will be other tradeoffs regarding element-specific recoveries, cost, etc.

Certainly another layer of complexity is added when comparing reconstructed mass from samples collected at one flow rate to the mass collected by the $PM_{10-2.5}$ FRM at a different flow rate, with this being more of a sampling artifact issue than a detection limit issue.

5. Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?

The minor flow still has all of the coarse PM pulled through the inlet (i.e. upstream of the virtual impactor).

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

The core species measurements should be elements, ions, and ECOC, consistent with the $PM_{2.5}$ speciation network. A key issue is whether XRF can provide adequate data quality for some of the trace elements for conventional mass loadings on the filters. This is less of an issue for mass closure but might be important for source identification.

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

The target list for ions is reasonable. While conventional wisdom says a denuder is needed for high quality nitrate measurements, work performed for the IMPROVE program has shown that certain inlets can be quite effective denuding nitric acid (although I don't know about the extrapolation of these results to urban environments). Sampling with and without denuders should be performed in the pilot network to determine whether they are warranted. Also, Nylon filters should certainly be used in the pilot network and then an evaluation can be made concerning the importance of ammonium nitrate.

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

I do feel strongly that we need a better characterization of the bioaerosol component. However, I have no specific comments on the method. Analysis for fly ash by SEM could be insightful, but perhaps used only in cases where trace element compositions suggest there are potentially significant fly ash contributions to PMc (I repsct there might be some issues in teasing out a fly ash signature from a soil signature from the elemental data).

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

I leave this question to those colleagues with more expertise than me on this matter.

5. 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 so, how should this interference be addressed?

It is generally accepted that the presence of such compounds can dramatically shift the carbon evolution profile during thermal analysis – whether this leads to errors in the EC/OC split is not clear. While not focusing on PMc, one option might be to examine data collected from continuous ECOC instruments in environments with high metal oxide loadings. Does the relationship between thermal EC and optical EC change in time with increasing time after a clean filter has been installed (presumably some of the metal oxides will remain on the filter and accumulate in time).

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

The focus should not be exclusively on sites with high PM_{10} and low $PM_{2.5}$. The pilot sites should be chosen to represent a broad range of aerosol compositions and environmental conditions, with the results being used to refine the recommendations for which Ncore sites should have PMc speciation. There are other considerations, such as providing data sets of use to health scientists, which would support the selection of sites to collectively include a range of PMc levels.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

See my introductory comment which addresses the timeline for network deployment. At this point, I have no additional comments about the network design.

Dr. Warren H. White

$PM_{10-2.5}$ Speciation Measurement

I will start by recognizing, and commending, the Agency's early consultation with this committee and its plan to start with a pilot study. An eventual network of 75 sites sampling at least one day in every three will represent a huge commitment of resources that might otherwise be devoted to more time-resolved measurements, or to biochemical assays and other new approaches to sample characterization, or to nuclei counters and other instruments more responsive to ultra-fine particles. Any one of these alternatives to the straightforward extension to $PM_{10-2.5}$ of current $PM_{2.5}$ measurements might yield greater insight into which particles should be of greatest concern to regulators. I urge the Agency to delay the general introduction of $PM_{10-2.5}$ monitoring at NCore sites until the pilot study has had adequate time to develop, explore, and assess a variety of sampling and analytical methods.

"Since EPA is requiring $PM_{10-2.5}$ speciation monitoring primarily for scientific purposes…"
It's not at all clear to me what those scientific purposes would be – source attribution? Assessment of hazardous components as called for by the NRC (2004)? The methods under discussion, largely derived from the existing $PM_{2.5}$ speciation network, don't seem very well adapted to either of these.

Source attribution: We have considerable experience with source attribution using speciated $PM_{2.5}$ data. That experience has taught us that it is hard to distinguish between different carbonaceous sources using EC and OC from thermal-optical analysis, and that it is hard to distinguish between different sources of dust using elemental analysis. But organic and crustal materials make up the bulk of $PM_{10-2.5}$ nearly everywhere. So what can the proposed level of speciation do? It can distinguish smoke from dust, but how often do local agencies encounter high $PM_{10-2.5}$ that they can't easily associate with obvious local and regional sources of smoke or dust?

Hazard assessment: Its 2005 assessment of the epidemiological evidence lead EPA to *"consideration of thoracic coarse urban particulate matter ($UPM_{10–2.5}$) as an indicator for a thoracic coarse particle standard … qualified so as to include any ambient mix of $PM_{10–2.5}$ that is dominated by resuspended dust from high-density traffic on paved roads and PM generated by industrial sources and construction sources, and to exclude any ambient mix of $PM_{10–2.5}$ that is dominated by rural windblown dust and soils and PM generated by agricultural and mining sources."*

In other words it judged that dusts of crustal origin, benign in rural settings, became contaminated in cities with surface coatings and other urban grime. It will be hard to detect such trace contaminants in $PM_{10-2.5}$ samples with the bulk chemical analyses currently used with $PM_{2.5}$; it will be still harder against a background of chemically-similar $PM_{2.5}$ mixed in with a PM_{10} sample. The pilot study should give particular attention to analytical methods that can target specific fractions expected to be enriched in $PM_{10-2.5}$, such as biological markers.

Reference

NRC (2004) *Research Priorities for Airborne Particulate Matter IV: Continuing Research Progress.* National Academies Press, Washington.

Dr. Yousheng Zeng

$PM_{10-2.5}$ Speciation Measurement

Among the four filter-based sampler types, dichotomous samplers should be used for speciation measurement. Dichotomous samplers produce physically separate coarse samples for speciation chemical analysis, which in turn reduces interferences and complications. They have been used for long time and are better understood.

Although the difference method is FRM for coarse particle mass measurement, it may not be most suitable for speciation measurement. When the levels of a component (or species) in the $PM_{2.5}$ sample and PM_{10} sample are close (i.e., the component primarily associated with $PM_{2.5}$), the difference between the two measurements may be too small compared to analytical uncertainty, making the speciation measurement unreliable. This problem is more significant when the chemical analysis has a sufficient method detection limit, but poor precision (repeatability). In that case, if dichotomous samplers are utilized, the results will be more reliable.

Even though dichotomous samplers are not FRM for PM mass measurement, their deviation from FRM, if any, is small. Considering uncertainties associated with many chemical analyses at low concentration levels, this possibly small deviation should be acceptable.

$PM_{10-2.5}$ Species

Speciation for organic portion seams lacking. If feasible, it would be useful to analyze for semi-volatile organic species and parameters typically obtained in ultimate analysis. The semi-volatile organic species should be useful in source apportionment. Also, ultimate analysis may help close the mass difference. I am not sure this will be feasible or practical. I just want to bring this up for EPA to consider for the pilot sites.

Network Design

For selection of pilot sites, high PM_{10} and low $PM_{2.5}$ sites should give more PM coarse fraction to work with. However, I think it is also important to select some pilot sites that represent low PM_{10} and high $PM_{2.5}$. At these sites the PM coarse fraction would be low. It would be a good test to see how the speciation methods perform when the coarse fraction is low (e.g., will method detection limits be low enough to cover some important species). Also, when EPA considers high or low PM_{10} or $PM_{2.5}$, EPA should consider not only the ratio between PM_{10} and $PM_{2.5}$, but also the mass levels of PM_{10} and $PM_{2.5}$. Both high mass level and low mass level sites should be included in the pilot program to fully assess candidate speciation methods.

Dr. Barbara Zielinska

$PM_{10-2.5}$ Speciation Measurement

1. *Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Are there additional $PM_{10-2.5}$ target species or methods that can be used to help identify the source of unidentified mass in order to obtain better mass closure?*

In my opinion, Table 1 is missing the speciation of $PM_{10-2.5}$ organic compounds. Taking into account that organic carbon (OC) constitutes significant portion of $PM_{10-2.5}$ mass, it is essential to have a general understanding what species comprise this organic mass. Are these species mostly of biogenic origin, biological material, or perhaps also anthropogenic? This knowledge may have important health implications and so far is missing. Since the primary objective for $PM_{10-2.5}$ speciation data is to support further research in understanding their chemical composition and source, the importance of the organic mass speciation should not be overlooked. It may help in source apportionment and in determining OM/OC factor. The organic mass speciation should be attempted during pilot study phase in some selected NCore sites that are representative of urban and rural settings. The EPA should not specify target organic compounds to be quantified (as it has been done so far), but should require the identification of as many organics as possible to get some knowledge of the organic mass composition of coarse particles in different locations. $PM_{10-2.5}$ is very different from $PM_{2.5}$ and the source tracers that worked for fines may not work for coarse particles.

2. *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. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?*

PM_{10} and $PM_{2.5}$ FRM are not appropriate for speciation of $PM_{10-2.5}$, since when the fine and coarse particles are mixed together, their composition can be potentially altered. Also, the determination of chemical composition by a difference method is inherently less precise and it is virtually impossible for organic compound's speciation. Although volatility issues are likely less important for $PM_{10-2.5}$, they are important for $PM_{2.5}$, which may bias the results of the difference method. Dichotomous sampler (or equivalent), which provides a separate $PM_{10-2.5}$ fraction are more appropriate for chemical speciation.
In addition, continuous methods for mass measurements and OC/EC speciation should be encouraged.

3. *What are the $PM_{10-2.5}$ speciation sampling artifacts that may be encountered using the samplers mentioned above and how should they be addressed? Is speciation by the difference method problematic for $PM_{10-2.5}$ speciation and if so what specific issues make it problematic?*

See my answer to Question #2.

4. *The current and most widely used $PM_{2.5}$ speciation sampler is the MetOne SASS and it has a flow rate of 6.7 Liters per minute (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 for $PM_{10-2.5}$ by difference, would the 6.7 Lpm flow rate be problematic, especially with the need to compare reconstructed mass to the mass collected by the $PM_{10-2.5}$ FRM?*

As stated above, I do not recommend speciation by the difference method. Dichotomous sampler with 16.7 Lpm flow rate is a better choice.

5. *Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?*

Since the total mass collected in the minor flow channel is a function of the inlet flow, this should not be a problem.

$PM_{10-2.5}$ Species or Components

1. Table 1 provides a list of proposed $PM_{10-2.5}$ species and analysis methods. Among these species, which are most important? Are there important $PM_{10-2.5}$ species or components missing from this list? Are there important analysis methods missing from this list?

Speciation of organic compounds is missing (see my answer to question #1 above). Such speciation is important from health effects point of view, as well as source attribution and mass closure.

2. In the consideration of potential ion measurements for $PM_{10-2.5}$ species, what ions should be on the target list? Are nitrate or ammonium ions important? If so, is an acid gas denuder and nylon filter required for the proper collection of these species in $PM_{10-2.5}$?

I don't think an acid gas denuder or nylon filters are required. The ions and their analysis methods listed in the corrected Table 1 (slide #9 in Joann Rice presentations) seem to be adequate

3. The 2004 CD included a list of important $PM_{10-2.5}$ components which included biological materials and fly ashes. If these species are important to characterize, what specific types of biological materials and fly ashes should be included? Is scanning electron microscopy (SEM) on Teflon filters sufficient to quantify and identify these species? Is the proposed total protein assay technique important to obtain a quantitative indicator of the total biological material present?

Fly ashes may only be important at sites close to some local sources (fly ashes were removed from Table 1 presented by Joann Rice). SEM on Teflon filters is not ideal for identification of biological materials - polycarbonate filters are better. Total protein assay may be important as an indicator of allergens, fragments of bacteria, etc. However, this assay is not adequate as an indicator of the total biological material present. Plant or soil derived material may be an important contributor. Analysis of sugars, sugar alcohols, phytosterols, triterpenoids, etc., may

help in quantification and identification of types of biological materials present in coarse particles.

4. Can the complication of particle size and absorption effects in XRF be resolved using absorption correction factors? If not, what other method(s) should be considered?

It would be desirable to compare ICPMS with XRF during a pilot study to answer this question.

5. *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 so, how should this interference be addressed?*

Metal oxides, if present in significant amounts may affect OC/EC split, however total carbon should not be affected. Humic material or carbonates are another potential interfering species. This question should be addressed during a pilot study.

Network Design

1. Are sites with high PM_{10} and low $PM_{2.5}$ good candidate sites for $PM_{10-2.5}$ speciation? Given that there will be some urban and rural NCore monitoring sites with $PM_{10-2.5}$ speciation, what other factors should be considered in selecting the pilot monitoring and long-term sites or locations?

It would be important to include both types of sites, with low and high PM_{10} to $PM_{2.5}$ ratios. Especially in urban locations and/or close to highways both types may be important. Variations in geographical distribution, costal and inland locations, urban and rural sites, proximity of mining sources, etc., should also be considered.

2. If there is an opportunity to modify the NCore $PM_{10-2.5}$ speciation monitoring requirements during a future rulemaking, should changes to the network design be considered? For example, changing the total number of required monitors and/or the required locations?

Flexibility was one of the major components of NCore design, so yes. However, prior to implementing 75 $PM_{10-2.5}$ speciation sites, the throughout evaluation of pilot study data should be completed. It seems that a goal of launching long-term $PM_{10-2.5}$ network by 2011 is not very realistic. We should learn first what works and what doesn't and allow enough time for scientific community to evaluate pilot study data and come to a consensus regarding the best methods of coarse particles monitoring and speciation.