

***Interactive comment on* “Determination of OM/OC ratios and specific attenuation coefficients (SAC) in ambient fine PM at a rural site in southern Ontario: implications for emission sources, particle aging, and radiative forcing” by T. W. Chan et al.**

Anonymous Referee #3

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Review of “Determination of OM/OC ratios and specific attenuation coefficients (SAC) in ambient fine PM at a rural site in southern Ontario: Implications for emission sources, particle aging, and radiative forcing” by Chan et al.

Overview of the manuscript

This paper describes ambient site observations derived from thermal analysis for OC/POC/EC, AMS for OM, and PSAP for particle absorption. The authors attempt

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to draw major conclusions from these three popular aerosol characterization methods from a very limited dataset. It is important to note upfront, that the sample collection methods for the three analyses are very different and also that this study was conducted at a site with very low OC concentrations ranging from 1 to 2.5 $\mu\text{g}/\text{m}^3$. From this dataset, the authors present arguments for a new OM/OC determination method and particle aging determination from correlations of POC with other data. Although this paper is interesting and potentially very important, the presented arguments are built on a poor foundation with many assumptions and uncertainties. The magnitude of the conclusions and the poor foundation for them bring me great concern. For this reason, I cannot recommend this paper for publication in ACP at this time. The paper is cumbersome with too much data and not enough error analysis and data validation. It seems to me that this paper needs to be broken into at least 2 separate papers to substantiate the arguments presented. Please see my comments below for more specific details to be addressed.

Detailed comments

1. Why did the authors chose to conduct this study at a rural site in southern Ontario? This question is important and specifically pertains to the reliability of the PSAP (Particle Soot Absorption Photometer) measurements which are known to be highly uncertain. Secondly, filter based absorption measurements are riddled with problems (because of the fibrous nature of the filters). Particles can travel deep into the pore spaces, flatten out on the surface, coagulate, and/or absorb to the individual fibers of the filter substrate. An excellent review of the associated problems with filter-based absorption measurements for thermal analysis and PSAP was presented by Subramanian et al. 2007 published in Aerosol Science and Technology.
2. Related to number 1, how do or will the authors address the differences between these two methods?
3. The determination of POC has been well understood to be problematic. As the au-

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thors point out the temperature step between 570C and 800C includes charred organic carbon and carbonate carbon. Additionally the laser attenuation correction is difficult because the charred OC can be often darker than EC on the filter. It appears to me that the new thermal analysis method reported in Huang et al., 2006 varies substantially from other highly used thermal optical method protocols such as IMPROVE and NIOSH. Since so many conclusions in this paper hinge on the correctness of the determinations of OC, POC, and EC, it would have been nice to see some comparison of the results between the analytical methods. I assumed this was done in the previous studies, but did not find it in the cited literature.

4. It has not been proven by Huang et al., 2006 or others (to my knowledge) that the POC is directly proportional to oxygenated organic compounds. The referenced paper states, "Most of the pyrolyzed organic carbon (POC), (formed through charring during the thermal evolution process), possibly some remaining OC-based compounds (e.g. high molecular weight refractory carbon), and carbonate carbon (CC) are released at 870 C." Further the Huang et al. paper reports very limited data corresponding to the POC time segment; the only oxygenated compounds they studied were sucrose and glucose. The nature of the OC is very important. A number of studies have presented findings of oligomers formed by esterification reactions. What about nitrooxy sulfates, organic sulfates, organic nitrates? How do these compounds behave in the thermal analysis? Since standards are not available it's difficult to say at present. But it is important to note, that there are many hundreds of unidentified oxygenated organic compounds that may evolve between the OC and/or POC temperature steps.

5. Given the high uncertainty of the AMS OM determination described by the authors in lines 378 through 391, the data collected by the alternate method cannot validate the OM/OC ratio determination directly from thermal analysis.

6. The long discussion of the ambient measurements does not add to this paper. The ambient measurements were divided quite substantially into sources by wind direction. The primary wind direction has to be at least 40% of the time. This is very low. Also the

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division of the samples makes the sample sets for correlation analysis small. Further, the source attribution assignments need to be confirmed with molecular marker analysis or AMS data. I did not understand it there is more related data or not in another paper, but if so the results should be at least summarized here.

7. Related to the site location and aerosol aging, the authors need to recognize that EC also undergoes chemical transformation in the atmosphere and may diminish with time (Decesari et al., Atmos Env. 2002).

8. There is a conceptual misunderstanding in the introduction. In lines 52-57, there is a description of the OC sources: primary emissions, “condensation of the low-volatility primary emitted organic gases, and secondary organic aerosol (SOA) formation via photochemical oxidation. . .” Gas to particle condensation of low volatility gases is not likely since dilution increases the volatilization of gases. This is governed by the partitioning equilibrium between a gas and a solid. Now on the other hand, partitioning from gas to liquid with aqueous transformation (aka aqueous SOA formation or cloud processing), may be possible. The aqueous phase pathways and other heterogeneous reactions alter the chemistry and particle morphology, thus potentially altering substantially the aerosol properties observed at a rural site. I recommend the authors review Poschl Angewandte Chemie-Int. Ed. 2005 to update the aerosol aging and transformation processes.

9. The abstract was poorly written. I would prefer to read first why the paper and findings report within are important, brief notes of the instrument method or unique analysis, and major conclusions and implications. There are a few sentences that read too much like other sentences in the text (methods and results) and a few that are worded strangely and thus are confusing. The description of the air masses from the south. . . and those from the north. . . need revision/clarification.

10. A decreasing trend. . . sounds better than a decrease trend. . . see line 38.

11. Biogenic influence versus SOA? Where do we draw the line? Obviously SOA can

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arise from either biogenic or anthropogenic emissions. As presented in a few papers, most notably Volkamer et al. GRL 2006 which was titled, "Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected," that SOA is quite substantial in anthropogenic emissions. Biogenic influenced SOA may look different, but the molecular properties are not well understood.

12. The authors indicate as a main objective to determine "the relationship between POC and the degree of oxygenation/aging." I don't see how this is possible. First, POC is not agreed upon nor proven. Second, the degree of oxygenation/aging cannot be estimated by thermal analysis, AMS OM determination, and/or PSAP. The chemistry is complex and cannot be presented without comparison to controlled studies.

13. Related to #12, the third objective of the paper is to "examine the influence of POC and sulfate as the impact of aerosol aging on the SAC to estimate the value of SAC of primary emitted soot particles." Here the authors extend uncertain conclusions to PSAP data collected in a relatively clean site. The uncertainty of the instrument is too high for "clean" sites.

14. PSAP data must be corrected. The Bond et al., 1999 citation is a good start, but it's not the definitive answer to PSAP correction. Generally, parallel absorption measurements using a photoacoustic or nephelometer are collected for an accurate determination of the correction factors. Since the applied correction factors are a vital component in your data QA process, they need to be specifically described here and compared if possible to other correction methods to substantiate the paper conclusions.

15. Related to sampling protocols and collection efficiencies, the authors compare 1-minute PSAP data to 24 hour integrated filter samples for thermal analysis? This sounds like another source of big error and uncertainty.

16. How was the biogenic period determined? The description in lines 274-276 is very short and refers to yet another outside paper. Related to the above comments, I recommend brief summary of key findings with the reference to substantiate these

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claims.

17. Line 288, “The difference in concentration. . .” What difference do the authors refer to?

18. Paragraph in lines 306 to 324, summarizes the data tables without adding much to my understanding of why this data is important. I recommend that a few key findings be presented with supporting data and leave the mundane in the table without additional description.

19. Correlations given in the paper tend to be fairly weak. Although, it seems likely that some relationships are identifiable, the cause of the relationships are not substantiated by the statistics.

20. Easy target: two AMS instruments don’t agree well with each other? This is a red flag that the cross comparison of the various methodology don’t necessarily agree well either. Collection efficiencies and sample collection intervals and times are very likely causes of the weak correlations. Also keeping in mind the rural site which is relatively clean, thus the uncertainties are quite substantial compared to the measured/determined values.

21. What is TE?

22. The ratio of toluene and benzene seems irrelevant with respect to the site’s emission sources. The particle aging that may be determined from this ratio is only that originating from vehicular emissions. Thus, there is a relative particle aging for some of the aerosol, but aerosol is a complex mixture (internal or externally mixed) of particles from several sources (vehicle emissions, biomass combustion, cooking, biogenic SOA, aqueous SOA (aka cloud processing), anthropogenic SOA, etc.).

23. If the authors can substantiate the POC determination and the babs measurement from PSAP, then I would find the relationship between SAC and POC to be more interesting. At this point, I feel this is highly speculative. Also the plots shown in Figures

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6, 7, and 8 are too scattered with too much information to be helpful. This section alone could be made into an excellent paper with more complete error analysis and after the ambient measurements are verified by at least the inclusion of the AMS data. Again a major stumbling block here is the validity of the PSAP data in a “clean” ambient environment.

24. Minor errors are found throughout the text. Some are simple grammar and some are typos. One important typo is the dates in Figure 1. Figures and tables don't show data. The authors present data in tables and figures. Line 493 found should be find. Line 337 is should be was. “Values in Table 2a represent. . .” in line 307 should be reworded. Line 166, last should be lasted. Just to name a few.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 14315, 2009.

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