UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK NC 27711

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OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

SUBJECT: Recommendations to Users of CSN and IMPROVE Speciation Data Regarding Sampling Artifact Correction for $PM_{2.5}$ Organic Carbon

FROM: Neil Frank, Air Quality Analysis Group, EPA (C304-04) /s/

TO: PM NAAQS Review Docket EPA-HQ-OAR-2007-0492

As part of the review of the national ambient air quality standards (NAAQS) for particulate matter (PM) completed in 1997, EPA established a $PM_{2.5}$ Chemical Speciation Network (CSN) to conduct routine speciation monitoring, primarily in urban areas across the United States (U.S.). Similar to the CSN, the Interagency Monitoring of PROtected Visual Environments (IMPROVE) program, a cooperative measurement effort managed by a steering committee composed of representatives from federal, regional, and state organizations, also conducts routine $PM_{2.5}$ speciation monitoring, primarily in non-urban areas across the U.S.[1]

For a number of years, EPA and IMPROVE Steering Committee representatives have been working together to ensure uniformity between the measurement and analytical procedures used in the CSN and IMPROVE programs.

In 2011, a committee was formed by the IMPROVE Steering Committee to review the existing procedures used by the IMPROVE program to adjust $PM_{2.5}$ organic carbon (OC) measurements for sampling artifact and to identify appropriate procedures that might be adopted for the U.S. EPA's CSN data to ensure comparability and consistency with the similar data collected by IMPROVE. The committee consists of representatives of EPA, National Park Service, Desert Research Institute, Cooperative Institute for Research in the Atmosphere (CIRA) and University of California-Davis. IMPROVE publicly reports its OC data with an adjustment for sampling artifact; while the EPA currently reports it OC data without such an adjustment. The attached document, issued in January 2012, provides the Committee's rationale and recommendations for those adjustments.

[1] The IMPROVE Steering Committee includes representatives from EPA, the National Oceanic and Atmospheric Administration, the Fish and Wildlife Service, the Bureau of Land Management, the National Park Service, the U.S. Forest Service, National Park Service, the National Association of Clean Air Agencies, Northeast States for Coordinated Air Use Management, Western States Air Resources Council, Mid-Atlantic Regional Air Management Association, and the State of Arizona.

Prior to the Committee's recommendations being issued, EPA reflected on the ongoing carbon measurement work of the IMPROVE program when conducting analyses as part of its ongoing review of the PM NAAQS. Specifically, in considering the adequacy of the current secondary (welfare-related) PM standards to provide protection against PM-related visibility impairment as well as alternative standards that were appropriate to consider based upon the available scientific information, the EPA staff made a nominal adjustment to the CSN's measured OC based on sampler-specific network-wide field blanks (US EPA, 2011, Chapter 4, Appendix G).[2]

For the aforementioned policy assessment, a nominal value of 0.4 µg/m3 was used to adjust OC measurements which were derived with EPA's IMPROVE-like monitoring method in the CSN. However, the attached technical committee report describes lower adjustment values based on monthly median backup filters or field blanks. Those would result in adjustments of ~0.32 µg/m^3 and 0.12 µg/ m^3, respectively, and the latter approach is tentatively recommended to adjust the data from both networks. Assuming a multiplier of 1.4 to convert adjusted OC into estimated extinction, the use of the two adjustment approaches both result in slightly higher estimate of organic mass (+0.1 to + 0.4 ug/m^3) and estimated extinction (+ 0.4 to + 1.6 Mm-1). Nevertheless, the latter change in visibility for locations with higher calculated extinction is extremely small for either approach when the results are expressed in deciview (dv) units. If the total aerosol-based extinction using the IMPROVE algorithm is 160 Mm-1 (28.3 dv), the change in calculated extinction using the alternative backup filter or field blank derived OC adjustment both result in a value of 28.4 dv (+ 0.1 dv). Thus, the tentatively recommended field blank approach is reasonable for the purposes of PM-related visibility assessment.

Attachment

[2] US EPA (2011). *Policy Assessment for the Review of the Particulate Matter National Ambient Air Quality Standards. Office of Air Quality Planning and Standards.* U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA 452/R-11-003. April 2011. Available: http://www.epa.gov/ttn/naaqs/standards/pm/s_pm_2007_pa.html.

Rationale and Recommendations for Sampling Artifact Correction for $PM_{2.5}$ Organic Carbon

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Background

Organic sampling artifacts occur during $PM_{2.5}$ sampling in the U.S. long-term urban Chemical Speciation Network (CSN) and non-urban Interagency Monitoring of PROtected Visual Environments (IMPROVE) networks. Organic sampling artifacts are interferences in the collection and quantification of particulate organic carbon (OC) due to adsorption and desorption of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) on to the quartz-fiber filter substrate. Estimates of organic sampling artifacts and their uncertainties are needed to estimate the mass contribution of particulate carbon in the calculation of aerosol-based light extinction with the IMPROVE algorithms in urban or rural areas (Pitchford et al., 2007). In addition, estimates of sampling artifacts are needed to understand compliance with the mass-based $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) and to determine long-term trends and chemical mass closure.

Organic vapor adsorption can occur during active sampling (with air drawn through the filter) and passive exposure (zero face velocity) (Chow et al., 2010; Watson et al., 2009). These vapors leave the sample during thermal analyses (Chow et al., 2007; 2011) and are interpreted as part of the measured particulate OC. This positive (additive) OC artifact yields higher values for $PM_{2.5}$ OC samples than exist in ambient air. SVOCs can be initially collected as particles, but portions can evaporate during sampling because of increases in temperature or decreases of their gas-phase concentrations in the sampled air, causing the particles to leave the filter and become part of the gas stream (Mader and Pankow, 2001). Evaporated SVOCs from sampled particles yield negative OC artifacts which tend to be multiplicative and could be reported as part of the particulate mass to represent ambient concentrations. A large number of investigations have been performed to address organic sampling artifacts based on: passive field blanks (FB), backup quartz-fiber filters (QBQ) placed behind the front quartz-fiber filter (QF), pre-filter organic denuders, and OC to $PM_{2.5}$ mass regression analyses, but the results are not consistent among the different studies.

CSN and IMPROVE Sampling, Analysis and Artifact Corrections

Efforts have been made since 2007 to obtain consistency of $PM_{2.5}$ carbon sampling and analyses between CSN and the IMPROVE network. As of October 2009, the URG3000N sampler (URG Corporation, Chapel Hill, NC; modified IMPROVE carbon sampler) has been operating at all CSN sites. The sampler uses 25 mm Pallflex® Tissuquartz™ filters at a nominal flow rate of 22 L/min for OC and elemental carbon (EC) detection following the IMPROVE_A thermal/optical

reflectance (TOR) protocol (Chow et al., 2007). This approach is consistent with procedures applied in the IMPROVE network.

Currently, carbon data is not artifact-corrected for CSN. For the IMPROVE network, monthly median OC from the quartz-fiber backup filter (OC_{QBQ}) is subtracted from all front filters in the network to correct positive organic sampling artifact. This approach assumes negative sampling artifacts are negligible. No artifact correction is made for EC.

For CSN, FB and QBQ filters were collected at a frequency of 20 percent at all sites during 2007–2010 and then reduced to a 10 percent frequency as of January 2011. For IMPROVE, QBQ were collected at six sites (1988 to August 2008), which increased to 12 sites with 13 sets of blanks (including 3 urban sites and one collocated sampler in Phoenix, AZ) from September 2008 onward. FB were collected at ~2–5 percent frequency at all sites from 1988 to 2008, and switched to the 12 QBQ sites after August 2008. Analysis of OC_{FB} and OC_{QBQ} for CSN and IMPROVE showed that:

- For CSN, median OC_{FB} (0.12 µg/m^3) is about 60 percent lower than median OC_{QBQ} (0.32 µg/m^3), accounting for 6.7 percent and 17.9 percent of OC_{QF} concentrations (1.79 µg/m^3, n=5043) during 2008–2010.
- For IMPROVE during 2005-2006, the median OC_{FB} (0.24 µg/m^3) was ~12 percent lower than OC_{QBQ} (0.28 µg/m^3) accounting for 24 percent and 26 percent of OC_{QF} concentrations (1.03 µg/m^3, n=41588) respectively. From September, 2008 through December 2010, the median OC_{FB} (0.13 µg/m^3) was 43 percent lower than OC_{QBQ} (0.22 µg/m^3) accounting for 16 percent and 28 percent of OC_{QF} concentrations (0.81 µg/m^3, n=47526) respectively.
- OC_{FB} levels are independent of front quartz-fiber filter OC, for both the CSN and the IMPROVE networks.
- OC_{FB} levels are lower than OC_{QBQ} so they represent a lower bound on the additive artifact.
- OC_{QBQ} increase with increasing OC_{QF} concentrations at some CSN and at all 12 QBQ IMPROVE sites and therefore overestimate the additive artifact.
- OC_{FB} are more consistent between sites and by season or day than OC_{QBQ}..
- There is a decreasing trend in median $OC_{F,}$ OC_{FB} and OC_{QBQ} from 2005 to 2010 for the IMPROVE sites. Median OC_F was 1.07 µg/m^3 in 2005 and 0.80 µg/m^3 in 2010. OC_{QBQ} was 0.29 µg/m^3 in 2005 and 0.22 µg/m^3 in 2010. OC_{FB} was 0.25 µg/m^3 in 2005, and 0.12 µg/m^3 in 2010.
- A sharp decrease in IMPROVE OC_{FB} was found during August 2008 as network FB collection is switched from a random selection of 2–5 percent of the sites to the 12 QBQ sites. Data analysis shows that changing the sites of collection for the FB is not likely the cause of the decrease.

Recommendation

Based on the above preliminary analyses, we tentatively recommend applying a monthly network median OC_{FB} for artifact correction for the CSN and IMPROVE networks, based on each networks OC_{FB} data. The use of OC_{FB} appears to adequately address the additive artifact. A data adjustment for the multiplicative artifact can be incorporated into the multiplicative

conversion of particulate organic carbon into particulate organic mass. For the original IMPROVE algorithm, this adjustment uses a 1.4 multiplier. The revised IMPROVE algorithm uses 1.8 (Pitchford et al, 2007). For its urban locations, CSN uses a 1.4 multiplier.

Additional Measurements and Analyses

It is recognized that these proposed artifact corrections utilizing a monthly median OC_{FB} may change upon additional field experiments and data analyses. The following questions will be addressed to better understand the behavior of the OC_{FB} in IMPROVE and CSN:

- Have there been changes in the physical properties of the quartz-fiber filters used by both CSN and IMPROVE (manufacturer and product purchased has not changed during the time periods addressed in this report) that caused changes in the OC_{FB}, particularly the sharp decrease observed in 2008? Tests to address this question include (but are not limited to):
    - Weigh archived laboratory quartz-fiber filter blanks from different manufacturer lots used in IMPROVE (2005-2010) and CSN (2008-2010) as an indicator of the reactive surface area available for organic vapor adsorption.
    - Perform optical microscopy and possibly other analyses on the archived filters to evaluate if physical properties have changed.
    - Determine if there is a relationship between mass or other properties of the filter and measured OC_{FB}.
- Did operational changes (changes from single to double quartz filter blanks, changes in sampler operations) in the IMPROVE network cause the sharp decrease in QF values 2008? Tests to address this question include (but are not limited to):
    - Single field blanks and double field blanks will be collected in parallel in the IMPROVE network and evaluated for differences.
    - Samples collected using the old sampler protocol and with the new sampler protocol will be collected in parallel and evaluated for differences.
    - Data from IMPROVE sites with FBs will be evaluated just prior to and just after the change in sampler protocol.

References

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