

Interactive comment on “Using in situ GC-MS for analysis of C₂-C₇ 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 greatly improved our manuscript according to them. Please, find below our answers to the general and specific comments.

The introduction could be improved if the authors incorporate a concise idea about VOAs in ambient atmosphere (origins, gas phase VOAs, particle phase VOAs, urban and rural VOAs). In many places throw-out the manuscript, some ideas were repeated or confusing (see my comments below). The authors are encouraged to incorporate in the introduction references and studies associated with VOAs in ambient atmosphere in a concise way.

-Introduction was improved by adding discussions on sources and fate of the studied

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VOAs in the atmosphere and several parts of the manuscript were clarified.

I was confused when the authors referring to VOAs in ambient air! It will be beneficial for the readers if the authors discuss the utility, importance and use of the technique for gas and aerosol samples? It was unclear in the text if both ambient gas and aerosol were sampled together? Although has noted by the authors, most VOAs may exist in the gas phase but due to partition and the presence of polar acidic group in these compounds, they may also be in the particle phase (aerosol).

-This methods was suitable only for gas phase samples. Small particles are lost in the FEP inlet lines and bigger ones follow the main gas flow when the sub-sample is taken to the thermal desorption unit. This is clarified in the section 2.1.

The sampling site is dominated by biogenic emissions including isoprene and monoterpenes (biogenics), and it will be great if the authors provide chromatograms associated with test samples and ambient samples in the manuscript. Are there other acids in the chromatogram? e.g. methylglyceric acid and other acids (peaks) from isoprene/other HCs oxidation? Is the technique can be used for dicarboxylic acids?

-Examples of the selected ion chromatograms of calibration and ambient air samples for m/z 59.9 and 73.9 were added as supplements and referenced in the section 3.1. In SCAN mode chromatograms the background was so high that peaks of the studied compounds or any other acids were not detected. This method is suitable only for gas phase samples and most of the dicarboxylic acids are in the particle phase or partitioning between gas and particle phases. Isoprene emissions at this boreal forest site are low and acids produced from mono- or sesquiterpenes are known to be less volatile (main products dicarboxylic acids) and partition between gas and aerosol phases. Therefore we did not try to look for those acids with this system. Other methods would be more suitable for their detection.

Specific comments: 1.Line 2, page 2. Is "Organic acids" comprise 25% of the non-methane hydrocarbons in the atmosphere? It's very high to me! It's true that 25% of the

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non-methane hydrocarbon in the atmosphere are organic acids (including gas phase and aerosol phase). Please check for accuracy! Is organic acids referred here are only compounds having carboxylic acid groups or with multifunctional groups including at least one acid group!!!

-Since 25% was not well-defined, we removed it.

2. "The VOAs react with hydroxyl radicals in the air or undergo dry or wet deposition." Needs reference(s)??

-References were added

3. Not sure what the authors refer in this sentence "Aqueous phase reactions provide a sink for water soluble VOAs, but reactions of other VOCs may also be a source of VOAs (Ervens et al., 2013)."

-This was removed, when the introduction was improved

4. Additional information of VOAs is suitable in the introduction mainly acids studied in this study.

-More information on sources and fate of studied VOAs was added to the introduction

5. The authors refer the role of acids in SOA formation, are the acids studied here relevant to SOA formation? Please elaborate?

- Studied VOAs participate into heterogeneous reactions on particles. This was clarified in the introduction.

6. It will be beneficial to clarify if gas phase or aerosol phase VOAs or both were measured here?

-This was clarified in the abstract, introduction and section 2.1

7. The discussion related to GC-MS sampling and analysis could be clarified. Confused about the sampling directly to the cold trap? Using test tubes etc.. How the

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samples were taken from the field site!!

-We clarified this in section 2.1 and added references into the introduction on the use of in situ GC-MS for other compounds

6. The paper could be improved significantly if the sampling method was clearly stated. A schematic diagram may be beneficial?

-We clarified this in section 2.1. and added a schematic diagram of the sampling system as supplement Fig. S1.

7. Is the PTRTOFMS discussion necessary in this study?

-We prefer to have detailed description also on PTR-TOFMS, since we compare the results to the GC results and the PTR-TOFMS is not yet widely used instrument. We included the results of the PTR-TOF as it displays similar variations in the acetic and propionic acid concentrations. Furthermore it shows the reader that the PTR-MS also has problems measuring volatile organic acids and the value of using a reliable method for measuring VOAs in ambient conditions.

8. What the authors refer here “The second port of the three way valve was used for this.” Page 5, line 2.

-This sentence was deleted

9. Please elaborate in “and their fragmentation pattern was not quantified” page 5, line 4

-When using PTR-MS most molecules (R) are charged by proton transfer, which adds an H⁺ to them. Certain oxygen containing compounds, like acetic acid and propanoic acid, can lose an OH during ionization. The ratio between those reactions depends on instrumental settings and affects the sensitivity of the compound directly. One way to characterize this ratio is by mixing pure acetic acid with VOC free air and measure it with the instrument. As we did not have pure acetic acid, we could not make this

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fragmentation test and therefore estimated it by using literature values. We refrain from adding such a detailed description to the manuscript, but cited a study which explains contains this information. We rephrased the sentence to: The calibration gas did not contain acetic acid or propanoic acid, therefore the sensitivity was estimated. As both molecules fragment when measured with PTR-MS (von Hartungen et al., 2004), the sensitivities were estimated to be 50% of the acetone sensitivity.

10. How the memory effect can be incorporated in this study? It depends on the acids concentrations in the previous runs? Please elaborate? How it was different from one acid to the other?

-There is some memory effect for all studied VOAs. Due to memory effects fast variations of mixing ratios would not be detected. However, this system is relatively slow (60 minute samples every other hour) and unable to detect fast variations anyway. Memory effect was clearly seen after running field standard gas which contained VOA, but it was only <3% already in the first run after the standard as shown by running blank gas (N2 6.0) after the field standard. We deleted always 5 samples after running this standard. In ambient samples variation of concentrations was much lower 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 compounds either. 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.

11. Confused about this statement "Using lower concentration for the calibrations would be expected to solve this issue." page 5, line 19? It did or did not solve the problem?

-Our standard gas for aromatic hydrocarbons, which were measured at the same time, contained high mixing ratios of VOAs as contaminant and it was not possible to lower the concentration in this case due to flow limitations and mixing ratios of other compounds in the standard. Nevertheless, as mentioned earlier more discussion on mem-

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ory effect was added to the main text and two supplement Figures (S4 and S5) to clarify this.

12. Which N2 flow the authors refers here?? “The precision (Uprec) was checked by injecting known amounts of acids into the N2 flow.”?

-This was clarified in section 3.1

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