10 February 2009 Preliminary Review Comments from CASAC AAMMS on the Key Issues Related to $PM_{10-2.5}$ Speciation Monitoring

Comments received:

Dr. Judith C. Chow 2
Mr. Henry (Dirk) Felton 15
Dr. Philip K. Hopke 18
Dr. Kazuhiko Ito 21
Dr. Thomas Lumley 24
Dr. Peter H. McMurry 26
Dr. Warren H. White 30
Dr. Barbara Zielinska 31
Dr. Delbert Eatough 33

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?*

Table 1 provides a comprehensive list of elements, ions, carbon, and bioaerosol indicators. 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. Oxides of major crustal components are used in the calculation for geological material. There are two commonly used metal oxide formulas that give similar estimates:

Geological Material = 1.89 × Al + 2.14 × Si + 1.4 × Ca + 1.43 × Fe (1)

Geological Material = 2.2 × Al + 2.49 × Si + 1.63 × Ca + 2.42 × Fe + 1.94 × Ti (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 19–56 μg/m^3. The variable nature of the OC/OM ratio introduces uncertainties in the estimation of $PM_{10-2.5}$ organic material. A 1.2 multiplier is appropriate for hydrocarbons (composed of H and C atoms), but the 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 and nitrogen atoms. 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?*

All of the 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 These 5 L/min units have well-characterized inlets.

Optical particle counters (OPCs, e.g., Grimm Dust Monitor, TSI DRX DustTrak II) should also be considered as they can detect short-duration events and can be comparable with filter measurements under certain circumstances (Grover et al., 2006; Peters et al., 2006; Teikari et al., 2003).

Other low- and medium-volume sampling systems are still in use (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 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). Nitric acid 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 difference method with inertial impactor or sharp-cut cyclone.

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 $PM_{10-2.5}$ particles 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., OMNI, PQ2000, Airmetrics) 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, 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). If the MetOne SASS is deemed adequate for chemical measurements with its larger filters and lower flow rates, then the higher areal concentration on the 37 mm filter and 16.7 Lpm flow rates would make the sensitivity for dichotomous samplers even better.

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 were submitted for 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 $PM_{10-2.5}$ samples (Motallebi et al., 2003a; 2003b; 2003c).

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

$PM_{10-2.5}$ Species or Components

6. *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?*

$PM_{10-2.5}$ 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 $PM_{10-2.5}$ components to be considered.

Cao et al. (2005) found that carbonate accounting 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 in non-urban IMPROVE sites (Chow and Watson, 2002), its abundances are expected to be higher in $PM_{10-2.5}$ and should be measured, especially for Asian dust intrusions (VanCuren, 2003; VanCuren and Cahill, 2002). Without acidification for carbonate analysis, the presence of carbonate could bias both OC and EC measurements (Chow and Watson, 2002).

Organic carbon in urban and rural PM_{10} road dust and agricultural soil 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). $PM_{10-2.5}$ b_{abs} measurements at various wavelengths might be considered, especially for locations where only Teflon-membrane filter samples will be collected.

7. *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 anions (i.e., Cl^-, NO_3^-, and $SO_4^=$) and cations (i.e., Na^+, K^+, NH_4^+) listed in 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 forms 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^{+2}, 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, it is recommended to use a 47 mm filter cassette (with an exposed area of 11.8 cm^2), which allows 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 analysis is considered.

8. *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 storage piles of fly ash nearby, but most modern industrial stacks have particle removal 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; 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.

9. *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. Table A shows an example of such correction factors for a specific analysis configuration and particle size distribution.

Table A. Correction factors applied for $PM_{10-2.5}$ or PM_{10} particles (after Dzubay and Nelson, 1974).

Element	Correction Factor
Al	2.439
Si	2.083
P	1.724
S	1.563
Cl	1.429
K	1.282
Ca	1.235

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.

10. *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 $PM_{10\text{-}2.5}$ mass and composition, respectively. The $PM_{2.5}$ Ca from CSN sites can be used to select sites for potential 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 $PM_{10\text{-}2.5}$ 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 $PM_{10\text{-}2.5}$ 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, 619-631.

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.

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.

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

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.

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.

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.

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.

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.

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,

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.

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.

Mr. Henry (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?*

Organic Carbon, volatile species

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 the SASS is the most appropriate choice if multiple filter media are required for each sample.

Continuous instruments with appropriate inlets - Particle Mass spec?

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?*

Mathematical adjustments to Dicot concentrations are less attractive for component analysis More volatile

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?*

At sites in the Northeast the coarse mode filter most likely will not have enough material for some of the component analysis.

$PM_{10-2.5}$ 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?*

This question is geographically, seasonally, health and urban/rural dependent. In the Northeast, the concentrations of elements in PMc tend to be around 30% of the mass. From a Northeast perspective, the only element missing from Table 1 is Vanadium which can have significant PMc concentrations in some areas. Soluble ions may be the least important group of species on the table. S, Cl and K can be estimated from the elemental data and ammonia data may be more accurate if the NATTs program initiates the planned 24-hr denuder sampling for ammonia.

Carbon is probably the most important overall group of PM components because it includes many compounds that are not well identified and are likely to be correlated with health effects. 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.

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 $PM_{10-2.5}$?*

This question is geographically, health and urban/rural dependent.

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 and 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?*

This is not much of a problem for sites in the Northeast. The XRF analysis for the more heavily loaded PM-10 filters is modified by extending the count time for the detector. If there is concern that this issue is becoming problematic at sites with heavier large particle loading, periodic digestive analysis should be used to validate the XRF results.

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.

<u>Network Design</u>

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?*

Yes, but these sites may not adequately challenge the sampling methodology. The sites for the pilot should be chosen to represent a range of the components of PMc, not just the range of the concentration of PMc. NCore sites are situated to represent large areas and generally will not have significant 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 situated to help ascertain the highest concentrations of likely PMc compounds associated with health effects. This strategy will help demonstrate the adequacy of the method as well as assist health researchers by providing data that is most likely to be relevant for their work.

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 more appropriate to tailor the PMc speciation program to the species which are prevalent and likely to be related to health effects in specific regions of the country. In North-Eastern 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. Health researchers are continually stressing a preference for daily data

Dr. Philip K. Hopke

$PM_{10-2.5}$ Speciation Measurement

3. *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?

4. *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.

5. *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.

6. *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.

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

Probably not.

$PM_{10-2.5}$ Species or Components

8. *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. Is 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.

9. *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.

10. *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.

11. *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.

12. 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

13. 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.

14. 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.

Dr. Kazuhiko Ito

$PM_{10-2.5}$ 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?*

Some of the non-exhaust traffic-related PM components may be either present in the coarse mode or attached to the surface of coarse particles. A recent review (Thorpe and Harrison, 2008) suggests that Cu and Sb may reliable tracers of the presence of brake wear particles in the urban environment. Schauer et al.'s study (2006) also showed the presence of Zn, Mn, Cu, Cr, V, Sr, Mo, and Sb in brake and tire wears.

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?*

No comment for now.

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?*

No comment on the first part of question. Regarding the second part, the relative quantity of some PM components in the two size fractions, depending on their detection limit, may be "problematic". For the coarse mass concentrations, I recall that the EPA showed that the difference method with low-flow samplers did not result in negative values. For certain species whose levels are very low in the coarse fraction, I imagine that the difference method may result in negative values. However, these negative values (within the range of statistical fluctuations around zero) simply means low levels, and I am not too concerned about them.

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 don't know this area enough to answer this question.

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

I don't know the data enough to answer this question.

$PM_{10-2.5}$ 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?*

See my comment on Question 1 of $PM_{10-2.5}$ Speciation Measurement section. In addition to the non-exhaust traffic species, we should also be concerned about other species that may be deposited on the surface of the coarse particles that are not of crustal origins. I may be wrong, but with XRF, don't we get all the species with not much more cost than that for just measuring those on Table 1? Why are we restricted to the mostly crustal materials? It is possible that minute amount of what's deposited on the surface may be more toxic than the mass of the crustal material. Also, some of the elements on Table 1 have either generally bad signal-to-noise ratio (e.g., P, Mg, Cr) or poor spatial correlation (e.g., Cr, Mg), so it would be difficult for these species to be "important."

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 $PM_{10-2.5}$?*

We don't know enough about possible effects of these species when they are on the surface of coarse particles to judge if they are important or not, I think.

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 don't know this area enough to answer this question.

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 don't know this area enough 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?*

I don't know this area enough to answer this question.

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?*

I would be most concerned about the spatial variation of coarse species, which would be more variable than that for fine mass species. The "spatial representation" of a coarse particle monitor may be different depending on the coarse constituents of concern in that locale. Therefore, I would recommend pilot monitoring in several different regions to uncover potential issues.

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?*

As far as I can tell, there are not many studies (aside from those mentioned in the white paper) that examined spatial variation of coarse PM constituents using many multiple sites in different regions. It is not coarse particles, but the NYC Dept of Health and Queens College is currently conducting multi-site (up to 150 sites, not all simultaneously but with a continuosly operating reference site) within NYC to monitor spatial variation of air pollutants including PM2.5 chemical species. Such results may be useful input for possible future revisions of location design.

References

Schauer JJ, Lough GC, Shafer MM, Christensen WF Arndt MF, DeMinter JT, Park JS. Characterization of metals emitted from motor vehicles. Res. Rep. Health Eff. Inst., 2006. 133:1-76.0000

Thorpe A, Harrison RM. Sources and properties of non-exhaust particulate matter from road traffic: A review. Sci. Tot. Environ. 2008. 400: 270-282.

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?*

I do not understand the rationale behind a focus specifically on the analysis fly ash particles by SEM. Perhaps there is some background I am not aware of. It seems arbitrary to identify fly ask as the sole target of SEM analyses. Similarly, particles originate from many types of sources. It seems odd to identify only fly ash as a type of particle to be analyzed.

Biological material is a poorly understood category of particulate matter that is likely to be significant. Matthias-Maser and coworkers (2000) 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) 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) 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 think some thought ought to be given to the analysis of water soluble organic carbon (WSOC). WSOC is believed to be secondary in origin and can contribute significantly to OC mass (Hennigan et al. 2008; Stone et al. 2008). Recent work suggests that the emissions of biogenic precursors may be correlated with secondary WSOCs (Carlton et al. 2007; Hennigan et al. 2008). Work of Turpin and coworkers shows that cloud processing may an important source of SOA, as it is for sulfates. The extent to which SOA is water soluble will play a role in determining their environmental effects.

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 Prof. 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 Prof. 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 such artifacts occur with the FRM mass sampler, then it would not be possible to achieve closure on mass and reconstructed mass based on speciation measurements. Thus, the ideal sampler could lead to "true mass" that might not agree with FRM mass. Speciation measurements

carried out 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 that is a preferable sampler. I am not certain that it does, however.

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?*

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?*

Missing: WSOC?
Questions:
-Specifying SEM for fly ash.
-Suitable analytical method for biological aerosols

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 important. Thought should be given to organic ions as well as WSOC. I will defer to others regarding the use of denuders (I recognize they would add complexity to the network). If needed to obtain accurate results, they should be included.

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?*

The contribution of biological species to aerosol particles is a poorly understood of potentially significant importance. I am not knowledgeable about analytical methods, so do not know if it is appropriate to mandate their measurement at this time. If a method is available, it would be desirable to measure them.

I do not see a clear reason for separating out fly ash as a source category.

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?*

Variability in likely sources of biogenic aerosols
Relative humidity
-impact on WSOC production
-impact on soil dust resuspension

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.

References

Carlton, A. G., B. J. Turpin, K. E. Altieri, S. Seitzinger, A. Reff, H. J. Lim and B. Ervens (2007). "Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments." *Atmospheric Environment* **41**(35): 7588-7602.

Fuzzi, S., P. Mandrioli and A. Perfetto (1997). "Fog droplets - An atmospheric source of secondary biological aerosol particles." *Atmospheric Environment* **31**(2): 287-290.

Hennigan, C. J., M. H. Bergin and R. J. Weber (2008). "Correlations between Water-Soluble Organic Aerosol and Water Vapor: A Synergistic Effect from Biogenic Emissions?" *Environmental Science & Technology* **42**(24): 9079-9085.

Hennigan, C. J., A. P. Sullivan, C. I. Fountoukis, A. Nenes, A. Hecobian, O. Vargas, R. E. Peltier, A. T. C. Hanks, L. G. Huey, B. L. Lefer, A. G. Russell and R. J. Weber (2008). "On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City." *Atmospheric Chemistry and Physics* **8**(14): 3761-3768.

Matthias-Maser, S., V. Obolkin, T. Khodzer and R. Jaenicke (2000). "Seasonal variation of primary biological aerosol particles in the remote continental region of Lake Baikal/Siberia." *Atmospheric Environment* **34**(22): 3805-3811.

Mohler, O., P. J. DeMott, G. Vali and Z. Levin (2007). "Microbiology and atmospheric processes: the role of biological particles in cloud physics." *Biogeosciences* **4**(6): 1059-1071.

Stone, E. A., D. C. Snyder, R. J. Sheesley, A. P. Sullivan, R. J. Weber and J. J. Schauer (2008). "Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment 2006." *Atmospheric Chemistry and Physics* **8**(5): 1249-1259.

Dr. Warren H. White

General comments

Since my subsequent comments will be lacking in enthusiasm for this proposal, 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 biochemical assays and other new approaches to sample characterization, or nuclei counters and other instruments more responsive to ultra-fine particles. It is not obvious to me that one or more of these or other less-straightforward extensions of current PM measurements might not yield a much bigger payoff in terms of understanding which particles should be of greatest concern to regulators.

"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, the Agency judged that there were critical differences between a mix of resuspended dusts from paved roads, construction, and factories, on the one hand, and resuspended dusts from agricultural and mining operations on the other. I think that it will be very hard to apportion $PM_{10-2.5}$ samples among these closely related fractions on the basis of bulk composition, particularly if the analyses themselves are performed on separate samples of PM_{10} and $PM_{2.5}$.

Reference

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

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 organic compounds that are present in coarse particles. 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. This speciation should be attempted 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 require the identification of as many organics as possible to get some knowledge of the organic mass composition in different locations.

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 may not be 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. 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 seems to be more appropriate for chemical speciation.

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?*

In my opinion, 6.7 Lpm is rather low for detailed chemical speciation. Although some species can be measured by combining multiple filters and extracting them together (i.e. ions, organic species), mass, OC/EC and elements by XRF have to be done using separate filters. Thus, it is necessary to collect sufficient $PM_{10-2.5}$ mass for these analyses.

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.

Dr. Delbert Eatough

6 February 2009

Comments by: Delbert J. Eatough

On: Consultation on Coarse Particle Speciation

General:

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 some 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.

While many components of coarse particles will be unaffected by the sampling protocols used, this is not true for all components. Thus, 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 this may be very important.

In the review of these two areas in the material to follow, I have relied mainly on our past work. I have done this because of the short time available to provide comments and my not having immediately available references to related work by others. However, it should be recognized that the effects noted below have been observed by several investigators.

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 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.

Such sampling should be done at at least some of the NCORE sites.

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 particle phase can be lost from particles during sampling making it difficult to measure). The composition of coarse particles may also include semi-volatile material, 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. 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 $PM_{10-2.5}$. A dicot based FDMS has now been release by Thermo which will also measure both $PM_{2.5}$ and $PM_{10-2.5.}$ 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.

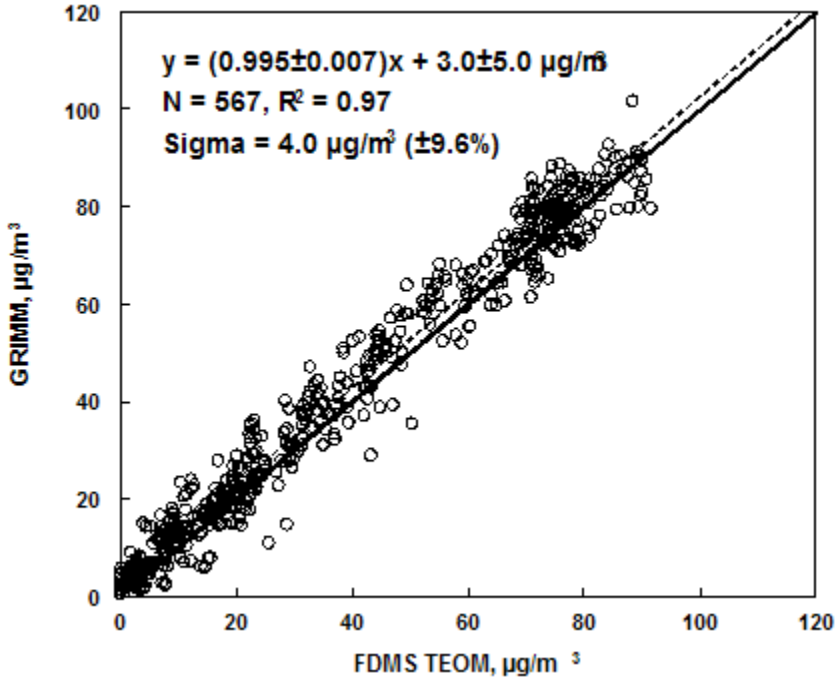

Figure 1. Comparison of $PM_{2.5}$ hourly average mass measurements by an FDMS-TEOM and a GRIMM monitor for the 19 January through 16 February 2007 study at Lindon, Utah. The linear regression fit to the results are given in the Figure

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.

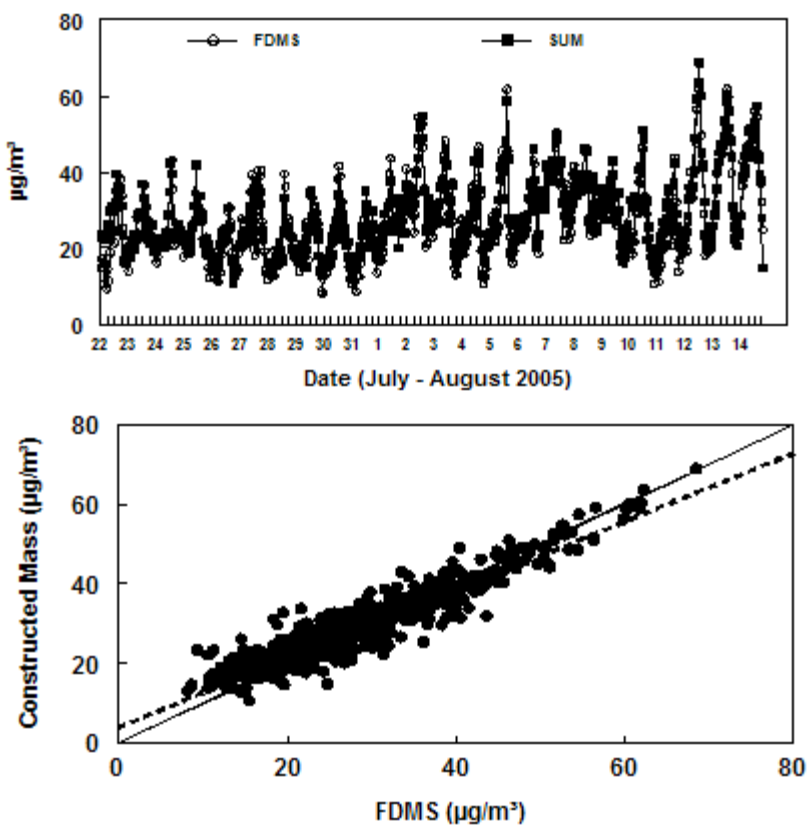

Figure 2. Semi-continuous constructed mass (y axisin both plots) vs. FDMS measured mass. Constructed mass is the sum of all the major components of the aerosol including; NVOM, SVOM, EC, NH_4NO_3 and ammonium sulfate.

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 ablility 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 °C), 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 convention 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, with some of the points showing a bias towards higher SVM concentrations for the PM_{10}. 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 particle semi-volatile material is organic.

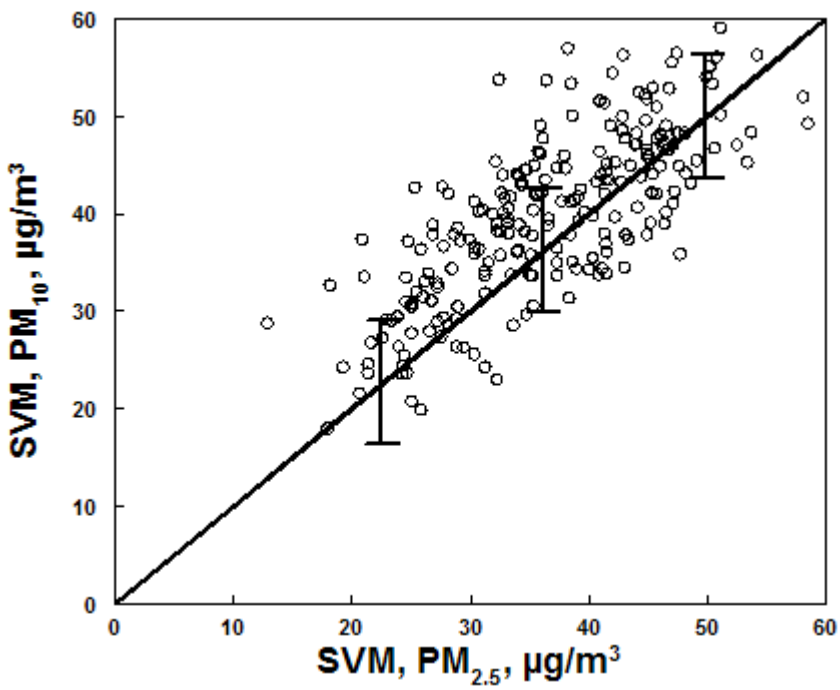

Figure 3. Comparison of the calculated concentrations of $PM_{2.5}$ and PM_{10} semi-volatile material at Lindon UT, see text.

Comparisons such as those shown here should be obtained in the EPA 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.

Responses to Charge Questions.

$PM_{10-2.5}$ 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?

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.

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. 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 sem-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 the fly ash particles.

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?

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 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?

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 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?

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. 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 is a function of the inlet flow and not the minor flow, I would not think this would be a problem.

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?

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 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?

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 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 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?

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 PM10-2.5 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.

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?

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 PM10-2.5 speciation monitoring requirements during a future rule making, 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.