Mr. Dirk Felton Updated Review Comments for AAMMS Coarse Particle Consultation

$PM_{10-2.5}$ Speciation Measurement

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

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

2. *Various sampling devices, including dichotomous samplers, MetOne SASS speciation monitors, PM_{10} and $PM_{2.5}$ FRMs are potential sampling devices (with the appropriate filter types) for $PM_{10-2.5}$ speciation. Among these sampler types, which should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?*

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

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

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

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

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

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

During the recent FEM equivalency evaluations performed by ThermoFisher Scientific, Franklin, MA,

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

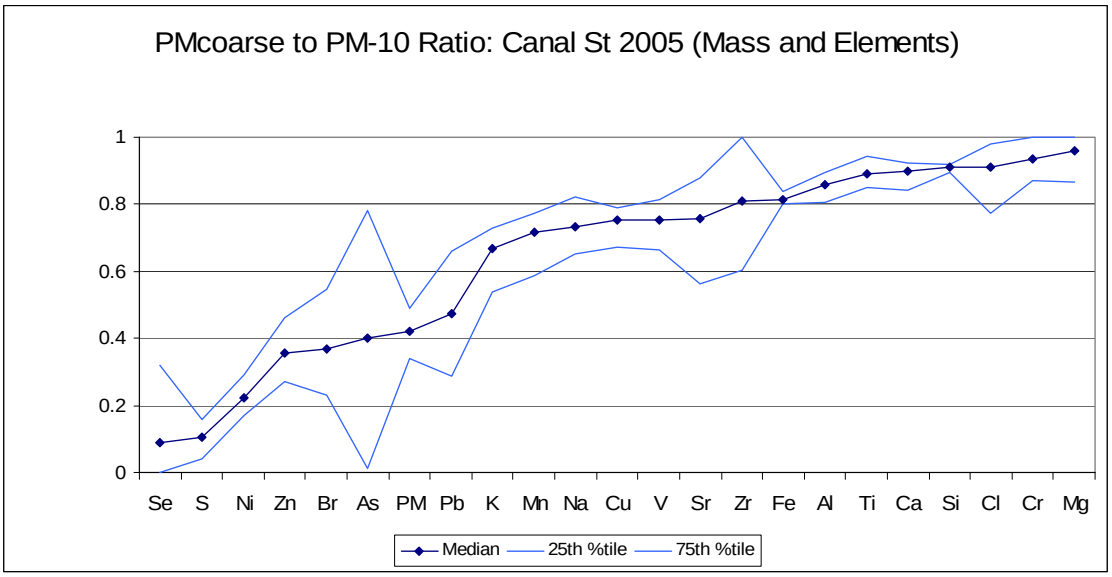
5. *Is the amount of particle mass collected on the dichotomous filters (especially the minor flow) sufficient for speciation chemical analysis?*

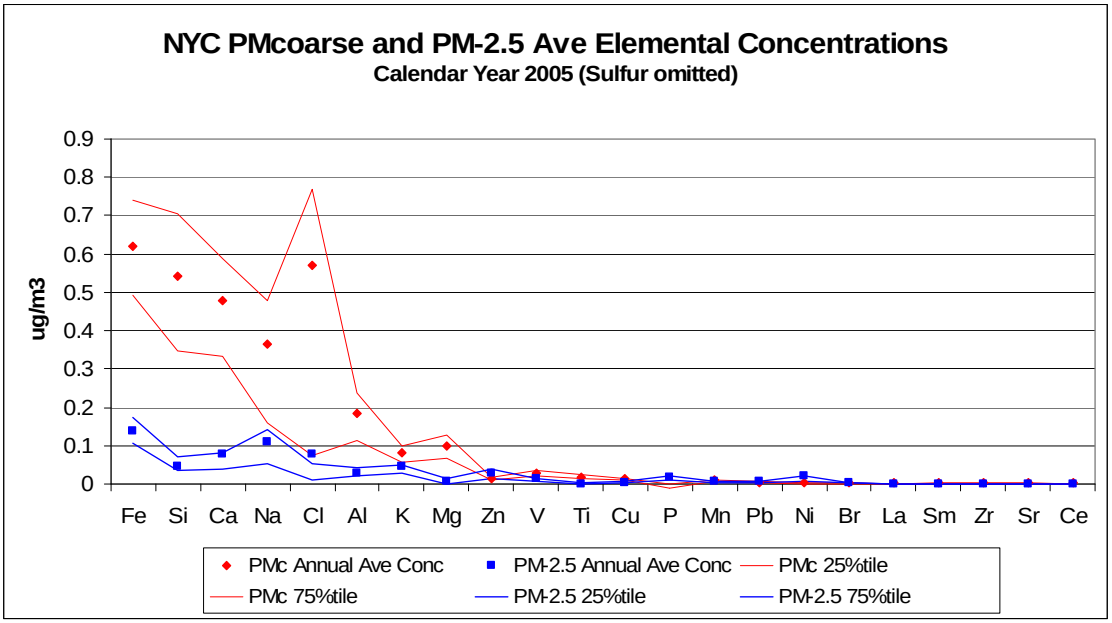
During the Thermo Fischer Scientific FEM evaluation in Queens NY last summer, the correlation between the virtual impactor Coarse mode data and PMc by filter difference was not as good as the correlation with the fine mode. This is not too surprising considering the low PMc concentrations and the issue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

$PM_{10-2.5}$ Species or Components

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

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





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

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

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

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

As with all PMc data, the relative importance of one component over another is dependent on location and sources. In and around industrial areas and large, older urban areas such as cities in the midwest and northeast, fly ash and oil soot are found in significant concentrations in the air. Often the majority of these particles are larger than 10 microns and are likely to be excluded in PMc measurements. Since these particles may be correlated with health effects, the pilot monitoring program should consider

evaluating concentration differences in results between samples collected with PMc samplers and samplers with low volume TSP inlets such as the URG-2000-30DG.

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

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

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

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

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

5. *Are metal oxides a significant source of interference in thermal-optical analysis (TOA) of $PM_{10-2.5}$ for OC and EC given the large expected soil component? If so, how should this interference be addressed?*

The IMPROVE program should have some insight into this.

<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?*

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

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

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

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

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