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Interactive comment on “Chemical evolution of organic aerosol in Los Angeles during the CalNex 2010 study” by R. Holzinger et al.

Anonymous Referee #2

Received and published: 19 June 2013

General Comment:

This paper characterizes the evolution of the chemical composition of organic aerosol measured at the Pasadena ground site during the CalNex field campaign. Measurements from a TD-PTR-MS are analyzed extensively using AMS measurements as a basis for comparison. The mass associated with the ions measured by the PTR represent 25-60% of the OA mass measured by the AMS. The two main conclusions of the manuscript are (1) the photo-chemical age of OA decreases during the middle of the day, and (2) the PTR measured higher N concentrations than the AMS, which the authors attribute to multi-phase chemistry involving ammonium ions. This manuscript is well written and contributes to our understanding of OA formation and evolution in a major urban area. The paper can be published once the comments below have been

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addressed.

Comments:

End of Introduction: "Thus much more organic chemical information is preserved relative to the AMS. We focus on the comparison of AMS and TD-PTR-MS and our results illustrate the potential of TD-PTR-MS for elucidating different chemical pathways of aerosol formation.", At the end of this paragraph please include a few more sentences that list the measurements, insights, and potential chemical formation pathways the TD-PTR-MS data will show that the AMS can't, and in what section this information will be discussed.

The data suggests that chemical fragmentation gains importance over functionalization as OA photo-chemical age increases, but also that the photo-chemical age of OA decreases during daytime hours due to rapid production of SV-OOA. Does this imply that fragmentation is to some extent less important than functionalization in terms of understanding the formation and evolution of OA in Los Angeles?

Page 12870, Line 8-10: Please provide 1-2 more sentences explaining why heterogeneous and multi-phase processes are poorly represented in most atmospheric models.

Page 12871, Line 11-12: Please include the range of operation temperatures here since you mention 600 C for the AMS above.

Page 12871, Line 22: "16 June 2010", abstract says 15 June.

Page 12872, Line 7: What is the purpose of a dual inlet?

Page 12873, Line 14-15: Please estimate what fraction of the aerosol would have evaporated for a typical aerosol concentration.

Page 12875, Line 12-13: "...reaction rate constant may be different for different fractions of organic aerosol (OA).", Which OA components do you expect to have higher/lower reaction rate constants?

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Page 12875, Line 15: “~30%.”, Please confirm that this refers to the measure OA mass concentrations. How is this accuracy determined? What about aerosol that doesn’t vaporize below 350 C?

Page 12876, Section 2.5: How is the m/z calibration carried out in analysis? - Are there ions inherent in the instrument that are used? If so, list what they are?

Page 12880, Line 13: The scatter plot shown in Figure 2 seems to be displaying 2 correlations? Can the authors attribute this to anything (e.g. daytime vs night time, weekend vs weekday)? Also please change “total OA” to “AMS-OA” in the legend of Figure 2.

Page 12882, Line 15-16: What fraction of the PTR-MS mass do the excluded ions represent?

In Figure 3a-f, are the PTR timelines averages or summations? Also, did all temperature ramps for one ion correlate with the same AMS profile?

Page 12884, Line 1: Should “above 90” by “above 190”?

Page 12886, Line 11-18 through Page 21, Line 1-2: This paragraph is an important distinction between what information you can get with an AMS and what you can get from a PTR. Please add a sentence or two highlighting this.

Figure 5: Should PTR-OA be on another axis? Should the y-axis label be “fraction of total PTR-OA signal”?

Page 12888, Line 5-7: This sentence is slightly confusing as written. Is it correct to interpret this to mean that LV-OOA mass forms from the oxidation/functionalization of SV-OOA mass, but that at some point, the LV-OOA becomes so oxidized that any additional LV-OOA mass the forms is offset by LV-OOA mass that is lost due to fragmentation. This should be consistent with (LV-OOA ions)/delta(CO) plotted as a function of photo-chemical age increasing and then leveling off at some point. I recommend including a figure in this manuscript that is similar to the subfigure in Figure 8 in [Hayes

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et al.(2013)] using the groups of ions discussed in this study and coupling it to the discussion in section 3.3.

Page 12888, Line 27-28: Is this because it measures less OA than the AMS due to the lower vaporizer temperatures?

Page 12889, Line 5-8: Has there been a calibration for different types of compounds into the PTR-MS to see what the uncertainty for O:C and H:C is?

Figure 1: Please include a subfigure for the gas-phase because it is difficult to see what typical gas-phase thermograms look like in the current figure.

Figure 4: Please use different colors for the SV-OOA and LV-OOA ions because the purple and maroon are difficult to distinguish where they overlap.

Figure 10: Why isn't PTR-OA the largest?

Please correct all instances where "which" is used when "that" should be used. For example, Page 12872, Lines 20-22 is the correct usage of "which", while Page 12871, Line 25 is the incorrect usage.

References:

Hayes, P. L., et al. (2013), Organic Aerosol Composition and Sources in Pasadena, California during the 2010 CalNex Campaign , J. Geophys. Res.-Atmos., In Press., doi: 10.1002/jgrd.50530.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 12867, 2013.

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