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Interactive comment on "Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols" *by* Q. Zhang et al.

Q. Zhang et al.

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We first thank the reviewer for his/her rapid review and thoughtful comments. Below we include our responses to each point after reprinting the reviewer's comments in italics.

Reviewer Comment*: Overall, this is an extremely well written manuscript. There are minimal errors and the paper is extremely well laid out and clear. The content of this study is timely as the roll of organic material in atmospheric aerosol is currently of interest in atmospheric science. The paper will make a good addition to the literature and is appropriate for ACPD.*

Response: We thank the reviewer for this comment

***Reviewer Comment**: 1. AMS aerosol characterization is laid out in this paper up to 1000 nm. I notice from previous work that the AMS is increasingly inefficient above (numbers vary) about 600 nm. Why is 1000 nm used? A cryptic statement is made in the Experimental about inlet size differences and references to other papers.*

Response: The AMS has partial particle transmission beyond 600 nm (Jayne et al., 2000). Indeed, as shown in Figures 4-8, signals above 600 nm are clearly seen for all species. The first paper on the AMS showed about 50% transmission at 1000 nm, which is typically referred to as PM1 (Fig. 9 on Jayne et al., 2000). Slightly different aerodynamic lens designs have been used in the AMS, including during the Pittsburgh study, and each lens may have different particle transmission characteristics. This is a subject of ongoing research. This point will be clarified in the revised manuscript.

***Reviewer Comment**: 2. It appears many of the figures (e.g., 1 and 13, 2 and 3, 5 and A1, etc.) hold exactly the same information plotted in either identical or very similar ways. As a consequence this results in a much longer paper than it need be.*

Response: The AMS data are complex and multi-dimensional, containing information of concentrations vs. composition (inorganic and organic) vs. size vs. time. Any plot from AMS data is a 2 or 3-dimensional slice of this 4-dimensional data space. In our work we find that it is very necessary to project the 4-dimensional data in multiple ways in order to fully understand and illustrate their meaning. We also find that audiences at our presentations understand our points better if we "slice" the multidimensional data matrix in different ways.

Even though similar data are shown in some figures, each is presented in a different context to support different points. For instance,

1. Figure 1 provides an overview of the temporal variations in HOA and OOA mass concentrations while Figure 13 focuses on the similarity of the daily decrease in HOA and CO concentrations, which supports our point that we did not see

ACPD

5, S2806–S2813, 2005

clear evidence of rapid HOA oxidation in Pittsburgh. The later point cannot be appreciated in Figure 1 due to the compression of the time axis.

2. The scatter plots in Figure 3 are a necessary supplement for Figure 2 as they provide a complementary view of these extremely important correlations, and better show the degree of scatter and/or deviations from linear relationships.

3. Figure 5 presents the average particle size distributions for selected inorganic ions, HOA and OOA. We use this figure to discuss the similarities and differences between PM species, and the processes that may produce them. Figure A1 shows the good agreement between the average size distributions of TOTAL organics (which are not shown in Figure 5) estimated by 2 different approaches - the standard procedure used by most AMS users and an improved procedure presented in this paper that uses the HOA and OOA size distributions.

***Reviewer Comment**: 3. It is my understanding that the AMS does not efficiently measure EC. Although the topic is mentioned in passing throughout the paper I can find no single description of how HOA is related to POA is related to EC and why it is expected that the AMS would be used to determine the quantity of this species. Conversely, it is expected that OOA is SOA which is accessible to the AMS. Specifically, there is a comparison of the POA/SOA to EC/OC ratios made but if, as is my understanding, the AMS can not quantify EC then why is it expected that this comparison can be made?*

Response: We do not state nor imply that the AMS measures EC. This paper does explore the correlations between HOA (measured by the AMS) and "Primary Organic Carbon" (POC). POC can be estimated from EC measurements made by the Sunset Labs carbon analyzer, by using the "EC tracer method" (Since POC is typically adsorbed on EC, POC = EC * estimated POC-to-EC-Ratio; see e.g. Cabada et al. 2004a referenced in the manuscript). This is discussed in detail on page 8439 of section 3.4. In this manuscript, the correlations between HOA and POC are used to present evidence that most HOA is likely from primary emissions in Pittsburgh. This is discussed

ACPD

5, S2806–S2813, 2005

in detail in section 3.4. We will revise this section to improve its clarity in the revised version.

***Reviewer Comment**: 4. It would be useful for the authors to comment on the need for yet another AMS publication from Pittsburg (from the references there appear to be at least two others plus a fourth paper on the HOA / OOA method). It is not clear why all this work is not presented in a comprehensive work from Pittsburg or, otherwise, why is the HOA / OOA method not described for all recent AMS work in a single comprehensive manuscript (a reference is made to a paper (Dzepina 2005) that would appear to be this same paper but using data from Mexico). To be clear this is an excellent paper but this group of authors needs to begin to self impose a restriction on the shear number of recent papers from AMS instruments that are appearing in the literature. A quick scan of recent ACPD papers illustrates this point as well as anything. It will be highly disappointing if this paper is but the first of many individual papers on HOA vs. OOA from a multitude of field locations. If this is the authors plan I would HIGHLY recommend that they remove this paper and a SINGLE comprehensive manuscript be written.*

Response: We disagree with the reviewer on these points. We believe that each paper should be judged on its own merit, and on whether it has scientific and/or technical content that is substantially different from that of previous publications.

The four Pittsburgh AMS papers from our group discuss different scientific topics and have been written and published over the course of more than 3 years. Shown below are the citations in chronological order:

1. Zhang, Q.; Stanier, C. O.; Canagaratna, M. R.; Jayne, J. T.; Worsnop, D. R.; Pandis, S. N.; Jimenez, J. L. Insights into the chemistry of new particle formation and growth events in Pittsburgh based on Aerosol Mass Spectrometry; Environ Sci Technol 2004, 38, 4797-4809. (submitted on December, 2003; 13 pages in print)

ACPD

5, S2806–S2813, 2005

2. Zhang, Q.; Canagaratna, M. C.; Jayne, J. T.; Worsnop, D. R.; Jimenez, J. L. Time and size-resolved chemical composition of submicron particles in Pittsburgh - Implications for aerosol sources and processes; J. Geophys. Res. 2005, 110, doi:10.1029/2004JD004649. (submitted on February, 2004; 19 pages in print)

3. Zhang, Q.; Alfarra, M. R.; Worsnop, D. R.; Allan, J. D.; Coe, H.; Canagaratna, M. R.; Jimenez, J. L. Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry; Environ Sci Technol 2005, 39, 4938-4952, doi:4910.1021/es048568l. (submitted on September, 2004; 15 pages in print)

4. Zhang, Q.; Worsnop, D. R.; Canagaratna, M. R.; Jimenez, J. L. Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: Insights into sources and processes of organic aerosols; Atmospheric Chemistry and Physics Discussions 2005. (this manuscript, submitted on August, 2005)

This series of papers has emerged over the course of 3 years from very careful analysis of the data, and a gradual buildup of knowledge and understanding of the dataset and the atmospheric characteristics of the study site (US EPA Pittsburgh Supersite). There is very little (unless necessary) overlap in results/discussions among these papers. The scientific merit of all these papers is high and each one of them reports new information and discusses new insights regarding atmospheric aerosols. Specifically:

1. Paper #1 is the first paper that investigated the chemistry of new particle growth in the atmosphere by using an AMS and two SMPS systems. These results were selected for the cover of the special issue of Journal of Geophysical Research on the EPA Supersites (even though the paper was published in EST), which involved hundreds of scientists and instruments. This paper was published in September 2004 and has already been cited 10 times (from ISI Web of Science), and only one of the 10 citing papers is from our group.

ACPD

5, S2806–S2813, 2005

2. Paper # 2 discussed the general characteristics of submicron aerosol species (inorganic ions + organics) in Pittsburgh. It presented the most detailed comparison between an AMS and collocated instruments at the time of publication. It is also the first paper to our knowledge that uses highly-time resolved chemical speciation data to evaluate the potential importance of SOA formation on acidic particles in the ambient atmosphere.

3. Paper # 3 presents a novel data analysis technique that yields information on HOA and OOA from AMS data. This is a methodology paper, constrained in length by the page limits for EST articles, that is focused on the mathematics and validation of the deconvolution method. The automated deconvolution technique presented in paper 3 is of particular interest and utility since it greatly simplifies the otherwise extremely complex AMS organic spectra into a physically meaningful and much smaller set of results. Thus it is important for the technique to be thoroughly described in the peer-reviewed literature.

4. Paper # 4 (this paper) is the first that presents a detailed report on the characteristics of HOA and OOA at a well characterized location (Pittsburgh) and discusses in depth how the deconvolved HOA and OOA components can be related to the possible sources and processes of organic aerosols at that location.

Presentation of the above material in 4 separate publications, has allowed:

1) Timely dissemination of information

For example, there was no reason to wait to publish some of the first measurements of the chemical composition during new particle growth (Paper 1, 2004) until the mostly unrelated analysis of HOA/OOA (this paper) were finished. The HOA/OOA results have taken > 1.5 yrs after the nucleation results were ready. The HOA/OOA deconvolution method was developed after the submission of the first two papers and a comprehensive analysis of HOA and OOA in Pittsburgh was finished after the publication of both.

ACPD

5, S2806–S2813, 2005

2) Clarity of presentation

A massive paper with many unrelated or loosely related themes and topics can be confusing and ineffective. Important findings/discussions on specific subtopics tend to be drowned in the mass of text and figures in such papers. However, they can be much better communicated in stand-alone shorter papers. When we submit very long papers, the reviewers and editors often ask us to consider breaking them down into two parts. A single paper from Pittsburgh, combining the four papers listed above into a 60+ (printed) page article would be much less effective at communicating our findings than the four papers we have published so far.

Following the referee's suggestions, the introduction of this manuscript will be revised to briefly specify how this manuscript relates to the three articles on Pittsburgh PM published earlier.

In terms of the reviewer's question, *"why is the HOA/OOA method not described for all recent AMS work in a single comprehensive manuscript"*, our response is that the details of the mathematical method itself have been effectively discussed and evaluated using the AMS data from Pittsburgh only (Paper 3), and there is enough new science to report using the Pittsburgh dataset alone. We are currently writing a comprehensive manuscript on HOA/OOA from many sites in collaboration with 10+ groups in the AMS community, which will not be a paper on the organic aerosol deconvolution method, or on the details of each site. It will be a paper that overviews and compares the HOA and OOA characteristics in various atmospheric environments and discusses the underlying science. In addition, while the authors of this paper do collaborate with several of these groups, we find the reviewer's suggestion (that we should or can impose publication limitations on any of these independent research groups) unreasonable.

Regarding the reviewer's concern over the publication of a large number of AMS related papers, and the possibility of future publications of many individual papers on HOA/OOA, our expectation is that the HOA/OOA results (as well as those of more

ACPD

5, S2806–S2813, 2005

powerful deconvolution algorithms along the same lines) will be part of future papers that analyze AMS ambient PM data. Since these results add new unique information to each study, we can't see why this would not be the case.

Within this context, while several papers using AMS results have been published in ACPD recently, they address vastly different topics. E.g. Allan et al. report on the composition of new particles at the Hyytiälä boreal forest (a topic and location that has spawned a large literature on its own); Salcedo et al. report on the size-dependent composition of particles during an intensive field study in Mexico City; and other papers address CCN closure in Toronto, and density changes of aerosol upon chemical reaction.

We strongly believe that the scientific merit, rather than the number of papers that focus on results from a given instrument should be judged. We are confident that the reviewers of the various papers will do so and that papers that merely duplicate previous work will be rejected in the peer review process.

References:

Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, Aerosol Science and Technology, 33, 49-70, 2000.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 8421, 2005.