

## ***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.***

### **Anonymous Referee #2**

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The authors present the use/development of an in situ GC-MS technique to measure ambient volatile organic acids (VOAs). The method is based on a cold trap technique followed by GC-MS analysis. The method was tested and validated on standard acids. Although the technique used in this study seems to lead to the analysis at "pptv" levels of C<sub>2</sub>-C<sub>7</sub> monocarboxylic acids in the ambient atmosphere, the paper could benefit from a major revision mainly to improve the organization, editing as well as scientific discussion. 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 throughout 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. I was confused when the authors referred to

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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 as 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). 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?

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 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!!! 2. "The VOAs react with hydroxyl radicals in the air or undergo dry or wet deposition." Needs reference(s)?? 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)." 4. Additional information of VOAs is suitable in the introduction mainly acids studied in this study. 5. The authors refer the role of acids in SOA formation, are the acids studied here relevant to SOA formation? Please elaborate? 6. It will be beneficial to clarify if gas phase or aerosol phase VOAs or both were measured here? 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 samples were taken from the field site!! 6. The paper could be improved significantly if the sampling method was clearly stated. A schematic diagram may be beneficial? 7. Is the PTR-TOFMS discussion necessary in this study? 8. What the authors refer here "The

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second port of the three way valve was used for this.” Page 5, line 2. 9. Please elaborate in “and their fragmentation pattern was not quantified” page 5, line 4 10. How the memory effect can be incorporated in this study? It does depends on the acids concentrations in the previous runs? Please elaborate? How it was different from one acid to the other? 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? 12. Which N2 flow the authors refers here?? “The precision (Uprec) was checked by injecting known amounts of acids into the N2 flow.”?

The method developed here is of great interest, however at this stage, I believe a major work need to be done before its acceptance.

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