

***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.***

**Anonymous Referee #2**

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Review of Vogel et al 2012

This paper presents a new combination of two existing instruments: APCI-IT-MS for measurement of molecular species in aerosols, and mVACES aerosol concentrator that is used to improve detection limits and enable measurements by the first instrument under ambient conditions, where it would otherwise not be able to do so. The instrument combination is described and is well placed in the context of the previous literature and other instruments. Data is presented from two studies, the HUMPPA-

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COPEC-2010 field campaign in Hyttiala and a laboratory reaction chamber study. The field data are compared to those from a widely used AMS instrument. The paper describes and characterizes a new measurement combination for important atmospheric molecules and is reasonably well written, and thus it is appropriate for AMT. I recommend publication after the following issues are addressed:

#### Major issues

- 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 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.

- 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.

- 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

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as 'approx. a factor of 2').

- 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..  $\sim 2/3$  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.

#### Minor comments

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

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- 6155-3, the quoted value is a flow speed, not a flow rate
- 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)
- 6157-28, units should be  $\mu\text{g m}^{-3}$ , not  $\text{cm}^{-3}$
- 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.
- 6166-18, principal should be principle
- 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.

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