Comments regarding monitoring methods for the measurement of PM lead in the atmospheric

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Re: Draft Federal Reference Method (FRM) for Lead in Pb-PM_{10}

1. What are your comments on the use of the low-volume PM_{l0c} FRM sampler as the Pb-PM_{10} FRM sampler?

The application of the PM10c FRM sampler is an acceptable approach for the monitoring of lead. It leaves open the possibility of missing Pb exposure from PM_Pb > 10 μm diameter particles. Measuring the concentration of PM_Pb as a function of particle size at a select number of representative monitoring sites would address this size cut issue and the data would likely be informative to the health community as well.

2. What are your comments on the use of XRF as the Pb-PM_{10} FRM analysis method?

I do not agree with this choice. I recommend that ICP-MS be the FRM for the analysis of Pb and that XRF be considered as a FEM. The ICP-MS has better overall quality assurance and quality control (QA/QC) and traceable standards than the XRF method. In addition, the extraction and digestion of Pb compounds in ICP-MS analyses has proven to be quite effective and efficient (Qureshi, et al., 2006).

Among the issues raised regarding XRF, the uniformity of material on the filter collection surface and the potential role of large particle contributions to this non homogeneity remain of greatest concern. It would seem prudent to study these issues prior to formally committing to a decision on sampler type and the performance requirements of the analytical methods. The fact that the TSP Pb measurement has been of historical poor quality in terms of particle size sampling, should not be used as a rationalization that any incremental improvement in PM_Pb monitoring is better than the status quo.

3. What are your comments on the specific analysis & details of the XRF analysis method contained in the proposed Pb-PM_{10} FRM analysis method description?

An effort should be made to archive and test filter blanks by batch number.

4. Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?

The approach described is adequate for characterizing the performance of the XRF analysis for Pb under ideal filter sample collection. It is clear from discussions among committee members that significant uncertainties remain with regard to XRF's quantification. These include potential effects of sampling inlets, Pb particle size and the uniformity of collected PM on the filter. D. Felton's comments, present data which

indicate the extreme sensitivity in precision and accuracy with respect to ambient Pb concentration levels and certainly makes the case for the need to reconsider the statistical measures for precision and accuracy for the low Pb concentrations typical observed in urban areas (e.g. figure 1 below)

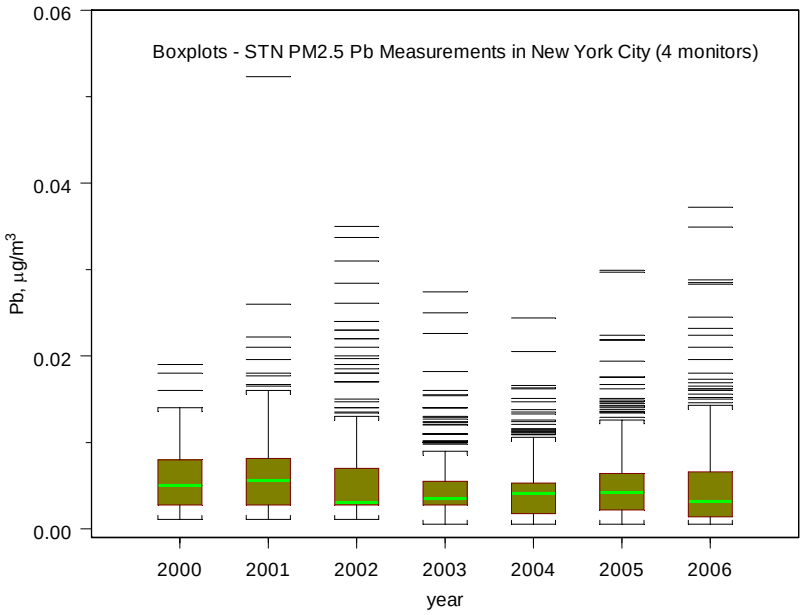

Figure 1. Boxplots STN PM2.5 Pb Concentrations in New York City

5. Are there any method interferences that we have not considered?

All standard sources of interference have been identified. The low levels ambient PM Pb in the atmosphere will continue to be a challenge and require maintaining filter blank quality and monitoring the integrity of sample handling and potential contamination sources within the sample collection system.

Qureshi, S., V. A. Dutkiewicz, K. Swami, K. X. Yang, L. Husain, J. J. Schwab, and K. L. Demerjian, 2006. Elemental Composition of $PM_{2.5}$ Aerosols in Queens, New York: Solubility and Temporal trends, Atmospheric Environment, 40, S238-S251.