

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

A. L. Vogel et al.

vogelal@uni-mainz.de

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The authors thank the referee #1 for thorough reading and improving the manuscript by constructive comments. The manuscript will be revised based on the referee's comments as follows:

Comment 1: In section 3.1, the calculation of the analyte concentration from the measured signal intensities is introduced. The explanation is somewhat confusing. If con-

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centrations 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.

Reply: In order to determine the absolute mass concentration ($\mu\text{g m}^{-3}$), the mass of the deposited analyte and the volume in which the analyte is vaporized into needs to be determined, as the referee noted. However, the authors tried to clarify this section by merging Eq. 1 and Eq. 2 and rewriting the p.6160, l.17 to p.6161, l.2 as follows: “Equation (1) is used to determine the instruments response towards the absolute mass concentration. During the calibration procedure (Fig. 2), the mass of the deposited organic acid on the deposition plate is m (μg), and the denominator expresses the volume (m^3) in which the analyte is evaporated into: the product of flow rate f (SLPM) and average time interval t (min) (red boxes: 5 min; black boxes: 10 min), resulting in the concentration c ($\mu\text{g m}^{-3}$). Based on the assumption that the average intensity I (counts) during the calibration procedure equals the same mass concentration during the online measurement, the linear interpolation (slope s and y intercept b) was applied on the ambient online intensities to determine the ambient mass concentration.”

Comment 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

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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!

Reply: a) when the mVACES was sampling from the chamber, the sampling flow rate was ~ 11 SLPM, whereas the sampling flow rate from the chamber without mVACES was only 1 SPLM. Therefore the input flows into the chamber were adjusted to keep a constant pressure throughout the experiment. Thus, the average residence time of the precursor gases in the chamber varied during the experiment, depending on mVACES on / off. Consequently, the SOA mass concentration varies due to the different residence time as well. Therefore, (b) the selection of the time interval must be chosen at the time when the aerosol concentration can be regarded as nearly equal. (c) The fact that the intensity of the monomers at the end of the 5 min intervals when mVACES is off is at the same magnitude as at the end of the 5 min interval when mVACES is on does not mean that the monomers do not get enriched at all. It rather indicates that more aerosol is produced during the time when mVACES is off due to a longer residence time of the precursor gases in the reaction chamber. However, the referee is correct that one might argue that mass spectra measured with and without mVACES are different by comparing lower and higher molecular weight species. We think that this is mainly driven by the higher volatility of semi-volatile monomers. Consequently, gas-phase losses of semi-volatile monomers in the saturator are more distinct compared to the low-volatile dimers. Subsequent reequilibration (evaporation of particulate SV-OOA) might result in negative artifacts of SV-OOA when using the concentrator. This can be seen in Fig. 4 at minute 10, where the signal of the monomers is higher than the dimer signal (mVACES off) and vice versa when the mVACES is switched on. In order to better address possible artifacts of SV-OOA and to call for future studies, the passage p.6162, l.18 to p.6163, l.2 was rewritten to: "Another aspect that should be considered when a VACES system is used, are the losses of semi-volatile and at least partly water soluble compounds during the mVACES preconcentration by absorption within the saturator. An estimation of this amount based on the Gormley-Kennedy

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equation (diffusion coefficient $D=0.058 \text{ cm}^2/\text{s}$ at a flow rate of 11.0 SLPM) results in a notable loss of 30% of the gas phase fraction, assuming that the wet sponge acts as a perfect sink for gaseous organic acids. Subsequent re-equilibration between gas- and particle-phase (evaporation of SV-OOA from the particle phase) might result in negative artifacts. An indication for negative artifacts of semi-volatile organics can be seen in Fig. 4 at minute 10: Before switching the concentrator on, the signal of the monomers is higher than that of the dimers, and vice versa after switching on. Further concerns about possible changes in gas/aerosol partitioning might be raised by multiple temperature changes during the passage through the concentrator. Contrary to negative artifacts, Khlystov et al. (2005) showed that the concentration of water soluble semi-volatile material can be increased at small sizes after passage through the concentrator. Their maximum observed amount of positive nitrate artifacts (relative to sulphate) on a polluted day reached a factor of 2.6, organic material showed significant less positive artifacts (factor 1.2). These positive artifacts are most probably attenuated due to losses of gas-phase organics in the saturator. Further investigation on artifact formation of the semi-volatile aerosol fraction in a water based concentrator is needed for a more precise determination of the concentration factor of semi-volatile organic compounds.”

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

Reply: The referee is correct that in the estimation that 60 % of the total organic aerosol consists of organic acids some kind of uncertainty approximation is missing. However, the mentioned loss of 30 % of gaseous molecules might bias the organic acid fraction in the aerosol particles, since organic acids can evaporate from the particle-phase due to re-equilibration between gas- and particle-phase. But without detailed knowledge

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on evaporation dynamics it is not possible to determine this kind of error quantitatively. Furthermore, the estimation that 60 % is organic acids, relies on other assumptions, e.g. pinic acid as a surrogate for all organic acids, as it is stated in the manuscript. To make this estimation more clear, the abstract will be extended by “The campaign average contribution of organic acids measured by APCI IT MS to the total sub-micron organic aerosol mass was estimated to be about 60%, based on the response of pinic acid.” Furthermore, Fig. 5 was extended with estimated uncertainty bars of both instruments, AMS and APCI-IT-MS. For the AMS a maximum uncertainty of +/- 20 % was estimated and for the APCI-IT-MS +/- 50 %. Future investigations and mass closure experiments between APCI IT MS and other mass based instruments can help to characterize the sensitivity of the APCI-IT-MS, but when measuring ambient aerosol the largest uncertainty remains due to high molecular mass compounds and their unknown ionization efficiency.

Comment 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.

Reply: The referee is correct- the text in section 3.4 is extended by the consideration that oxidation of other VOC precursors might result in the m/z 115 fragment as well: “Due to the diversity of biogenic emissions at the Hyytiälä station, oxidation products from other volatile organic precursor molecules might also contribute to the m/z 115 fragment, e.g. myrcene-, camphene-, sabinene- or sesquiterpene derived acids.”

Technical comments:

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

Reply: Done.

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Comment: 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.

Reply: Flow rate in Fig. 1 was wrong- corrected.

Comment: 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".

Reply: Corrected.

Comment: 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)".

Reply: Corrected.

Comment: p.6157, l. 29: "maximum of $23.1 \mu\text{g cm}^{-3}$ " should read "maximum of $23.1 \mu\text{g m}^{-3}$ ".

Reply: True- corrected.

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

Reply: Corrected.

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

Reply: Replaced.

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

Reply: Sentence was rewritten to: "possibly induced by the extreme heat and biomass burning events during summer 2010"