

# **Replies to referee comments on Holzinger et al., ACPD 13, 12867–12911, 2013: “Chemical evolution of organic aerosol in Los Angeles during the CalNex 2010 study”**

## General Remark:

We appreciate the effort of the three reviewers to provide very useful comments that help further improving our manuscript. Below we answer their comments point for point. For clarity we reproduce the referee comments in ***bold italic*** style.

## Replies to Referee #1, Giuseppe Petrucci:

***Organic Nitrogen: The results of this study show significant disparity in the ambient levels of organic nitrogen (ON) in OA (as well as OA subgroups, such as LV-OOA) as determined by PTR compared to AMS, with PTR detecting higher ON concentrations than the AMS. The authors state that ON is probably underestimated by PTR for several reasons, including fragmentation of alkyl-nitrates in the ionization process which “often produces a neutral nitric acid fragment and an alkyl ion which is detected by the mass spectrometer, or an NO<sub>2</sub><sup>+</sup> ion and a neutral organic fragment: : :” (This would also contribute towards an overestimation of inorganic nitrate).***

***What is the current state-of-knowledge regarding the extent of fragmentation of ON from different chemical classes (e.g. alkyl nitrates, amines) during electron impact ionization (which is employed in AMS)?***

Aiken et al. (ES&T 2008) reported measured N/C ratios for pure nitrogen-containing species and found that the N/C ratio of the detected ions corresponded well with the molecular N/C ratios (4% bias, 22% precision quantified as the average absolute value of the relative error). One important type of species not studied by Aiken et al. are organic nitrates. As discussed by Farmer et al. (PNAS 2010) alkyl nitrates fragment extensively during electron impact ionization in the AMS producing NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> ions. Ambient AMS analyses these ions are typically dominated by ammonium nitrate. In some cases (e.g. Fry et al., ACPD 2013) organic nitrates can still be quantified based on their distinct NO<sub>x</sub><sup>+</sup> fragment ratios, however such an analysis was not possible for CalNex due to the presence of sea salt nitrates that also modify the NO<sub>x</sub><sup>+</sup> fragment ratios (Hayes et al., JGR 2013). Thus, and as already described in the ACPD manuscript, one possible explanation for the differences in N/C between the PTRMS and AMS relates to the possible importance of organic nitrates that may be reported as organic N by the first but not the second instrument for this study.

***Are any of the methods to constrain ON discussed by Farmer et al.1 (e.g. NOx+ fragment ratios, ON ions, HNO3+ ions, and ammonium balance of the nominally inorganic ions)***

**applicable to this study?**

Unfortunately, the methods outlined in Farmer et al. (PNAS 2010) rely on assumptions that do not hold for the measurement site in our study. As discussed in Hayes et al. (JGR 2013) Pasadena, CA is impacted by aged sea salt, which includes sodium nitrate. The sodium nitrate also fragments to produce  $\text{NO}_x^+$  ions in the AMS, but with a different ratio than organic nitrogen compounds or ammonium nitrate. Given the variable and unknown relative amounts of at least 3 nitrate types present at the site, this prevents determination of organic nitrogen concentration by analyzing relative fragment intensities. In addition, the sodium from sodium nitrate impacts that the ammonium balance calculation, since sodium nitrate is vaporized in the AMS but the concentration of sodium is difficult to quantify from the mass spectra. (There is an interference from sodium ions released by the materials used to construct the AMS vaporizer). It is very difficult, in general, to quantify organic nitrogen using an AMS when sea salt influences the air mass over a measurement site.

Sea salt does not interfere with one method that is proposed by Farmer et al., namely, the utilization of organo-nitrate ions measured in the AMS. However, some of these ions can also be produced from reduced nitrogen species, and amines were observed at the Pasadena ground site (Hayes et al. JGR 2013). Overall, it appears that none of methods from Farmer are applicable to this study, unfortunately.

***The authors also explain that the high nitrogen content of LV-OOA is derived from multiphase chemistry, in which liquid-phase ammonium ions may play an important role. The authors should reference prior studies (for example, references 2, 3) that showed the importance of ammonium ions in forming ammonium salts in OA (particularly SOA, which becomes highly oxidized with ageing, like LV-OOA). Also, were ammonium ions detected directly by AMS and/or PTR?***

This information (including references) has been included to the revised version of the manuscript. Ammonium is detected by both instruments (AMS  $m/z$  15-17, PTR  $m/z$  18).

***LV-OOA and SV-OOA: There were several counterintuitive results regarding the LVOOA and semivolatile OOA (SV-OOA) subgroups. This includes the observation of LV-OOA ions desorbing at lower temperature than SV-OOA ions. This result is opposite to those of several studies that showed that LV-OOA has the lowest volatility of the commonly described OA subgroups (for example, references 4-6). ... Can this effect be an artifact of the ramping scheme employed by this study? Do the authors have future studies planned that employ reference aerosols with components of known vapor pressures (across a range of volatilities, representative of LV-OOA and SV-OOA) where they measure thermal-desorption temperature under variable ramping schemes?***

It is hard to imagine that these observations would be different when applying a different heating cycle. Therefore our suggestion is that the release of LV-OOA species is driven by chemical processes (e.g. thermal decomposition or pyrolytic processes).

We have done first experiments to measure the desorption of C<sub>12</sub>-C<sub>24</sub> alkanes from the CTD cell and found the expected behavior of increasing desorption temperature with increasing carbon number. More experiments with different compound groups and an extended volatility range are planned in the near future.

**Sulfate and sulphate: both spellings are employed in the text. The authors should consistently use one spelling. Page 12885, Line 11: “: : rather identifies the best ion makers of SV-OOA: : :” should be “: : :markers of SV-OOA: : :” Page 12879, Line 15: “: : :assumed oxidation state of Nitrogen within: : :” Nitrogen should not be capitalized. PTR-OA, AMS-OA: Italicized and normal text are employed for these abbreviations; consistently use one form. Page 12880, Line 21: (Jimenez et al., 2003) Page 12893, Line 9: “: : :LV-OOA-ions are: : :”**

All corrected.

## Replies to Anonymous Referee #2:

***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 requested information was already given in the conclusions and in the abstract. We feel that repeating this at the end of the introduction would be redundant.

***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?***

This is an interesting, however, very complex question. Both mechanisms certainly occur in the LA region. Whether functionalization or chemical fractionation dominates, depends on many different factors: existing conditions (gas phase precursors, aerosol composition and state of

oxidation), type of chemistry (gas phase, heterogeneous, multiphase), reactant (O<sub>3</sub>, OH, NO<sub>3</sub>, NH<sub>4</sub> etc.), and physical parameters (temperature, relative humidity, etc). Therefore it is not possible to characterize this aspect more precisely than it has been done already.

***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***

The importance of SOA formation has not been realized until a few years ago. Meanwhile most models have parameterizations for SOA formation but this is mostly based on volatility and physical phase partitioning. We realise that our text may suggest that there may be a deeper reason for the poor representation of heterogeneous processes and we changed the wording to avoid such misunderstandings.

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

Done.

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

Abstract corrected

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

The main purpose is a higher time resolution. This information has been added to the manuscript.

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

This is variable but from thermodenuder experiments we can deduce that probably of order 50% of the organic aerosol mass can be evaporated under such conditions. Information added to the manuscript.

***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?***

The reaction rate constant basically depends on factors like size, polarizability, and the distribution of charge in the molecule (polarity). This information and a reference (Su and Chesnavich, 1982) has been added to the manuscript.

***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?**

This estimation is based on the consideration that reaction rate constants for proton transfer are within a relatively narrow range and on comparison with SMPS data during smog chamber experiments. We clarified the statement in the manuscript. The accuracy applies to components that are actually measured. We do not account for constituents that do not desorb at 350 degrees or are lost for other reason. This information is already given at the end of the same paragraph.

**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?**

For a rough calibration we use the signals of  $\text{H}_3^{18}\text{O}^+$  and  $\text{C}_3\text{H}_7\text{O}^+$ . We fine-tune the calibration by varying the parameters to maximise the matches with a library containing  $\text{C}_x\text{H}_y\text{O}_{1-3}$  ions. The underlying assumption is that many detected peaks are  $\text{C}_x\text{H}_y\text{O}_{1-3}$  ions. The Procedures are described in Holzinger et al. (2010b) and we refer to this work in our manuscript.

**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.**

The different slopes in the insert of Figure 2 represent rather synoptic episodes than the difference between day and night. This can be seen in the timeline presented in the main graph (Fig 2).

The legend was adjusted as suggested.

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

This information can be derived from the supplement tables. The fraction is ~12%. The information has been added to the manuscript.

**In Figure 3a-f, are the PTR timelines averages or summations?**

The timelines are the sum of all ions in the respective group.

**Also, did all temperature ramps for one ion correlate with the same AMS profile?**

No. We often observed that a particular  $m/z$  correlated best with e.g. HOA at 150 and 200C and

with SV-OOA for the higher temperatures. The full information can be retrieved from the supplement tables.

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

The text is correct as written. The mass spectrum of the LV-OOA component in the AMS is dominated by small ions.

**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.**

We feel that the text is already clear in the current version.

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

The graph is correct in the current form. However, we added the sentence below to the figure caption to avoid misunderstanding:

“The y-axis represents the fraction of the total signal of the respective ion-group; i.e. the points of each ion group sum up to 100%.”

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

This sentence means to say that there may be limits to further oxidation of LV-OOA in the sense that further oxidation produces volatile fragments that do not remain in the particle phase. All major PTR-ion/deltaCO ratios (HOA-, SVOOA-, and LVOOA-ions) increase as a function of photochemical age up to 0.5 days. The leveling-off of LV-OOA and HOA as observed by Hayes et al. (2013) is not reproduced by the PTR ion groups. So both, the leveling off in Hayes et al 2013, and the narrow distribution of LV-OOA ions in the nC versus OSc space (Figure 6) remain interesting findings that are currently not well understood.

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

*lower vaporizer temperatures?*

No, this is not considered the major reason. Rather we think that losses of O and H at temperatures below 350C play a larger role.

***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?***

A thorough investigation of this is yet to be done.

***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.***

Gas-phase measurements were done in the standard PTR-MS mode. So, there are no thermograms.

***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***

We apology for the difficulties. We darkened the maroon in Figure 4 a bit, but generally we prefer to keep the colors as we use the same colors throughout the paper. Purple and maroon were chosen because these colors are similar to the colors that are used by the AMS community to code SV- and LV-OOA.

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

Because Fig 10 display the ratio of N/C (as labeled for the Y-axis), and not the total amount of N.

***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.***

We double checked and corrected the language.

**Replies to Anonymous Referee #3:**

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

The Hayes paper was submitted more than 6 months earlier than this paper, and we had

expected it to be published by the time our paper was under review. Unfortunately the reviewing process of the Hayes paper in JGR was very slow. Thankfully the article is now in press and can be viewed online at <http://onlinelibrary.wiley.com/doi/10.1002/jgrd.50530/pdf>

**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.**

We agree with the reviewer's reasoning. On the other hand the AMS PMF has been compared with many other aerosol and gas phase data, and the AMS community has accumulated a great deal of experience on the application of PMF. This means that the correct derivation and interpretation of the PMF factors has been tested and confirmed with other techniques. Therefore it made sense to rely on the PMF components derived by AMS and building a lot of our conclusions around the correlation analyses.

We consider PMF analysis on the TD-PTR-MS data as important next step. We have in fact performed preliminary analyses with this dataset. However, the details of such an analysis are far not trivial and require very careful analyses. See for example the following detailed papers for PMF analysis of gas-phase unit-resolution PTRMS data: Slowik et al. ACP 2010 <http://www.atmos-chem-phys.net/10/1969/2010/> and its very extensive public review/discussion <http://www.atmos-chem-phys-discuss.net/9/6739/2009/acpd-9-6739-2009-discussion.html>; Bon et al. ACP 2011 <http://www.atmos-chem-phys.net/11/2399/2011/> and Yuan et al. JGR 2013 <http://onlinelibrary.wiley.com/doi/10.1029/2012JD018236/abstract>, but when successful we hope that PTR-PMF will be capable of revealing further detail. PMF of high-resolution thermal-desorption aerosol data will have to deal with additional complexities, and thus it should be the focus of its own study.

**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.**

There is a slight misunderstanding here: for almost all ions we attributed the signal at different temperatures to different OA components. For example the signal detected at m/z 183.998 was attributed to HOA for temperature levels 100, 150, 300, and 350 C, and to LV-OOA at 200 and

250 C. There are only a very few ions that have been attributed to one component for all temperatures (e.g. 98.025 to LV-OOA). The full information on which ions and temperature levels have been attributed to a particular component is given in the supplement tables. Therefore we do not think that our correlation analysis biases the thermograms.

***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?***

We prefer to stick to the terminology established and tested by the AMS community. Thermo denuder experiments suggest that LV-OOA is less volatile than SV-OOA when suspended particles are evaporated in air. Therefore we think that the PTR thermograms rather reflect chemical desorption from the CTD cell (rather than physical evaporation). The residual signal is very noisy and comprises about 12% of the total detected signal (see supplemental tables). No diurnal patterns have been observed but most of the residual signal is observed at desorption temperatures of 100 and 350C, where signal to noise ratios are the lowest.

***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, 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 NH3, amines, HONO, HNO3 are sampled by the technique and interfere with particulate signal? An uptake of NH3 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 NH4” in the AMS. The AMS data could be used here to check for such indications of NH3-uptake by organic particles. Also the detection of such molecules as NH4 in the AMS and respective assignment to inorganic particle components, might explain (part) of the differences in observed N/C.***

The suggested tests are subject to future laboratory studies. From the available data we do not find evidence that the suggested processes play a significant role. Empirical formulas of the LVOOA-ions are given in the supplement. Many detected ions are rather saturated and do not contain many oxygen atoms. There is no significant correlation between gas phase NH3 and any

of the reported ion groups, which does not suggest an artifact related to NH<sub>3</sub>. Furthermore, we did not observe any excess NH<sub>4</sub> with the AMS. However, excess NH<sub>4</sub> is not a definitive metric in field measurements for NH<sub>3</sub>-uptake, because there are other factors that can influence the NH<sub>4</sub> balance as typically performed with AMS field data (e.g. presence of sea salt, amines, organosulfates, and organonitrates and unneutralized H<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>HSO<sub>4</sub>). The other factors could lead to a low measured/predicted NH<sub>4</sub>, and could probably mask excess NH<sub>4</sub> from NH<sub>3</sub> chemistry, unless it was very large compared with the amount of NH<sub>4</sub> in ammonium sulfate and ammonium nitrate (which is not expected to be the case at this site). On the other hand, the measurements by Mensah et al. (2012) were carried out in a different environment and the Dutch site Cabauw is known to be dominated by inorganic nitrogen chemistry. Altogether, we agree with the reviewer that this issue requires substantial follow up research, which is (unfortunately) beyond the scope of this work.

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

We provide temperatures now.

***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?***

We prefer to keep this part. The discussion of artifacts from gas phase contamination is important.

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

We deleted this section and specified the details at the first occurrence in the text.

***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 between experimental methods.***

This information is provided now: minutes for TD-PTR-MS, tens of seconds for thermodenuder, and less than a millisecond for AMS.

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

R<sub>2</sub> is different for each of the 208 ions. The full information is provided in the supplemented tables. A reference to these tables is given in the beginning of section 3.2.

**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.**

Done

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

A cumulative plot would be an alternative way to present the same data (no additional information). We tried both ways and we feel that the current presentation clearer. Therefore we prefer to keep the current plot.

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

The statement has been corrected: “Compounds constituting newly formed SOA are relatively volatile...”

**Page 12886 line 15: check sentence**

We made the paragraph clearer.

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

Even though our correlation analysis attributed relatively few ions to the SV-OOA, this was the dominant group at the site (compare Figs 3 g-l).

**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.**

For practical reasons we decided to stick with the current date format.