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Comment

# ***Interactive comment on “Ambient measurements of aromatic and oxidized VOCs by PTR-MS and GC-MS: intercomparison between four instruments in a boreal forest in Finland” by M. K. Kajos et al.***

## **Anonymous Referee #2**

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### General Comments:

The study by Kajos et al. seeks to address the reliability of ambient measurements of aromatic and oxygenated VOCs when different instruments are employed for measuring air in the same environment through a field intercomparison exercise. In their experiments conducted in a boreal forest site, the authors intercompared ambient data acquired using two proton transfer reaction mass spectrometers and two GC-MS systems. Such a study is laudable as it is never easy to undertake an intercomparison ex-

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ercise during field measurements and the outcome of such studies is valuable for highlighting technique specific strengths and limitations under ambient conditions. While the manuscript is generally well written, I feel the manuscript needs to be strengthened in several aspects before it can be published in AMT. Several questions/concerns arise in the present version pertaining to the robustness of the results and the validity of the conclusions for practitioners of these analytical techniques.

#### Major Concerns:

1) Calibration data of the individual instruments are not presented and discussed in detail. In an intercomparison of techniques, the raw measured data acquired during calibrations often holds clues to instrumental issues, in particular if the calibration experiments are carried out under relevant ambient regimes encountered at a site ( e.g. at different relative humidities and ambient temperature). The authors mention that calibrations were performed atleast thrice during their month long study. It would be instructive to present and analyze the data from the calibration experiments in the paper. How long were the lines conditioned with flow of VOCs during the calibration experiments? How do chromatograms measured by the two GC-MS systems compare while measuring from the same VOC standard and for the common ambient periods? Are the peaks always equally well separated by both GC-MS systems on occasions where there was poor agreement? The QA/QC employed by the operators of the different instruments for both the calibration experiments and ambient data need to be documented in more detail in the paper for the reader to have confidence that all known precautions were followed and the results are really specific to instrumentation and not operator skills/know-how.

2) For periods where there is better agreement between instruments and periods where the agreement was not good, were the ambient air conditions significantly different in terms of humidity and temperature? Perhaps a trace of the ambient temperature and RH could be added to Fig 2 and Fig 3. Water vapour is a common problem for several instruments and for VOCs such as methanol and benzene measured with the PTR-

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MS the effects can be very different on the sensitivity as also acknowledged by the authors. Were calibration experiments performed over different RH ranges (0% to 90% RH) specifically to test for the magnitude of such effects in different instruments?

3) Toluene discrepancy ; the authors state that being an anthropogenically emitted VOC they do not expect toluene variability to be high over short time scales in the forest where they were measuring. I am not entirely convinced that this is true all the time even in a remote biogenic setting. A number of studies have shown that under stress, many plants including Scots pine (a major tree species at their site) can emit benzenoid compounds such as toluene (see for example: Heiden et al. GRL, 1999). As the sampling time varied between the different instruments, this could explain part of the discrepancy

4) The use of  $r$  values for interpreting correlation/ agreement between instruments is a bit misleading to me. For example, an  $r$  value of 0.5 for acetaldehyde reported by the authors is still interpreted as a correlation, while to me  $r$  of 0.5 is actually only an  $r^2$  of 0.25 , which implies only 25 % of the data co-varied (which is more lack of a correlation than any correlation ! I would suggest use of  $r^2$ , even though it may not look better.

5) Fig 5 has very poor resolution in the web version, and much of the information was obscured so it should definitely be made more legible.

6) An outcome of a paper of this kind should be to inform the community about detailed technical aspects and potential artefacts intrinsic to different types of instrumentation so that lessons can be passed on to the community at large. This aspect is really in short measure in the current version of the manuscript and I would encourage the authors to collectively strengthen the same by focusing on suggestions made above and in the other review.

Technical corrections: I could not find any that have not already been pointed out by Reviewer 1.

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