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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 #3

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The paper presents a detailed analysis of TD-PTRMS data of organic aerosol measured in Los Angeles during the CalNex 2010 campaign. Utilizing the high resolution of the ToF-MS, elemental composition is determined for individual ions. The time series of individual ions are correlated with AMS results and thereby interpreted as contributing to aliphatic (HOA), local (LOA), semi-volatile oxygenated (SV-OOA) and low volatile oxygenated (LV-OOA) factors of the observed organic aerosol. The results are interesting to the community and deserve publication after consideration of the following major points.

Overall it is difficult for this reviewer to judge the comparison of PTR with AMS results, as the AMS results are only very briefly mentioned and the cited literature could not be found (Hayes et al 2012 or Hayes et al 2013, not clear from the manuscript). A more

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detailed coverage of the AMS results would certainly be justified and help the reader.

Main comments:

1. It remains unclear why the PMF results from AMS data are considered as complete picture with respect to the factors/sources present in the observed aerosol. As PTRMS features a softer ionization technique and thereby enhances possibilities to identify individual molecules in the aerosol, one should assume that the level of detail that can be extracted from such a data set goes beyond the level of source understanding obtained from AMS data. One very straight forward thing to do would be to apply PMF analysis to the PTR data independent of AMS results. The identification of the same number and time series of factors in both data sets would thereby strengthen the overall interpretation of the observations. While the suggested approach may go beyond the scope of this paper, it certainly deserves mentioning in the manuscript.

2. In the same line it seems unlikely to this reviewer that the chosen approach of assigning ions that correlate with a certain factor to one factor only at all times and at all desorption temperatures is revealing the full information content of the data. The chosen approach could be one reason for surprising results obtained such as the finding that LV-OOA ions are detected at lower desorption temperature than SV-OOA ions. In this respect the terminology of LV-OOA and SV-OOA needs to be reconsidered and it is unclear to this reviewer why the authors would term a fraction of their observed signal LV-OOA-ions when they desorb at relatively low temperatures. One is tempted to suggest different terminology here. Information that would be useful in this context is, is the residual signal of PTR ions not assigned to either of the AMS factors dependent on diurnal patterns, temperature, desorption temperature, or any other parameter?

3. With respect to the observed higher N/C ratio in the PTR compared to AMS and the suggested NH₄-driven in particle chemistry as underlying reason for the observed organic nitrogen, the finding is indeed interesting and of importance if substantiated. One aspect related to instrumental issues that needs to be discussed in this context is,

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in how far the humidification and sampling steps pose “contamination” risks that could drive water soluble gases into the particulate phase and enhance in particle (in sample liquid phase to be exact) chemistry. Have the authors performed laboratory studies to test in how far e.g. gas phase NH_3 , amines, HONO , HNO_3 are sampled by the technique and interfere with particulate signal? An uptake of NH_3 in organic particles – regardless if happening in the atmosphere or in the sampling system – should be correlated with organic acid concentration in the particle (e.g. Mensah et al. 2011, Mensah et al. 2012). Therefore information on the functionality of ions that contain N and/or correlate with N-containing organic peaks would be highly interesting. As also discussed in Mensah et al 2012, such an uptake is likely seen as “excess NH_4 ” in the AMS. The AMS data could be used here to check for such indications of NH_3 -uptake by organic particles. Also the detection of such molecules as NH_4 in the AMS and respective assignment to inorganic particle components, might explain (part) of the differences in observed N/C.

Specific comments in order of appearance in the manuscript:

Abstract lines 16 and 20: lower and higher is not informative here without providing an absolute value of a reference temperature.

Figure 1: it is unclear why the authors chose an ion (protonated acetone) that is not considered as informative particulate signal for this figure. Why not chose a more representative ion and skip discussions of artifacts here?

Section 2.9: the two sentences describing the statistical methods do not deserve a separate section. Either elaborate or integrate in other subsection.

Page 12881: discussion on volatility and temperatures: while the authors correctly state that a comparison of volatilization temperature needs to consider the dimension of time during which samples or particles are exposed to certain temperatures, they do not provide information on comparisons of time scales in the approaches they compare. This should be added to give the reader at least some impression of the differences

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between experimental methods.

Page 12883 line 2: “correlated best with LV-OOA” this should be supported by providing e.g. R2 for each of the factors.

Figure 4: the separation of normalized spectra on one y-axis makes it impossible to see quantitatively which fraction a certain ion contributes to the factor mass spectrum. Each spectrum should be plotted with its own y-axis for clear display.

Figure 5: A cumulative plot of the fraction desorbed would be more informative here.

Page 12884 line 15: “Compounds constituting primary organic aerosol are relatively volatile...” This sounds surprising. Is e.g. pollen volatile?

Page 12886 line 15: check sentence

Page 12893 line 17 ff: how does this fit with SV-OOA ions being a minor fraction of the OA-ions?

Figures 2, 3, and A1: Actual date would be a more convenient x-axis, assuming that is what the cited AMS paper would also present.

References:

Mensah, A. A., Buchholz, A., Mentel, T. F., Tillmann, R., and Kiendler-Scharr, A.: Aerosol mass spectrometric measurements of stable crystal hydrates of oxalates and inferred relative ionization efficiency of water, *Journal of Aerosol Science*, 42, 11-19, 10.1016/j.jaerosci.2010.10.003, 2011

Mensah, A. A., R. Holzinger, R. Otjes, A. Trimborn, Th. F. Mentel, H. ten Brink, B. Henzing, and A. Kiendler-Scharr, Aerosol chemical composition at Cabauw, The Netherlands as observed in two intensive periods in May 2008 and March 2009, *Atmos. Chem. Phys.* 12 (10), 4723-4742, 2012

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

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