UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

MEMORANDUM

SUBJECT: CASAC Consultations on Monitoring Issues related to Ozone Network Design and Coarse Particles ($PM_{10-2.5}$)

FROM: Lewis Weinstock
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TO: Kyndall Barry
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Attached are materials for review by the Clean Air Scientific Advisory Committee's (CASAC) Ambient Air Monitoring and Methods (AAMM) Subcommittee. These materials will be the subjects of consultations by the AAMM Subcommittee, scheduled for teleconferences to be held on February 10 and 11, 2009. I am requesting that you forward these materials to the AAMM Subcommittee to prepare for these consultations.

The first project, entitled *Monitoring Issues related to Ozone (O_3) Network Design*, has been requested by EPA's Office of Air Quality Planning and Standards (OAQPS), within EPA's Office of Air and Radiation, as a follow-up to the revision of the O_3 NAAQS that occurred in March, 2008. This consultation will cover several issues that will be included in an upcoming notice of proposed rulemaking affecting ambient monitoring regulations supporting the revised NAAQS. Specific issues include minimum monitoring requirements in urban and non-urban areas, and the length of the required O_3 monitoring season. Based on the projected rulemaking schedule, EPA plans on finalizing the O_3 monitoring rule in late 2009 or early 2010.

The second project, entitled *Monitoring Issues related to Coarse Particles ($PM_{10-2.5}$)*, has also been requested by EPA's Office of Air Quality Planning and Standards (OAQPS), within EPA's Office of Air and Radiation, as a follow-up to the revision of the ambient monitoring requirements that were finalized in October, 2006. This consultation will cover a range of issues related to the deployment of monitors to assess the speciated components of $PM_{10-2.5}$, a topic that was widely discussed during the 2006 review of the PM NAAQS. At that time, EPA finalized new monitoring requirements that included speciation sampling for $PM_{10-2.5}$ at the 75 NCore multi-pollutant stations. EPA specifically requests that monitoring issues related to $PM_{10-2.5}$ species, analysis methods, samplers, and potential network design be addressed during the

consultation. This information will be used to assist with EPA's implementation of the $PM_{10-2.5}$ speciation monitoring component of the NCore network, which is required to be fully operational by January 1, 2011.

We appreciate the efforts of you and the Subcommittee to prepare for the upcoming meeting and look forward to discussing these projects in detail on February 10, 2009 (O_3) and February 11, 2009 ($PM_{10-2.5}$). Questions regarding the enclosed materials should be directed to Mr. Lewis Weinstock, EPA-OAQPS (phone: 919-541-3661; e-mail: mailto:weinstock.lewis@epa.gov

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Documents Associated with Subcommittee's Consultations:

- **Attachment 1 –** ***Network Design Options Under Consideration (Memo to Docket EPA-HQ-OAR-2008-0338)***

Background and Summary: EPA is considering the modification of minimum O_3 monitoring requirements to require one monitor to be placed in MSAs of populations of between 50,000 and less than 350,000 in situations when there is an absence of a design value. EPA may propose that Regional Administrators have the authority to waive requirements for reasons including the presence of a nearby monitor. States will likely have to install some new monitors and/or have the option to relocate existing monitors under certain conditions.

Charge Questions:

Considering the ozone minimum monitoring requirements that are already promulgated through 40 CFR Part 58, is the considered change to these requirements sufficient to ensure a minimally adequate network in urban areas?

We are considering a timeline that would require newly required ozone monitors to be operational no later than January 1, 2011, based on the expectation that final rulemaking will be completed in 2009 or early 2010. Is this schedule appropriate or should EPA consider providing an additional year for new monitors to be deployed (or relocated)? What would be the advantages or disadvantages of a staggered deployment schedule?

Background and Summary: EPA is considering the addition of requirements that each State operate a minimum of three non-urban O_3 monitors in addition to the current and proposed urban O_3 monitoring requirements. The first required non-urban monitor could be located in areas such as some Federal, State, or Tribal lands, including wilderness areas that have O_3-sensitive natural vegetation and/or ecosystems; lands with other ownership may also be appropriate. The second required non-urban monitor could be required to be placed in a Micropolitan Statistical Area expected to have O_3 design value concentrations of at least 85 percent of the NAAQS. The third required non-urban monitor could be required to be located in the area of expected maximum O_3 concentration outside of any MSA, potentially including the far-downwind transport zones of currently well-monitored urban areas. EPA is also considering flexible options for monitoring agencies in meeting the proposed requirements, including the potential relocation of monitors, use of monitors to meet multiple objectives, and use of existing monitors such as CASTNET to fulfill State requirements.

Charge Questions:

We are considering a new requirement that each State operate a minimum of three non-urban ozone monitors to meet certain objectives (described above). Considering the stated objectives of the non-urban ozone monitoring requirements, is three required monitors per state sufficient?

What factors should be considered in the siting of ozone monitors to assess impacts on ozone sensitive vegetation in national parks, wilderness areas, and other ecosystems?

In addition to the objectives that have been described for non-urban ozone monitors, what other objectives should be considered in the final network design? How would the consideration of additional objectives, if any, effect the minimum number of non-urban required monitors?

Current ozone monitoring regulations (described in Appendix E of 40 CFR part 58) include requirements for station and probe siting (e.g., vertical distance of inlets, set-back distances from roadways). Are these requirements (that have been developed for urban monitors) appropriate for non-urban ozone monitors? What changes, if any, should be considered?

We believe that States should have the option of designating that existing non-urban ozone monitors that are potentially operated by another agency (e.g., CASTNET monitors operated by the National Park Service) be utilized for meeting certain non-urban minimum monitoring requirements. What factors should States use to determine if such monitors are appropriate to include in their networks?

Background and Summary: EPA is considering changes to the required State O_3 monitoring seasons. The changes entail a proposed decrease of one month for Minnesota, an increase of one month (19 states), two months (6 states), four months (3 states), and five months (Wyoming). O_3 season requirements are currently split by Air Quality Control Region in Louisiana and Texas. Included in the above State-by-State accounting is the proposal to lengthen the required season in the northern part of Louisiana by one month (southern Louisiana O_3 monitors would remain on a required year-round schedule) and the proposal for the required season in Texas to become year-round for the entire State.

Charge Questions:

We are considering changes to the required ozone monitoring seasons based on analyses of the patterns of ozone exceedances and occurrences of the Moderate level of the Air Quality Index, during periods outside of the currently required seasons. What other factors should be considered, if any, in the determination of the length of the required monitoring season for each State?

We believe that ozone monitors that are located at NCore stations should be operated on a year-round monitoring schedule. Under what circumstances might it be appropriate to require year-round monitoring at other stations beside NCore?

We are considering that changes to the required ozone monitoring season be applicable to existing monitors beginning in 2010, one year ahead of the deployment schedule for newly required ozone monitors. Is this schedule reasonable for existing monitors?

- **Attachment 2 – K*ey Issues Related to $PM_{10-2.5}$ Speciation Monitoring (Memo to Docket EPA-HQ-OAR-2007-0492)***

Background and Summary

As part of the recent revision to the Ambient Air Monitoring Regulations, $PM_{10-2.5}$ speciation monitoring is required at National Core (NCore) multi-pollutant monitoring stations by January 1, 2011. EPA has prepared a draft whitepaper on $PM_{10-2.5}$ speciation monitoring. The whitepaper paper describes the $PM_{10-2.5}$ speciation monitoring requirements specified in the ambient air monitoring rule and provides an overview of the monitoring issues, a discussion of the potential use of existing $PM_{10-2.5}$ speciation sampling and analysis techniques in a pilot study to inform the implementation and decision-making process, and potential research questions to inform the planning and implementation process.

One of the next steps for development and implementation of a long-term $PM_{10-2.5}$ speciation monitoring program at NCore is the development of a pilot monitoring study. Several issues need to be addressed in order to develop the long-term $PM_{10-2.5}$ speciation implementation plan. Prior to long-term monitoring, it is appropriate to have a pilot network of a few sites to improve our understanding of the issues associated with $PM_{10-2.5}$ speciation monitoring and to determine the most appropriate way to measure $PM_{10-2.5}$ species at NCore.

$PM_{10-2.5}$ Speciation Measurement Issues

The EPA Office of Research and Development (ORD) has conducted a multi-site field evaluation of candidate methodologies for $PM_{10-2.5}$ mass (U.S. EPA 2006b). $PM_{10-2.5}$ mass measurement approaches initially selected for study included virtual impaction (dichotomous sampling), difference, and continuous methods. In addition to continuous monitoring devices, integrated filter-based monitors were used to collect filters for subsequent speciation analysis. ORD has found that when reconstructing $PM_{10-2.5}$ mass using the speciation results (sum of species), there is a significant portion (10-50%) of the mass that is unaccounted for or unidentified in some locations. This includes uncertainties associated with the factors used in reconstructing mass (e.g., the factors used in conversion from OC to OM and those used to estimate metal oxides). Although the level of agreement between the reconstructed mass and the measured mass was not always high, linear regression comparisons between constructed mass and measured mass did show high correlation.

The current $PM_{10-2.5}$ Federal Reference Method (FRM) or difference method, dichotomous sampler, and current speciation filter-based samplers serve as logical choices for the basis of a $PM_{10-2.5}$ speciation sampling design. Modification of the $PM_{2.5}$ speciation sampler inlets to PM_{10} was suggested by CASAC (EPA-SAB-CASAC-CON-04-005) as an option for $PM_{10-2.5}$ speciation by difference. This may be a viable alternative as long as both speciation samplers have identical flow rates, filter sizes, and filter handling procedures. One potential limitation of the most widely used $PM_{2.5}$ speciation sampler (MetOne SASS) is the difference in flow rate (6.7 Lpm) from the $PM_{2.5}$ and PM_{10} FRMs (16.7 Lpm). Differences in flow rates result in differences in filter face velocity and pressure drop across the filters, which may adversely affect volatile species and subsequent comparison of reconstructed mass with the FRM total mass; however, volatility issues may be less important for $PM_{10-2.5}$ particles than for $PM_{2.5}$.

The viability of $PM_{10-2.5}$ speciation by a difference method requires further evaluation. However, preliminary regression comparisons for speciation by difference and the dichot method have shown high levels of agreement and high correlation for predominant species. While there is currently no consensus on whether the mixing of $PM_{2.5}$ and $PM_{10-2.5}$ aerosols causes a bias in either measurement, CASAC

mentioned the need for sampling separation and collection of filters with only coarse particles to avoid mixing of $PM_{2.5}$ and coarse particles and the potential for subsequent chemical interaction. Allen et al. (1999) also mentions the importance of maintaining filter flow rates greater than 10 Lpm, preferably 16.7 Lpm, to avoid degraded precision.

Charge Questions:

Table 1 below 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?

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. Which of these sampler types should be included or excluded from the pilot network design? Are there other sampling devices not listed here that should be considered?

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 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?

$PM_{10-2.5}$ Species or Components

A list of coarse particle constituents was provided in the 2004 Criteria Document (CD) and included suspended soil or dust; fly ash; nitrates/chlorides/sulfates; soil components (Si, Al, Ti, Ca, Fe); sea salt; tire/brake/road wear debris; and biological materials. Table 1 provides a list of candidate $PM_{10-2.5}$ species. The specific species that need to be measured for $PM_{10-2.5}$ must be identified in order to design a pilot or long-term monitoring program. For example, ions (e.g., nitrate and sulfate) have been identified as only minor components of $PM_{10-2.5}$ in some locations. It is not clear whether the resources to measure ions are needed to support research or data use needs for $PM_{10-2.5}$ speciation.

Table 1. List of Proposed Filter Types, Species, and Analysis Methods

Filter Type and Species		**Analysis Method**
Teflon	Mass	Gravimetric
	Elements	Vacuum XRF
	Ions (Na, Ca, Cl, K, SO_4, NH_4, NO_3) *	Water extraction with Ion Chromatography (IC)
	Total Protein (Surrogate for total biological)	Protein assay (NanoOrange®) of IC extract above with Fluorometry and/or SEM
Quartz	Organic and Elemental Carbon	Thermal Optical Analysis (IMPROVE_A TOT/TOR)
	Carbonate Carbon	Acidification followed by TOA

* Any volatile species present will be compromised by vacuum XRF

Potential issues with XRF measurement of particles have been identified. Large or coarse particle size effects may be problematic for XRF. Larger particles (greater than 3 micrometers) may absorb some of the incident and emitted x-rays for light elements such as sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium (Chow 1995). Absorption corrections procedures for particle size effects on XRF results can be applied (Van Dyck et al., 1985).

$PM_{10-2.5}$ organic and elemental carbon (OC and EC) species can be measured using the same thermal-optical analysis (TOA) method that is used for $PM_{2.5}$ speciation. Han et al., (2007) reports an interference with metal oxides (e.g., iron oxides) and TOA analysis; where certain metal oxides can serve as a source of O_2 in the helium atmosphere. The soil component of $PM_{10-2.5}$ is expected to be significant. Biological materials (bioaerosols) are collected with the filter-based particle sampling techniques used for $PM_{10-2.5}$ or $PM_{2.5}$ monitoring and included as part of the OC measurement, but not quantified separately from other components. If bioaerosol species (e.g., pollens and molds) need to be qualitatively or quantitatively identified for the $PM_{10-2.5}$ speciation program, an appropriate measurement technique will need to be identified (or developed) and evaluated. Some biological materials can be identified using the scanning electron microscopy (SEM) technique (U.S. EPA 2002). Total protein has been measured from filters with an assay technique and used as an indicator of total biological material (Menetrez et al, 2007).

Charge Questions:

Table 1 provides a list of proposed $PM_{10-2.5}$ species. Which of these species are most important? Are there important $PM_{10-2.5}$ species or components missing from this list?

If ions are important $PM_{10-2.5}$ species to measure, what ions should be on the target list? Are nitrate or ammonium ions important?

Of the proposed analysis methods in Table 1, which methods should be excluded or included? Are there important analysis methods missing from the list?

The 2004 CD included a list of important $PM_{10-2.5}$ components which included biologicals 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 (or something similar) important to obtain a quantitative indicator of the total biological material present?

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?

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 the interference be addressed?

Network Design Issues

The final monitoring rule contains a requirement for $PM_{10-2.5}$ speciation at NCore multi-pollutant monitoring sites in 2011. As compared to the proposed rule, the final rule increases the number of monitoring sites from ~20 to ~75 and shifts the focus from urban monitoring to both urban and rural monitoring locations. Manually-operated $PM_{10-2.5}$ speciation samplers must operate on at least a 1-in-3

day schedule and be collocated with $PM_{2.5}$ speciation at NCore stations. The NCore will have about 75 sites mostly in urban areas, with a subset of about 20 rural sites. The candidate NCore locations may not be optimal for $PM_{10-2.5}$ speciation. Initially in 2009, a few pilot monitoring sites will be selected for a field test program.

The EPA held a workshop on Air Quality Monitoring and Health Research in April 2008. One suggestion from the session on Thoracic Coarse Particle Components and Potential Health Impacts was to consider that when evaluating potential locations for $PM_{10-2.5}$ monitoring, that areas in attainment for $PM_{2.5}$ but not for PM_{10} be considered. $PM_{10-2.5}$ monitoring in these locations may provide insights regarding sources that may be contributing to non-attainment.

Charge Questions:

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, are there other factors to consider in selecting the pilot monitoring and long-term sites or locations?

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?

References

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U.S. EPA 2002. Guidelines for the Application of SEM/EDX Analytical Techniques to Particulate Matter Samples, Office of Research and Development, September 2002; EPA-600/R-02/070.

U.S. EPA 2006b. Multi-site Evaluations of Candidate Methodologies for Determining Coarse Particulate Matter (PM10-2.5) Concentrations: August 2005 Updated Report Regarding Second-Generation and New PM10-2.5 Samplers; September 2006; EPA-600/R-06/093.

Attachments

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