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Comment

Interactive comment on “Positive sampling artifact of carbonaceous aerosols and its influence on the thermal-optical split of OC/EC” by Y. Cheng et al.

Anonymous Referee #1

Received and published: 13 August 2009

Overview:

This paper reports on a study in which a denuder sampler and parallel port filter samplers were used to measure organic carbon and organic sampling artifacts. This paper explains well the issues with the accurate measurement of organics, and more studies of this type are needed in a variety of locations. The authors do a very good job, with a few exceptions, of crediting knowledge gained from past studies, and of explaining their results in the context of past work. The experiment was well designed. This paper is clearly appropriate for ACP and should be published with minor revisions.

Additional work needed on the following:

1. Although the introduction is very well done, it ignores one important issue regarding

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denuder performance. When using the denuder system, the filter plus backup adsorbant downstream of the denuder does provide the best estimate of particulate OC, BUT ONLY IF THE DENUDE EFFICIENCY IS 100% OR IS WELL KNOWN AND CORRECTION IS MADE FOR ORGANIC GASES THAT PASS THROUGH THE DENUDE AND ADSORB. Otherwise, a substantial portion of material collected on the backup filter or adsorbant can be from denuder breakthrough, and this can lead to a substantial overestimate of particulate OC. The authors are aware of this issue, because in their methods and results they take great care to look for denuder breakthrough, but this needs to be made clear to their readers. Likewise, on page 13749 the authors say "3) thus the positive artifact ...is calculated as..." This is accurate as long as denuder collection efficiency for organics that adsorb on the filter and backup is 100%, otherwise it can be quite inaccurate.

2. page 13743 - On line 1, the authors indicate that a variety of analytical methods have been developed to separate OC and EC and provide references. It would be far better to give credit to the developers of those first methods - the first that I am aware of are Novakov (thermal), Kochy Fong (thermal with MnO₂), and Huntzicker+Johnson (thermal-optical with pyrolysis correction). These are from the late 1970s and through about 1982 and should be referenced. Johnson and Huntzicker 1982? should be referenced when the authors say "Thermal-optical method has been developed..." These references should be easy to find in one of the 3 review papers or other early references already included in the paper (McDow, Turpin, other).

3. Methods - the face velocity needs to be included for the filters in each sampling port (in the text or in Table 1) - The size of the sampling artifact depends on face velocity, RH, Temp, and the filter loading. The more of this information that is given for this study (and if possible for the studies in table 2) the more useful it will be for mega-analyses. Also average values for DQ and BQ are given in Table 3, but average values for the other measures (QBQ, QBT,...) should also be given somewhere. What I mean is that the actual values of the measurements obtained should be made available, at least their

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averages.

4. How was the field blank handled? Was it subtracted from the values reported or not, and if so how?

5. page 13746 - Please be aware that it is possible to meet the criteria that the authors refer to as "suggested by Subramanian" and still get the wrong answer. For example, if the top temperature in He were too low, the last OC peak in He would have very long tail (like slowly bleeding out of the filter) and OC would be under-reported. The "ideal temperature" is still a matter of debate (based on my own experience and Robinson's work, I would suggest 700 rather than 580). Also, it would be better if the OC-EC split happened with the FID signal were low rather than high - this would lead to smaller uncertainties in the split. Both of these comments I provide as comments, and I do not insist in changes in the text. However, If the authors think they can modify the text to better inform the readers, that would be grand.

6. Page 13751-13752 - the suggestion that the particle loading on the front filter could alter adsorption on the front filter seems unlikely to me, but it is more likely as the particle loading increases. The particle loading could be quite high on these filters in China. It might help to evaluate this possibility if the authors could calculate the surface area of the filter and of the loaded particles. Another possibility is that the pressure drop across the Teflon filter causes volatile losses to be larger for the QBT than QBQ.

7. page 13753 line 23 - might be good to add the phrase "since not all PC is removed first" Also, it seems the attenuation coeff. for PC is likely to be larger because PC forms as a film on the quartz fibers - do the authors find any evidence of this? Also, It was not clear to me how the re-partitioning of EC and PC was accomplished (page 13754) and what the assumptions were. This needs clarification.

8. Conclusions - I disagree with the conclusion "implying an adsorbent backup filter should be used instead." I do not think this is necessarily supported by the paper. CIG or XAD-Q might collect more volatile OC (good) and might results in more denuder

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breakthrough (bad). Perhaps it would be better to say experiments similar to this one should be done with these. Also, the magnitude of the over and underestimate of the positive artifact should be provided in conclusions. By using a backup filter instead of a denuder, how close to the true value of particulate OC do you get? Likewise, "native EC was underestimated by TPT-split-EC" by how much? To what degree does the PC evolve before EC?

9. Discussion "More attention...semivolatle PC...considering its secondary nature..." Robinson and Donahue would probably disagree with this. In their Science paper they argue that primary OC is more volatile than secondary OC.

Minor Revisions needed:

1. Some terms are not spelled out or defined at first use, like: OC, EC and PC (abstract and Intro). What is meant by the TST filter (page 13748)
2. The grammar is quite good, except for the sentence on page 13741, line 3 - should be "monitors...provide" and line 6 - should be "network..and..network...provide", and line 9 - should be "projects, which are" Page 13748 line 5: instead of "or" the authors mean "specifically, organic vapors not removed..." And "Comparable OC were" should be "Comparable OC loadings were"
3. page 13741 lines 8-10 - yes, some supersites were designed to evaluate monitoring methods for their potential transition to routine monitoring networks, as indicated here - but this was not the only goal of the supersites - another was testing of models....
4. The review paper by Turpin et al 2000 should be referenced along with Huebert and Jacobson on page 13741 line 25, as it provides key background needed to understand the current paper. The authors might also want to reference the classic OM/OC paper by Turpin and Lim here as well (2000 or 2001?) published in Aerosol Sci and Technol.
5. The part # and company location for the MetOne carbon denuder should be given.
6. Page 13745 line 24 - I believe the authors mean to say they used the IMPROVE-

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A temperature protocol. I think IMPROVE uses TOR and this study uses TOT. If so, adding the words "temperature protocol" might reduce confusion.

7. I found the abbreviations like "(BQ-DQ)-OC" in text and figures to be a bit confusing. Perhaps it would be less so if the OC was a subscript.

8. Is Fig 1 referenced in the text? Is it necessary?

9. Fig 5 Define each y axis in the figure caption

10. Fig 6 - Other artifact studies have plotted QBQ or QBT vs BQ and percent artifact vs BQ. These figures would be more useful for comparison with other studies, if they can also show the points the authors are trying to make with respect to saturation, etc.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13739, 2009.

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