

## ***Interactive comment on “Using in situ GC-MS for analysis of C<sub>2</sub>-C<sub>7</sub> volatile organic acids in ambient air of a boreal forest site” by Heidi Hellén et al.***

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Thank you for the good comments. We have carefully considered all the comments and improved our manuscript according to them. Please, find below our answers to the general and specific comments.

One of my major concern is the question how quantitative is the presented method for the target analytes. The authors report by themselves that especially acetic acid showed a problematic behavior and that large deviations were observed. Just considering the sampling step in the “cold” trap at 25 C (to avoid water interference) in combination with the calibration using liquid standards injected into adsorbent tubes (purged with nitrogen – again to avoid water interference) results in the inherent difficulty to estimate a reliable recovery, since for both steps losses of the analyte (e.g. especially

C1

acetic acid) cannot be excluded (or better have to be expected!?). If no additional experiments can be performed, at least a comprehensive discussion about such losses are needed, which would certainly improve the manuscript.

-We added some chromatograms and calibration curves as supplementary material to better justify the method. Cold trap was filled with hydrophobic adsorbent, water goes through the trap and organic compounds are retained on it. However, excess water can block the cold trap if temperature of the cold trap is below the dew point of the sampled air. Therefore we kept this hydrophobic cold trap at 25°C. We have seen already in earlier measurements (with e.g. monoterpenes) that if we use lower cold trap temperature during warm summer days, water can block the cold trap. Also calibration samples from the adsorbent tubes were directed to the cold trap at 25°C and before that adsorbent tubes (filled also with hydrophobic adsorbents) were purged with nitrogen to remove excess water used as solvent (1 µl injected into the tube). This was so small amount (1 µl) that most probably this would not have been even needed. The main issue of the adsorbent tubes was high background values and not losses. We added to section 2.1 the explanation for water removal in our study.

Specific remarks:

Page 6: “Some memory effect was found”. Please describe more quantitative these effects since especially for the highly polar and sticky analyte molecules such a behavior has to be known in detail.

-There is some memory effect for all studied VOAs. This was clearly seen after running field standard gas of benzene and toluene which contained VOAs as contaminant, but the memory effect was <3% already in the first blank run after the standard. We deleted always 5 samples after running this standard. In ambient samples variation of concentrations was much lower than difference between standard gas and ambient and therefore we expect that memory effect is not as big problem in ambient air samples as after standard gas. In inlet tests we did not detect any major losses of these

C2

compounds even with humidified samples. Discussion on memory effect was added to the text and figures of blanks and first runs after field standards were added to the supplementary material.

Page 8, line 20: As also discussed later in the manuscript: High concentrations during nighttime are not necessarily a consequence of nitrate chemistry (e.g. transport).

- It is true that the lower boundary layer present during the night may also explain higher nighttime mixing ratios, but since this clear peak was not found for any other compounds than for butanoic acid, we believe that there was an additional butanoic acid source during that night. An explanation for this was also added to the text in section 3.2.1.

Please check the whole text for typos (using a spell checker!?)

- This was done.

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