Dirk Felton: CASAC AAMM Individual Written Comments:
(Prepared for the July 14th teleconference)

***Peer Review* of the Draft Federal Reference Method (FRM) for Pb-PM10; *Consultation* on Approaches for the Development of a Low-Volume Ambient Air Monitor for Pb in Total Suspended Particulate (TSP) FRM or Federal Equivalent Method (FEM)**

Attachment 1 - Draft Federal Reference Method (FRM) Lead in PM-10 (Pb-PM10)

Background and Summary: In order for monitoring data to be used in determination of attainment with the NAAQS, the data must be collected with a FRM or FEM. A number of options under consideration for the Pb NAAQS indicator would require the EPA to develop a FRM and FEM criteria for the measurement of Pb in PM_{10}. The EPA has proposed language for a FRM for Pb- PM_{10} based on the existing FRM sampler for low volume PM_{10c} in Appendix O to Part 50 of the Code of Federal Regulations (CFR) coupled with analysis by x-ray fluorescence (XRF). The attached document includes the proposed regulatory text for the FRM for Pb in PM_{10}.

Charge Questions:

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

The PM_{10c} sampler is adequate for use as the Pb-PM_{10} FRM sampler. Many States already use this sampler for NATTS PM_{10} metals sampling. The sequential versions of the samplers should also be designated as FRMs because future Pb PM_{10} FEM evaluations should use the FRM samplers and protocols most predominantly utilized in the national network. Future FEM evaluations should be designed with the identical sample collection interval (midnight to midnight) and filter handling procedures as followed by the majority of the data providers for the national network.

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

Specifying XRF would make analytical problems stemming from non-uniform loading, spectral overlap and non-ideal filter loading densities an inherent part of the FRM. ICPMS should be the analysis method for the FRM and for the PEP audit samples. ICPMS is more accurate and it does not require the filter to be uniformly loaded. XRF should be designated as a cost effective FEM that is routinely compared to ICPMS through the periodic collocation of the PEP audit program.

It should also be noted that gravimetric mass determination of the sample filter is not required for Pb analysis.

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?

The section on background measurement and correction states that 20 – 30 clean blank filters are kept in a sealed container and are used exclusively for background measurement and correction. These should be replaced with filters that are representative of the "batches" of filters that are used for the current measurements. It is likely that filter qualities such as thickness, density and contaminant concentrations will change over time.

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

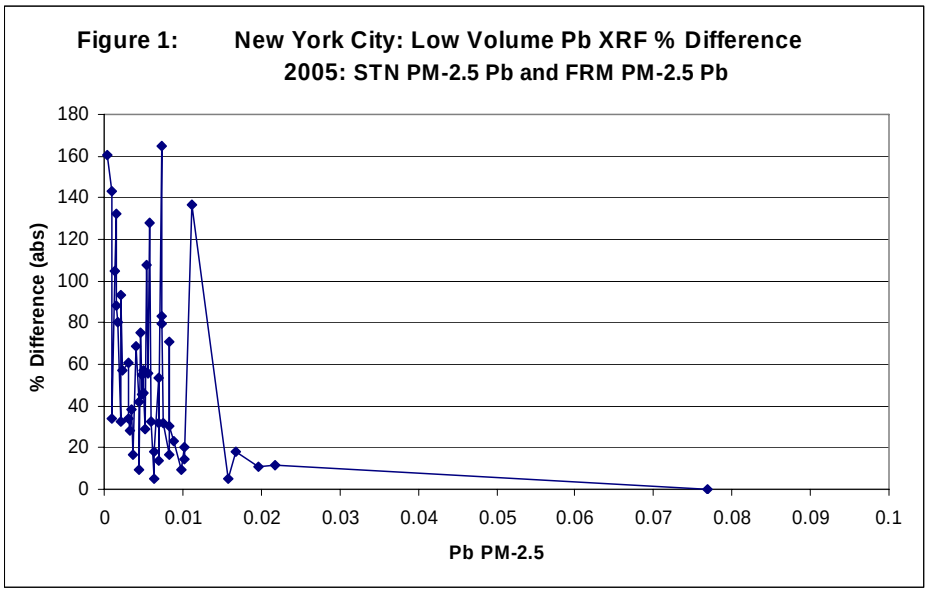
XRF is not the most accurate method for use in a Pb FRM and if selected it should be viewed as a compromise between cost effectiveness and accuracy at concentrations below about 0.01 ug Pb/m^3. For low concentration measurements, it is preferable to use ICPMS which is more accurate and does not require the filter to be uniformly loaded for the FRM. XRF should be designated as an FEM and be permitted for use unless accuracy at very low concentrations is necessary for specific monitoring objectives.

The MDL for Pb XRF as stated in the draft Reference Method is 0.001 ug Pb/m^3. At this concentration the Pb data is not accurate enough to be used reliably for anything other than to demonstrate that the amount of Pb in the air is low. The EPA should consider establishing a minimum reporting level for XRF Pb no lower than 0.005 ug/m^3. Levels below this can be reported but flagged as between detection limit and reporting limit or set to zero if they are below 0.001 ug/m^3.

The draft PM_{10} method references the procedures in Appendix A Part 58 for use in precision calculations. CFR Appendix A Part 58 (1997 - section 5.3.1.1) states that the concentrations of both collocated pairs of Pb data must be above 0.15 ug/m^3 in order for the data to be used in precision calculations. This concentration will be too high for most of the sites in the new Pb monitoring network. A lower value can be selected but the precision of the measurement will decrease rapidly at lower concentrations. In Figure 1 below, STN $PM_{2.5}$ Pb is compared to data from a collocated $PM_{2.5}$ FRM in which the filters were analyzed for Pb by XRF. This data should emulate what we would expect to see for the precision calculations for a clean site in the proposed low volume PM_{10} Pb network. As we can see, the Percent Difference rapidly increases below about 0.02 ug Pb/m^3. This is only one example but it serves to demonstrate that the proposed method's precision determination will have to account for XRF's increase in error at low concentrations.

The EPA may have to revise the way statistics are calculated for Pb or other NAAQS developed in the future for individual components of PM. The typical

ambient concentrations of Pb are of course much lower than those for gravimetric mass and are closer to instrument and method detection limits. The statistics used to determine precision and accuracy may have to be specified as a range; looser at low concentrations where much of the ambient data will be and tighter at higher concentrations closer to the Pb NAAQS.



Are there any method interferences that we have not considered?

The sampler components and the shipping and handling materials for the filter samples must be free of Pb that can affect the integrity of the sample. The metal used to produce the sampler inlet is of particular concern and there should be a specified limit for the amount of trace Pb that is permissible for any component of the sampler including o-rings and greases. It would also be advisable to restrict the use of brass upstream of the sample filter or in any part that experiences wear and is exposed to the sampler exhaust such as in cooling fans and motor brushes.

Document Associated with Subcommittee's Consultation:

Attachment 2 - Options for the Development of a Low Volume Lead in Total Suspended Particulate (Pb-TSP) Sampler

Background and Summary: Problems with the current high-volume Pb-TSP sampler have been highlighted as part of the on-going Pb NAAQS review. As part of the NAAQS review, EPA proposed network design requirements that could result in the need for a significant expansion and/or reallocation of Pb monitors. Due to the concerns over the existing high-volume Pb-TSP sampler, EPA requested comments on the need for a FRM

or FEM low-volume Pb-TSP sampler. The attached document discusses options for the development of a low-volume Pb-TSP sampler for use in the Pb network.

Charge Questions:

Would a low-volume Pb-TSP sampler be an improvement over the existing high-volume Pb-TSP sampler? What advantages and disadvantages do you see associated with a low-volume Pb-TSP sampler?

> Yes, low volume sampling is always preferred because it is intended to represent the air and associated pollutants a typical human is exposed to through breathing. Pb-TSP data collected at 16.7 l/m is more useful for health researchers because it more accurately reflects the Pb exposure from air sources and it minimizes the potential bias due to sampling at other flow rates.
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> Low volume sampling has many advantages over high volume sampling. The low volume samplers have volumetric flow control, are available in sequential versions and provide data that is more compatible with other national monitoring datasets.

What inlet designs would be best suited for a low volume Pb-TSP sampler? What designs are not appropriate for a low-volume Pb-TSP sampler?

> There is no currently available inlet that is suitable for a low volume TSP sampler. The low volume PM_{10} inlet with the size fractionator removed is not appropriate because it does not have a water trap and it may not capture large enough particles to ensure that TSP is fully characterized.

What is your preferred approach for the development of a low-volume Pb-TSP sampler, and why?

> The health community should provide the target upper bound of particle size necessary for a TSP measurement as well as the acceptable inlet efficiency at that particle size. It is likely that if particle sizes above 20 microns are necessary for characterization of TSP then it will be necessary to accept lower collection efficiencies for the larger particle sizes. The inlet design specifications should also include requirements for directional sensitivity, collection efficiencies at smaller particle sizes, water and snow rejection, ease of maintenance and cost. EPA ORD should then design or provide a competitive mechanism in order to have a low volume inlet designed that can meet the needs of the health community and the specifications of the regulators and the monitoring community.
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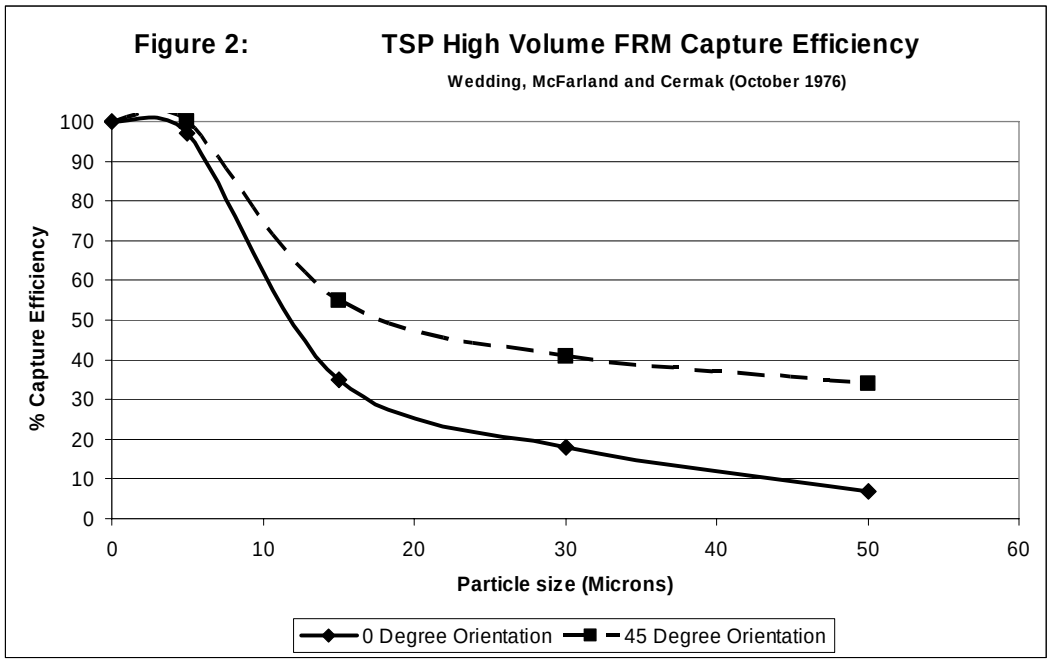
> I realize that it is difficult for the health community to come to a consensus on the issue of determining the appropriate size of particles that must be captured in a future TSP measurement since many researchers investigate different exposure

paths. In the absence of a consensus from the health community, collection efficiencies for the particle sizes required to be collected in a future TSP sampler should at a minimum be equal to or better than the existing TSP FRM. Wedding, McFarland and Cermak evaluated several samplers including the high volume TSP FRM sampler in a wind tunnel in October 1976. They found that the high volume TSP only collected 18% of 30 micron particles when the sampler roof was parallel to the wind direction and 41% of the 30 micron particles when the sampler roof was oriented 45^0 to the wind direction. Their data is presented in Figure 2 below:



Design specifications for a future low volume TSP inlet should require that the inlet capture efficiency curve be higher than the Hi-Volume sampler (oriented at 0^0) curve (solid line). This will be a vast improvement over the existing FRM sampler since the resulting data will not be wind direction dependent and yet the magnitude of the data will still be as comparable as possible to existing TSP FRM datasets.

If the EPA were to develop a low-volume Pb-TSP FRM, how important is it that the sampling capture efficiency be characterized for varying particle sizes?

It is very important to characterize the capture efficiency of sampling inlets for different particle sizes, particle shapes and densities. It will not be possible to design one inlet that has the same capture efficiencies for all particles in the TSP class and it is very likely that the capture efficiency will drop off for the larger

particles. This is acceptable as long as the relationship between the particle size and density and the inlet capture efficiency are well documented and there is enough particulate matter collected in each size fraction. In fact, it is preferable to have a predictable relationship between particle size and collection efficiency with a new inlet than the current situation where the TSP concentration varies tremendously with wind direction in addition to wind speed and particle size. The current FRM's sensitivity to wind direction causes much of the method's uncertainty and makes it more difficult to use the data for source attribution.

It is acceptable for a potential new TSP inlet to have decreased capture efficiencies for larger particles. The new Pb monitoring network is primarily source oriented and most of the monitoring locations will be positioned at the point of maximum expected impact from the emissions from a single source. At these locations, the samplers will be exposed to the full range of particle sizes emitted from the source because the largest particles have not yet been lost significantly to surface deposition. The largest particles which tend to be emitted non-uniformly also weigh a great deal more than the smallest particles. These heavier, larger particles will still be accounted for in gravimetric measurements even if their capture efficiency is well below the capture efficiency of the smaller particles.

If the EPA were to develop a low-volume Pb-TSP FRM, should the new FRM replace the existing high-volume Pb-TSP FRM, or should the EPA maintain the existing FRM?

A new low volume Pb-TSP FRM should replace the existing high volume Pb-TSP FRM. Since the biggest drawback of the existing FRM is its directional sensitivity which cannot easily or reliably be accounted for in data analysis, the use of the old FRM should be discontinued.

Is it appropriate to accept alternative sampler and inlet designs as FEM?

Yes, there is the possibility that continuous or semi-continuous Pb samplers could be available in the future. The FEM specifications need to be written with performance based criteria that permit the use of different technologies, inlets, averaging times etc.

Are the proposed FEM testing criteria for Pb methods adequate to ensure equivalence of alternative sampler and inlet designs? If not, what additional testing requirements should be considered?

No, since the existing Pb-FRM does not provide data that is wind direction independent, a candidate sampler cannot be expected to compare favorably to the existing FRM. The EPA should develop performance based inlet and sampler specifications for candidate FRM and FEMs. The specifications should be evaluated in wind tunnels using state of the art particle generation and measurement techniques.