

***Interactive comment on “Online atmospheric pressure chemical ionization ion trap mass spectrometry (APCI-IT-MS<sup>n</sup>) for measuring organic acids in concentrated bulk aerosol – a laboratory and field study” by A. L. Vogel et al.***

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The authors thank the referee #2 for thorough reading and improving the manuscript by constructive comments. The manuscript will be revised based on the referee's comments as follows:

Comment: 6153-27 and 6164-1, the issue of possible artifacts in the mVACES concentrator is glossed over by citing the study of Khlystov et al. (2005). In that study the

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artifact was quantified relative to the total aerosol concentration, which included a large fraction of non-volatile ammonium sulfate and LV-OOA. However in their Fig. 1 these authors show that in 2 out of 3 experiments, the concentration of semivolatile ammonium nitrate increased by a factor of 2, due to repartitioning of HNO<sub>3</sub> and NH<sub>3</sub> from the gas-phase. Further the authors present a model study that shows that the magnitude of the artifact for semivolatile studies may depend strongly on the ambient conditions and could reach a factor of 5 (their Figure 3). The potential artifact for organic acids has not been studied in detail, but for semivolatile soluble acids it could potentially be as large as for HNO<sub>3</sub>. Therefore the importance of this issue is really unknown, and it is not known that it is a minor effect. It needs to be discussed on a more balanced manner, and calling out for future studies that look at this issue in detail.

Reply: The authors agree that the issue of potential artifacts of semi-volatile organic acids is not sufficiently discussed. Due to limited literature on mVACES artifact assessment, the authors did not want to overinterpret the study by Khlystov et al. by assuming that the inorganic nitrate artifacts can be equally considered as organic semi-volatile compounds. Semi-volatile organic acids are less water soluble than nitrate, therefore we came to the statement that artifacts are a minor issue by looking at the organic matter in Fig. 1 of Khlystov et al. (2005) in which all three cases show significant less artifacts than the semi-volatile nitrate. We are aware that LV-OOA is less vulnerable than SV-OOA towards possible artifacts. However, in contrast to what would be expected for positive artifacts (i.e. a larger fraction of SV-OOA in the particle phase) we observed surprisingly high concentrations of semivolatiles in the gas phase after the concentrator. Therefore, we believe that these artifacts are smaller for SV OOA than for nitrate. However, to better address the issue of artifacts, the revised paper will be more cautious in describing possible artifacts and will be calling out for future studies to characterize artifacts of semi-volatile organic material in water based aerosol concentrators. The rewritten part at p. 6153, l. 26 is now: “Khlystov et al. (2005) investigated the VACES technology with focus on artifacts due to repartitioning from gaseous compounds into the particle-phase. They observed significant positive arti-

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facts for semi-volatile nitrate, based on the enrichment factor of sulfate. Artifacts for organic material were less pronounced, however, the artifacts of semi-volatile organics were not investigated by Khlystov et al. and further fundamental studies are needed in order to clarify those issues.” p. 6162, l. 26 to p. 6163 l. 2 was rewritten as well (see reply on comment 2 by referee #1).

Comment: 6154-11, is the O<sub>2</sub><sup>-</sup> reagent ion exclusive to acids? The paper appears to assume this, but a reference should be provided, since it is plausible that O<sub>2</sub><sup>-</sup> could also react by charge transfer or other mechanisms, and this affects the interpretation of the comparison with the CTOF-AMS.

Reply: In order to better address the ion chemistry, and which analytes are accessible by the O<sub>2</sub><sup>-</sup> ionization, the experimental part is extended by the following section (starting from p. 6154, l. 13) also including further literature: “Briefly, O<sub>2</sub><sup>-</sup> ions are formed at atmospheric pressure by a 3 kV corona discharge between a needle and the transfer capillary (Fig. 1). Gaseous analytes, which have a higher gas-phase acidity than O<sub>2</sub><sup>-</sup>, become ionized by proton transfer reactions. Remaining excess energy of the proton transfer reaction is transferred by collision to a third neutral molecule. The O<sub>2</sub><sup>-</sup> reagent ion is selective towards organic acids, inorganic acids, nitrophenols and combination between those compound classes (e.g. organosulfates). Veres et al. (2008) described a similar CI-MS method using acetic acid as reagent ion. Due to a lower gas-phase acidity of O<sub>2</sub><sup>-</sup> compared to acetic acid (Bartmess, 2011), most atmospherically relevant organic acids are detected by the O<sub>2</sub><sup>-</sup> ionization method. Both techniques show limited response on organic acids which rapidly undergo thermal decomposition, e.g. oxalic acid or malonic acid.”

Comment: 6163-13. The total organic acid concentration is estimated using the sensitivity of pinic acid. The uncertainty on this total acid concentration is not quantified. More detail is needed here, on what is known about variations in sensitivity of different acids using O<sub>2</sub><sup>-</sup>, as well an error bar on the resulting concentrations (even if it is rough, such as ‘approx. a factor of 2’).

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Reply: Unfortunately, there is very few literature about ionization efficiencies of different organic acids using APCI. Furthermore, most of the signals which were measured during the HUMPPA-COPEC campaign can't be assigned to identified compounds. Therefore it is difficult to estimate the uncertainty. However, Fig. 5 was extended by uncertainty bars: +/- 20% AMS uncertainty and +/- 50% APCI-MS uncertainty (see also reply on comment 3 by referee #1).

Comment: Abstract and p 6165, a conclusion is reached that fast reacting or unknown VOCs must account for a substantial fraction of the acids measured in this forest, based on the observation in the field of additional MS/MS peaks compared to limited laboratory experiments. However only ozonolysis experiments were performed in the lab, while in the field a large fraction of the terpenes are expected to react with the OH radical: according to Atkinson & Arey (Atm. Env., 37:S197-S219, 2003) approx.  $\frac{2}{3}$  of the  $\alpha$ -pinene and 80% of 3-carene will react with OH under ambient conditions, the remainder reacting with O<sub>3</sub>. While some OH is produced during the ozonolysis reactions, the composition of the products from the ambient oxidant mixture can be expected to be different, with much higher importance of products that have undergone more than one OH reaction. In addition some NO<sub>3</sub> may be present in or upwind of Hyttiala, producing some additional products that have not been characterized in the lab either. Finally aerosols have a long lifetime of a week, so under certain conditions of continental transport some of the aerosol molecules may be due to transport of anthropogenic pollution from distant sources. Unless the authors can show that the precursor + oxidant mixtures studied are actually representative of those likely to affect their field observations, this conclusion is unwarranted and should be removed from the abstract.

Reply: For the laboratory studies, the precursors  $\alpha$ -pinene and  $\Delta^3$ -carene were chosen, based on the ambient observations by Yassaa et al., as it is discussed in the manuscript. They showed that those two monoterpenes are the most abundant precursors at the Hyttiälä station. Further precursors such as limonene and  $\beta$  pinene

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were studied, since those compounds are strongly emitted by single tree species in the surrounding area. Using OH-scavengers in the chamber ozonolysis did not show a different product distribution. Of course, only the OH is scavenged which is produced by the ozonolysis, and higher OH levels due to photochemistry were not investigated. Furthermore, OH-reactivity measurements during the HUMPPA-COPEC campaign indicated that a high amount of OH reactive species are not known (Nölscher et al.). We want to stress that the HUMPPA MS/MS spectra are the result of gaseous and particulate compounds on  $m/z$  185. Recent field experiments at Mt. Kleiner Feldberg (less remote than Hyytiälä) showed that the 28 Da fragment does not occur in  $m/z$  185-MS/MS of the particle phase only. Therefore it is very likely, that this particular fragment at Hyytiälä originates from gaseous compounds and long range transport of anthropogenic pollution seems rather unlikely. To conclude, we think that other precursor compounds are a major source of those unidentified fragments but we don't want to rule out that photochemistry is the reason for different oxidation products. Therefore the abstract was rewritten to: "Possible explanations for those unaccounted fragments are the presence of unidentified or underestimated biogenic SOA precursors or that different products are formed by a different oxidant mixture of the ambient air compared to the chamber ozonolysis."

## Minor comments

Comment: 6149-7, the detection limits are 'improved' or 'decreased', not 'increased'

Reply: corrected to "improved".

Comment: 6150-21: NMR and FTIR as applied to aerosols are not capable of detecting single molecular species. These techniques provide alternative characterizations of the bulk OA with some functional group or other chemical resolution, and are more similar to the AMS, as described in Hallquist et al. (2009), see their Figure 4.

Reply: Sentence was rewritten to: "Common offline techniques for measuring single organic compounds from filter samples are liquid- or gas-chromatography coupled

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to mass spectrometry (LC/MS, GC/MS), off-line techniques for measuring bulk properties such as functional group contributions are nuclear magnetic resonance spectroscopy (NMR) or direct filter analysis using Fourier transformation infrared spectroscopy (FTIR) (Hallquist et al., 2009, Hoffmann et al., 2011).”

Comment: 6153-8, Hohaus et al. describe a coupling of an aerosol collector to a GC/MS, not a PTRMS. They only mention a PTRMS as a possibility for future coupling.

Reply: Corrected.

Comment: 6155-3, the quoted value is a flow speed, not a flow rate.

Reply: Corrected.

Comment: 6157-23, a more recent parameterization of the effect of acidity and other composition effects on the AMS CE has been published by Middlebrook et al. (Aerosol Sci. Tech. 46, 258–271, 2012)

Reply: The paper was added, although the AMS data are not that much affected by RH or ammonium nitrate.

Comment: 6157-28, units should be  $\mu\text{g m}^{-3}$ , not  $\text{cm}^{-3}$

Reply: Corrected.

Comment: 6158-1, the mass concentration measured by an AMS is not ‘the total aerosol mass’ but the ‘submicron non-refractory mass’. Refractory species such as dust, BC are not included, nor are supermicron particles.

Reply: The referee is correct, the sentence was rewritten to: “On average organic species explained 69% of the submicron non-refractory mass, sulfates accounted for 20% of mass and ammonium compounds and nitrates for 7% and 4% respectively.”

Comment: 6166-18, principal should be principle

Reply: Corrected.

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Comment: 6179, Fig 3 is very small and hard to read in the ACPD print version, the authors should reformat it so that it can be better read in the ACP version of the paper.

Reply: The authors will have an eye on Fig. 3 after the setting of the paper. It should have the same width as Fig. 4.

Literature:

Bartmess, J. E.: Negative Ion Energetics Data, in: NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Linstrom, P. J. and Mallard, W. G. (Eds.), National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, 2011 (retrieved January 7, 2013).

Veres, P., Roberts, J. M., Warneke, C., Welsh-Bon, D., Zahniser, M., Herndon, S., Fall R., de Gouw, J.: Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, *Int. J. Mass Spectrom.*, 274, 48-55, doi:10.1016/j.ijms.2008.04.032, 2008.

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Interactive comment on *Atmos. Meas. Tech. Discuss.*, 5, 6147, 2012.

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