**Atmospheric
Measurement
Techniques
Discussions**

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

Anonymous Referee #1

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Vogel et al. present an interesting study measuring aerosol organic acids both in field and laboratory experiments. They apply a well-established atmospheric pressure chemical ionization ion trap mass spectrometer and compare the ion trap results with a compact time-of-flight aerosol mass spectrometer. For increased detection limits during the field experiments in Hyytiälä, an mVACES aerosol concentrator is coupled to the ion trap MS, and MSxMS spectra of selected m/z ratios of field samples are compared to MSxMS spectra of laboratory studies.

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The manuscript is well structured and clearly written. The presented results are a valuable contribution to an improved characterization of the atmospheric organic aerosol. The authors show that APCI-IT-MS is a valuable analytical tool both in field and laboratory studies. I therefore recommend publication of this manuscript in AMT after taking into account the following comments:

1) In section 3.1, the calculation of the analyte concentration from the measured signal intensities is introduced. The explanation is somewhat confusing. If concentrations are indeed derived from the linear regressions presented in Fig. 3b, the concentration c is simply (I-b)/s (which is presented as the first part of Eq. 1). Thus, the explanation could be simplified. If, however, the signal intensities are related to the absolute mass of the analyte, then indeed the sampled volume has to be determined (Eq. 2) to arrive at the concentration. Please clarify.

2) The concentration enrichment factor of mVACES was tested in lab experiments presented in Fig. 4. Several questions arise: (a) Why is it that the addition of mVACES changes the flow rates and reaction times in the continuous flow chamber? (b) The selection of the time intervals to compare total ion currents with or without mVACES seems somewhat arbitrary. Is this really the most appropriate selection to evaluate the concentration enrichment factor? (c) From Fig. 4, it seems that the lower molecular weight range (m/z 160-240) termed monomers is not enriched at all with mVACES. By the end of the 5 min intervals switching between mVACES on/off, the monomer signal intensity is more or less the same with or without mVACES. Taking this into account, one must speculate that mass spectra measured with and without mVACES are in fact different due to a different contribution of lower and higher molecular weight compounds. One could argue that mVACES enriches high molecular weight compounds, but not low molecular weight compounds!

3) The authors note that losses of semivolatile and/or water soluble compounds can be an issue when using mVACES, e.g. a "notable loss of 30 % of the gas phase fraction". Taking this into account, how reliable is the result that on average organic

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acids contributed about 60 % of the total organic aerosol during HUMPPA-COPEC. Please add some kind of uncertainty figure.

4) In section 3.4, the authors discuss the m/z fragment 115 found in the laboratory MSxMS spectrum of limonene, and also in the Hyytiälä spectrum. Given that there are many additional fragments not assigned to certain compounds, the m/z fragment 115 in the field measurement may also be an oxidation product of a VOC other than limonene. This should be added to the speculative discussion.

Technical comments:

p.6155, l.15: Replace "and a temperature of ca. 30 °C" by "and a temperature of approximately 30 °C".

p.6155, l.27: In the text, the authors quantify the minor flow rate of the PCVI Q=0.8 SLPM, while Fig. 1 gives a flow rate of 1 SLPM. Please adjust accordingly.

p.6157, l.9/10: Replace "to particulate time of flight chamber. Resulted high He signal" by "to the time of flight chamber. The resulting high He signal".

p.6157, l.16: Replace "AMS data analysis see (e.g. Allan et al., 2003, 2004)" by "AMS data analysis see e.g. Allan et al. (2003, 2004)".

p.6157, l. 29: "maximum of 23.1 μg cm-3" should read "maximum of 23.1 μg m-3".

p.6159, l.24: Replace "based on with following assumptions" by "based on the following assumptions".

p.6163, l.3: Replace "During HUMPPA-COPEC" by "During the HUMPPA-COPEC".

p.6164, l.8/9: What do you mean by "referring to the extreme conditions"? Please clarify.

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