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Atmospheric
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Discussions

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 thoughtful comments. Below we include our responses to each point after reprinting the reviewer's comments in italics.

Reviewer Comment: *General Comments: This manuscript describes an extensive and thorough analysis of AMS and gas phase data that yields detailed and quantitative insights into the nature and sources of organic aerosol particles measured during a short campaign in Pittsburgh. The results are a convincing and self-consistent picture of the organic (and sulfate) aerosol in this area. Quantitative estimates are made for the oxidized (essentially SOA) and hydrocarbon (essentially POA) components us-*

ing a recently developed approach and mass spectra provide further information on aerosol composition. The paper is one in a continuing series covering different aspects of methodology and demonstrations of the utility and power of the AMS technique, which may serve as a model for studies of ambient aerosol chemistry. Although the manuscript is long, it is a cohesive presentation and is well written. I think it is an important and well-done study and is certainly suitable for publication in Atmospheric Chemistry and Physics. I suggest the following comments be addressed.

Response: We thank the reviewer for this comment

Reviewer Comment: *Specific Comments: 1. In reading the introduction to this paper, I, like Reviewer 1, became concerned about the overlap with previous publications by this group. The posted response by the authors to the comment by Reviewer 1 clarify this matter to my satisfaction. The response should somehow be incorporated into the manuscript, however. The itemized response is too long in its current form, so I suggest simplifying it to a few sentences that will better place the current paper in the context of the earlier papers. This is important since there are many references to the earlier work and one should not expect that the reader has read them.*

Response: According to the reviewer's suggestion, we have now included in the last paragraph of the introduction a brief explanation of the topics of the other 3 papers and why this paper discusses HOA and OOA specifically.

Reviewer Comment: *2. Page 8432, bottom paragraph: Do the authors have any comments on why the HOA/CO, POA/CO, HOA/NOx, and POA/NOx ratios quoted here differ so much? Is this likely due to fleet differences, analytical methods, or something else?*

Response: According to the reviewer's suggestion, we now included at the end of the corresponding paragraph several possible reasons for the variations in various measured POA (or HOA)/CO and POA (or HOA)/NOx ratios.

Reviewer Comment: *3. Page 8433, lines 15-20: Since the vacuum aerodynamic diameter is a quantity that readers may not be familiar with, I suggest noting its relationship to the geometric diameter, and if possible, give an estimate of the geometric diameter corresponding to a vacuum aerodynamic diameter for organics and sulfates.*

Response: According to the reviewer's suggestion, we now discussed briefly how Dva is related to particle physical diameter right after the introduction of this term.

Reviewer Comment: *4. Page 8437: Is there any indication that a significant fraction of the m/z 46 signal comes from organic nitrates? What is the source of CO2+? Is it only from acids? Is CO+ from carbonyls or is it also a fragment from acids and other compounds?*

Response: Organic nitrates do produce a signal at m/z 46 in the AMS. However based on the correlation between the NO+ and NO2+ signals and the signals from ammonium, as well as the fact that nitrate was predominantly detected when the aerosol was neutralized by ammonium [Zhang et al., 2005b, referenced in the manuscript] indicate that inorganic nitrate was the main form of this species during the Pittsburgh study.

Regarding the CO2+ ion, the following text is taken from our previous publication [Zhang et al., 2005a, cited in the manuscript]: "(c) Association of m/z 44 with Oxygenated Organics. According to laboratory studies, the CO2+ ion (m/z 44) is observed intensely in the AMS mass spectra of di- and polyacids. The spectra of monoacids and other oxygenated organic compounds, including carboxylic acids, esters, carbonyls, and alcohols, also show signals at m/z 44, although at significantly lower intensity (Alfarra et al., 2004 [also cited in this manuscript]; and unpublished data from Philip Silva, Utah State University).

CO+ can be produced from carbonyls, acids and gas phase CO2 in AMS, due to electron ionization and pyrolysis. Detailed discussion is given in page 4941-4942 in Zhang et al. [2005] cited in the manuscript.

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Reviewer Comment: *5. Page 8437: The measured C:H:O ratio of 1:1.6:0.8 could also be presented in a way that allows the reader to better grasp what this means in terms of the nature of the oxidized products. For example, this is equivalent to a C:H:O ratio of 5:8:4, which is the molecular formula of glutaric acid. This is the least volatile C5 compound possible for this formula. It is also the molecular formula of a C5 dihydroxy-dialdehyde, which would be expected to be more volatile. However, compounds such as these are formed from the oxidation of aromatics and are thought to become less volatile by forming oligomers through heterogeneous reactions.*

Response: The reviewer brought up a very interesting point. However, our OOA component is likely a mixture of hundreds of compounds, and the C:H:O ratio represents the average of the bulk. We suspect that it is a coincidence that this ratio is the similar to that of glutaric acid. But we agree that using integers may help the reader making connections to real-world compounds. We therefore included the integer ratios in addition to the decimal ones that are normalized to one C atom.

Reviewer Comment: *6. Page 8438, Lines 1-5: I suggest also quoting the actual values of the OM:OC ratios obtained by Russell (2003), as is done for the Turpin and Lim values.*

Response: We now quote in text the OM:OC values given by Russell et al. (2003).

Reviewer Comment: *7. The observation that the mass spectrum of OOA formed during the new particle formation event is similar to that of aged organic aerosol is interesting. Considering that the time scale for this event is a few hours, and that the OOA products are highly oxidized, it would appear that the VOC precursors for OOA must either be freshly emitted aromatics such as trimethyl benzene or oxygenated compounds present in the background air. Only these compounds could form such highly oxidized condensable products (consistent with the C:H:O ratio) on this short time scale. Do the authors have any thoughts on the VOC sources of OOA?*

Response: Unfortunately we sampled in Pittsburgh by the end of the PAQS study,

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when VOC monitoring had already stopped. Thus no VOC data are available to address this question. A relatively clean air mass arrived on the morning of Sep. 12. According to back-trajectory analyses (HYSPLIT) this airmass originated in Northern Canada, and likely contained biogenic VOCs, in addition to the anthropogenic VOCs locally emitted in Pittsburgh. Thus the source of the VOCs resulting on SOA production during this day are unclear.

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