

The following comments pertain to the ACPD submission, Chemical evolution of organic aerosol in Los Angeles during the CalNex 2010 study, by R. Holzinger et al.

General Comment: The submission by Holzinger et al. is a detailed characterization of organic aerosol (OA) as part of the CalNex study (Los Angeles area ground supersite, May 15 to June 16 2010), which places emphasis on comparing and correlating the results determined from a deployed thermal-desorption proton-transfer-reaction mass spectrometer (TD-PTR-MS; hereby simplified to “PTR”) with those from an aerosol mass spectrometer (AMS). This work has presented some unique insights to the chemical evolution of OA and contributes to expanding our knowledge base of this important component of atmospheric aerosols. Notably, in this reviewer’s opinion, the most interesting results (especially those worthy of pursuing in follow-up studies) are those that are counterintuitive and that contrast with prior studies of OA. Some of these are highlighted below, including some points where clarification is needed. A list of errata follows that discussion.

Specific Comments:

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_2^+ 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)? Are any of the methods to constrain ON discussed by Farmer et al.¹ (e.g. NO_x^+ fragment ratios, ON ions, HNO_3^+ ions, and ammonium balance of the nominally inorganic ions) applicable to this study?

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?

LV-OOA and SV-OOA: There were several counterintuitive results regarding the LV-OOA 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, references⁴⁻⁶). Holzinger et al. did extend their analysis by correlating PTR-ions with AMS-PMF components (and excluding AMS-OA components), which makes the group of SV-OOA larger; however, this extended group of SV-OOA still desorbed at a higher temperature than LV-OOA. 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?

Errata: These minor errors that should be corrected. Underlining is for emphasis.

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..."

References

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