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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantification of organic carbon sampling artifacts in US non-urban and urban networks" *by* J. C. Chow et al.

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Author's Note: The revised manuscript is attached as supplemental material to this comment

General: What is your criterion for defining an "urban" site and a "non-urban" site?

Although there is not an absolute definition of "urban" and "non-urban" sites, we followed the definition found in 40 CFR Part 50 (National Ambient Air Quality Standards for Particulate Matter; Final Rule. U.S. EPA, 2006) and documented in the U.S. EPA Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10} (U.S. EPA, 1997). Specifically, these terms were used to contrast the non-urban and urban sampling sites located in the IMPROVE network and STN/CSN, respectively. Out of

the 181 IMPROVE sites, over 93% (170 sites) are located in National Parks and wilderness areas that represent different regions in the U.S. These sites are far away from population centers or local pollution sources, and are often at high elevations. These non-urban or regional sites are defined to have a zone of representation of pollutant levels within a 100 – 1000 km radius of the site. Regional or non-urban $PM_{2.5}$ sites are affected by a combination of naturally-occurring aerosol from wind-blown dust and marine aerosol, as well as particles generated in urban and industrial areas that may be more than 1000 km distant. The urban Speciation Trends Network (STN; part of the Chemical Speciation Network [CSN]) sites represent a mixture of particles from many sources within the urban complex, including but not dominated by neighborhood-scale (500 m to 4 km) sources. Urban-scale (4 to 100 km) sites are usually located on the roof-tops of two- to four-story buildings in cities, away from highly travelled roads, industries, and residential heating to represent human exposure, typically in an urban area with population $>$ 200,000 (Chow et al., 2002; U.S. EPA, 1997).

In order to understand air pollution epidemiology, the SEARCH network was designed to evaluate human exposure at urban versus rural environments in the southeastern U.S. (Mississippi, Alabama, Georgia, and Florida). Although in most cases it is easy to distinguish urban from rural/non-urban environments, we acknowledge that the distinction is sometimes ambiguous. For example, the outlying field (OLF) site, north of Pensacola, FL, in the SEARCH network is characterized as "suburban", which is somewhere between the urban and non-urban sites. We have added the site type descriptions in the Introduction Section of the revised manuscript (Lines 101 – 115) to facilitate understanding.

2) Page 27363, Line 9: Authors did not introduce this idea prior to hypothesis 3, and it strikes the reader as out of context. Please introduce this idea prior to this point (e.g., discuss SANDWICH method before introducing hypotheses)

A paragraph has been added to the Introduction Section of the revised manuscript that lays out the concept of the SANDWICH method:

Frank (2006) developed the SANDWICH method to estimate artifact-free OC or OC mass (OCM). This method assumes that all of the unaccounted $PM_{2.5}$ mass measured on a Teflon®-membrane filter (i.e., when weighted sums of elements and ions are subtracted) can be associated with the carbonaceous component. This is based on the principle that Teflon®-membrane filters are inert and their tendency to adsorb organic vapors is low. These filters are expected to have a minimal positive OC artifact, although their negative organic artifact might be larger than that of quartz-fiber filters. (Lines 89 – 95)

Additionally, Hypothesis 3 has been updated as follows:

H3: Artifact-free OC concentrations can be better estimated by the SANDWICH method (Frank, 2006) than by direct OC measurements. (Lines 152 – 153)

3) Comment: Do the authors know how 1-15 minutes ever became a standard exposure time for STN/CSN and SEARCH bQF? This seems way too short.

When the U.S. EPA established STN/CSN during 1999/2000, it did not define the standard protocol or specify the minimum exposure time for field blanks. By default, operators left the field blanks (bQF) exposed to ambient air for a few minutes during each site visit when new filters were installed. Anonymous Referee 1 is correct that the 1 – 15 minute exposure time is too short to represent passive deposition. As we note in footnote a of Table 1 of the manuscript,

As of October 2009, the modified IMPROVE Module C, URG 3000N sampler (URG Corp; Chapel Hill, NC) is placed at all STN/CSN sites using Pallflex ® Tissuquartz at a flow rate of 22.8 L/min on 25 mm filters for organic and elemental carbon (OC and EC) following the IMPROVE_A thermal/optical protocol (Chow et al., 2007b) (Page 23)

The representativeness of these bQF and QBQ will be evaluated after the completion of one year of sampling.

4) Page 27365, Line 3: What causes outliers?

Due to the large size of these networks (i.e., 181 IMPROVE sites and 239 STN/CSN sites), it is inevitable that some of the samples will be mixed or mishandled. The revised text now states:

Outliers are identified (i.e., values $>$ 3 or 4 times the standard deviation). The small number of outliers likely results from inadvertent contamination during filter shipping/receiving or sample loading/unloading and are excluded from the averages and standard deviations. (Lines 192 – 195)

5) Table3: Please include a footnote in Table3 to define ug/cm2 and ug/m3 as areal density and ambient concentration equivalent, respectively.

Footnotes d and e of Table 3 now read as follows:

d Areal density on filters in $\mu g/cm^2$ is based on the sample loading divided by the exposed area (e.g., 3.53 cm^2 for IMPROVE samplers, 11.76 cm^2 for STN/CSN speciation samplers, and 7.12 cm^2 for SEARCH PCM3 samplers as noted in Table 1)

e Equivalent ambient concentration in $\mu g/m^3$ is based on the sample loading divided by the nominal sampler volume (varies from 9.6 m^3 for MetOne SASS to 32.7 m^3 for the IMPROVE sampler as noted in Table 1). (Page 28)

6) Page 27366, Lines 11-12: include range for EC fraction of TC (e.g., 0 - 6% from looking at the table) and 7) Page 27366, Lines 13-14: suggest changing "can be used interchangeably" to "will be used interchangeably"

The sentences have been revised as follows:

EC values are at or near minimum detection limits (i.e., 0.06 $\mu g/cm^2$), accounting for 0 to 5% of TC, indicating that passive PM deposition is negligible. As a result, TC and OC are not statistically different and will be used interchangeably. (Lines 229 – 232)

8) Page 27367, Lines 16-17: May be worth noting this finding in the conclusions for hypothesis 1.

Done. The revised manuscript states that:

STN/CSN field and trip blank TC and OC concentrations are similar ($\sim$ 0.95 $\pm$ 0.23 μg/cm^2), within $\pm$5% for site averages. (Lines 409 – 410)

9) Page 27368, Line 9: suggest changing "abundance" to something like "fractional contributions"

Done. The new sentence reads: "There are no apparent changes in the fractional contributions of the IMPROVE thermal carbon fractions among the four seasons." (Lines 276 – 277)

10) Page 27368, Line 16: Authors originally stated a 30% difference between urban and non-urban SEARCH OC$_{bQF}$, now state 24%, but still looks like a smaller difference on the figure.

After examining the numbers, the sentence has been revised to: "Fig 4 shows little difference between urban and non-urban IMPROVE OC$_{bQF}$, but SEARCH OC$_{bQF}$ is 17% higher at non-urban compared to urban sites." (Lines 281 - 282)

REFERENCES

Chow, J.C., Engelbrecht, J.P., Watson, J.G., Wilson, W.E., Frank, N.H., and Zhu, T.: Designing monitoring networks to represent outdoor human exposure, Chemosphere, 49, 9, 961–978, 2002.

U.S. EPA: Guidance for network design and optimum site exposure for PM$_{2.5}$ and PM$_{10}$, prepared by U.S. Environmental Protection Agency, Research Triangle Park, NC, 1997.

U.S. EPA: 40 CFR Part 50: National Ambient Air Quality Standards for Particulate Matter; Final Rule, Federal Register, 71, 200, 61144–61233, 2006.

Watson, J.G., Chow, J.C., Chen, L.-W.A., and Frank, N.H.: Methods to assess carbonaceous aerosol sampling artifacts for IMPROVE and other long-term networks, J.Air Waste Manage.Assoc., 59, 8, 898–911, 2009.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/9/C11487/2010/acpd-9-C11487-2010-supplement.pdf

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