10 February 2009 Mr. George Allen Preliminary Review Comments on Coarse Particle Speciation

$PM_{10-2.5}$ 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?*

Species: None that I am aware of; uncertainties in OC [estimated] mass measurements (there are many) may be part of the missing mass puzzle. Methods: ICPMS may be needed to get robust measurements of some of the listed water soluble species at the range of concentrations expected from a dichotomous coarse channel filter.

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 PM-coarse, I strongly recommend using only a dichotomous sampler (virtual impactor) for coarse PM speciation sampling, since it has multiple advantages over a simple difference method (accuracy and precision, separation of pm-coarse from most of the pm-fine).

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?*

There are the usual fuzzy issues with OC artifacts, both positive and negative; we will probably have to live with these. The issue of how OC blanks will be created, handled, and applied to the data, and how samples are transported and stored (warm or cold) before analysis is important to clearly define. Another important issue is ammonium from Nylon filters. Ammonium from ammonium nitrate can not be measured with that media, despite the long held "conventional wisdom" that it would be; this assumption has no basis, and in fact the opposite (e.g., ammonium loss) would be expected. This has been confirmed: "The amount of ammonium lost at most sites could be explained by the amount of NH4NO3 present in the sampled aerosol." From: "Loss of fine particle ammonium from denuded nylon filters", Xiao-Ying Yu, Taehyoung Lee, Benjamin Ayres, Sonia M. Kreidenweis, William Malm and Jeffrey L. Collett, Jr. , *Atmospheric Environment*, Volume 40, Issue 25, August 2006, Pages 4797-4807.

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

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?*

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

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

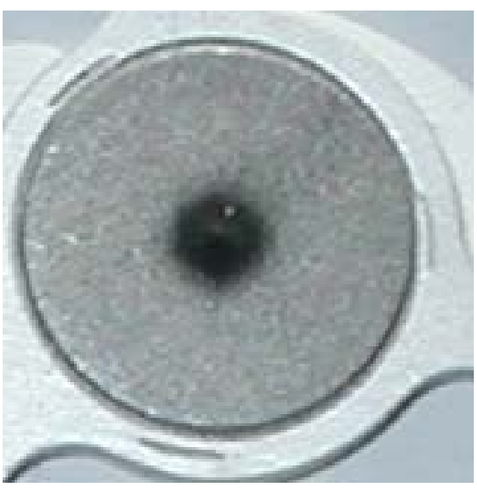
Yes it is, for the "classic" dichot inlet flow of 16.7 lpm. Note that although the coarse channel flow is only 1.67 lpm, the coarse channel dichot filter includes (in theory) all the coarse particles present in the 16.7 inlet flow. Thus, the low flow for the coarse channel is not a relevant issue, and the comment on page 8 of EPA's background document for this consultation about adequacy of XRF for dichot samples is not relevant.

$PM_{10-2.5}$ 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?*

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

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



Finally, it may not be worth the added analytical expense to fully characterize carbonate carbon with a separate analysis. A proper TOA run time-temperature profile (one that goes higher than 580C-helium) can give a reasonably useful indication of carbonate carbon. Carbonate comes off as a sharp peak at about 700-750 C, during the highest helium only temperature step in the Sunset Labs laboratory carbon analyzer protocol. With some care, the modest amount of OC that comes off in this last helium only temperature step can be differentiated from carbonate, since the OC usually evolves off more slowly than carbonate. Also, it is important to get carbonate off at this time in the run profile, since otherwise it could be classified as EC.

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?*

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

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?*

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

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

This may be a large problem for coarse pm speciation by difference, since PM10 loading will be larger than that on a pm-fine or pm-coarse dichot filter. It is less of a problem with a dichotomous sampler. As such, absorption correction factors are more practical for dichot filters. Still, ICPMS should be considered as an alternative analysis technique for water soluble components since it is both more sensitive and does not have any issue with self-absorption.

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

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

Network Design

1. *Are sites with high 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?*

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

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

I do not recommend the full suite of pm-coarse speciation measurements for the entire NCore network; it would be too resource intensive and require 5 pm-coarse samplers per site, an absurd burden on monitoring agencies. A subset of sites in very large urban areas with most of the measurements in Table 1 of the white paper (with 3 samplers?) might be useful to run on a daily basis. The remainder of the sites could run every third day with limited speciation -perhaps just XRF on Teflon, or maybe adding carbon -- keeping the number of pm-coarse samplers down to two. EPA must keep in mind that resources are limited and we will probably never be able to implement an optimal pm-coarse speciation network on a NCore-like scale.