Atmospheric
Measurement
Techniques
Discussions

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 #1

Received and published: 3 June 2015

Kajos et al. present comparison of concentrations of selected VOCs from a forested field site using 2 PTR-MS and 2 GC-MS instruments. The main conclusion from the paper is that independent settings, calibration approaches and variable instrument sensitivities can lead to relatively high uncertainties of reported concentrations, which could penetrate to models. Consequently, the collocated measurements with more than one instrument are advised to aid in confidence.

Simultaneous measurements of VOCs by multiple instruments are not usually performed, so the paper has a unique value to the PTRMS and GC community in learning

about the accuracy of long-term measurements. In addition, simultaneous measurements make it easier to diagnose problems (e.g. compounds breaking through in the microtrap, leaks, etc.).

It is unfortunate that the paper does not give a deeper scientific insight into observed discrepancies, as the recommendations could be synthesized to be even more useful for the community. Maybe this could still be done. While I recommended the paper is published subject to minor corrections, I do think the clarity of the paper has a high potential for improvement and may require a major effort.

General:

1) The authors did a good job with transparent presentation of concentrations from different instruments. Although for certain compounds comparison looks quite impressive, there are also some "scary" discrepancies highlighted. Significant problems should be identified and either pointed out since the beginning or excluded before the comparison is made. Otherwise the reported discrepancies might exaggerate how bad the accuracy really is. I think it is true that certain problems cannot be easily spotted if there is only one instrument, so acetone and methanol are probably good examples here to show. This leads me to a question: Has a strict quality control been performed on all the data (assessment of quality of zero air, breakthrough volumes, water condensations, leaks, contaminations, assessment of materials used in the sample lines, stabilization of "sticky" compounds in calibrations, etc.)?

2) The story is generally difficult to follow. While English is generally clear, there are language imperfections in various places. Consequently, the story, while generally interesting, makes impression of incoherent. It is surprising to see relatively little attention taken to comparing the actual results, the discrepancies and to an investigation of actual or potential problems behind those discrepancies.

3) Nowhere in the manuscript are shown the actual calibrations. Does the fact that they were performed relatively rarely (once per week?) is sufficient to say how stable the

sensitivities were? Did the sensitivities vary diurnally as relative humidity changed?

4) Typically much better agreements have been reported for methanol and acetone (e.g. Davison et al., 2009), but, here, it might be confusing that some instruments (PTRMS2) were not collocated and did not exactly coincide in timing, so perhaps a perfect agreement should not be expected? Also, it is surprising to see so drastically lower sensitivity for methanol in dynamic vs manual calibration which I guess might not have been an issue if the longer purging times and MFCs with appropriate materials (e.g. Kalrez instead of Viton o-rings) had been used.

Specific:

5) P3755 L2, Is this the best sentence to start the abstract from? What do you mean by "real time"? Even the fast GC is not a real time measurement or even close to real-time. Here, you show 1 hour data.
6) P3755 L14 "notably for methane" – methane cannot be measured by PTR-MS. Did you mean methanol?
7) P3755 L18 "This mismatch indicates that the systematic uncertainty in the sensitivity of a given instrument can lead to an uncertainty of 50–100 % in the methanol emissions measured by commonly used methods.". Is it if the Viton elements are used in MFCs or was there an issue with the equilibration time of methanol (e.g. if the calibration steps were short?)? I would suggest discussing more the reasons for these and how these could be avoided. This reviewer is not convinced that careful measurements of methanol can lead to so high uncertainties.
8) P3756 L14-23 I am confused by this paragraph. I guess you probably want to say generally that the inaccuracies in the models may often result from inaccuracies in measurements or do you suggest that earlier measurements might be inaccurate?
9) P3756 L24 "Traditionally . . ." and you cite fairly recent papers. Then (L.28) you have: "Recently,. . ." and you cite papers from 2 decades ago?

10) P3757 L17 "Typically, a long-term measurement setup consists of a single analyzer, which is periodically calibrated.". I do not think it is typical to calibrate rarely (e.g. 1-2 times a day may be more appropriate for long term measurements), but I agree that the discrepancies may derive from too seldom calibrations and zero air measurements. This is an important point to make in the paper from the beginning. A recommendation for frequent calibrations and zero air measurements have not been made by the authors but could be relevant for including in conclusions.
11) P3758 L3 "The main aim of this study was to evaluate how reliable the real-time measurements of aromatic and oxygenated VOCs are when a single stand-alone instrument is used.". It would be interesting to see a deeper insight into the actual reliability of the measurements in the light of the specific factors that influence it.
12) P3758 L5 again you refer to "real-time" measurements, but maybe you just mean "online" measurements or it might make sense to say "close-to-real-time".
13) P3759 L19 "cycle" is unclear and can be confused with the duty or MID cycle.
14) How much data is rejected between heights switching from PTRMS2? For example, is one minute data comprising all 60 s or is it something like 50 s or less?
15) P3759 L23. Were all the 6 lines of equal length (100 m)? Where in the set-up did the switching occur? What type of valve was used (what type of materials)? Was the tubing in any of the lines heated?
16) P3760 L12 ". . .cannot be used..." seems too strong here. Enhanced PTR-MS selectivity is possible in variable E/N mode (e.g. Maleknia et al., 2007, Misztal et al., 2012).
17) P3760 L21 120-140 Td. 110-140 Td has commonly been used (e.g. Ghirardo et al., 2010).
18) P3760 Until this point it is unclear to the reader what the dwell times were for each instrument and m/z (perhaps you could consider tabulating this information). Later in the text 2 s is shown as a dwell time for PTRMS2. Was it used consistently for all PTRMS instruments and m/z (including m/z 21)?
19) What was the cumulative dwell time for PTRMS2 per each tower level per

compound (i.e. dwell time of compound multiplied by the number of MID cycles in a minute (minus the trimming time due to height switching). It needs to be clear what 1 min data from each height effectively was. Possibly, it was just a few seconds for each mass per minute depending on the dwell time and how much you had to trim due to height switching.

20) P3760 L23 The sentence "Therefore both H3O + and H3O +H2O ions are taken into account in the data processing" is too general for general audience. I assume you mean the data are normalized to hydronium ions and hydrated hydronium ions to account for variation of the signal due to additional protonation of VOCs from colliding water clusters. Do you also consider humidity dependent sensitivities from calibrations at range of humidities (e.g. de Gouw et al., 2003) or was the zero-air source and standard gas of the same humidity?

21) P3761 L5-13. This paragraph refers to Taipale et al., 2008. However, some information should be more transparent without a reader having to refer to a separate paper, in particular:
a) Was the normalization done to water cluster at m/z 37, 38 or 39?
b) Was the ion at m/z 55 included to normalization for water clusters?
c) Was the normalization performed to drift pressure?
d) Was the procedure consistent for all PTR-MS instruments, their calibrations and ambient measurements?

22) When normalizing signal to primary ions, do you pre-average the signal at m/z 21 or do you divide by each point in an MID cycle. If the latter, how are the detection limits affected (i.e. if you are introducing the noise from m/z 21)?

23) P3762 L10. I like the idea to calculate the detection limits for each ZA air measurement. One thing to clarify is to say what period those detection limits correspond to. Unlike it is the case with the sensitivities, the detection limits will be different for differently averaged data, for example, 1 s and 1 min. Calculation of detection limits corresponding to ambient measurements at 1 min depends on the total counting statistics related to dwell time of each compound and the length of the MID cycle.

C1372

I could not find how much total time per compound is spent for each height (see earlier comment 21). Thus, it is unclear if the detection limits you report are just to characterize instruments or do you care to reflect the actual detection limits for the reported ambient data accounting for the exact number of samples (cycles) to average.

24) P3765 L10. It seems to me that you are describing here the white noise distribution, not the PTR-MS statistics distribution. When you average the data, the averaging filter is also a noise filter, so Poisson noise is reduced or eliminated with averaging. There is also a component related to true ambient variability of a compound at short time scales, but the precision must necessarily be much lower at short time scales.

25) P3765 last sentence: "Thus, the primary ion signal uncertainty is less than 1 % and it was neglected.". This is surprising. Even if overall the m/z 21 signals were similar, when you normalize to primary ions you introduce Poisson noise which, as mentioned above, will be different at different dwell-times and/or averaging times. Thus, I think you should consider including uncertainty in primary ion signal unless you did not normalize or you sufficiently pre-averaged the m/z 21 signal.

26) How many dilution steps of the standards were done and what was the duration of each step? Did the steps look well equilibrated (particularly methanol?)? Given the nature of the article I am surprised not too see any figures showing the actual calibration curves or steps from the instruments. These would be extremely useful (e.g. in SI).

27) Uncertainty of the PTR-MS measurement. This section seems a little bit vague. Not only the precision is important but also the accuracy. How about other things that impact uncertainty? For example, SEM voltage optimization if not done regularly can lead to decrease of sensitivities. Performance of MFCs in the dynamic calibration system should be assessed regularly (were those checked for leaks, crosscalibrated with an accurate flow meter?). What about line losses? Was the calibration done through the 100-m line? Finally, it is certainly interesting to see the variabilities in sensitivities, but the real question is how frequency of calibrations and zero air impact these uncertainties in terms of accuracy?

C1373

28) P3769 L14 "The concentrations measured with different instruments had temporal discrepancies, as all of the instruments had different sampling intervals. PTR-MS1 measured several compounds sequentially, each with an integration time of 2 s, which lead to a 1 min resolution." Do you mean you only got one point per one minute? In other words your 1 min data effectively contains only 2 s of the actual data?

29) P3769 L17 "The ambient concentrations were measured 43 times during each hour, after which the background was sampled 11 times." Do you mean that each compound was sampled effectively for 43*2s, so ~1.5 min per hour, or is it even less because you were switching the heights?

30) P3770 L20 "A constant ratio was assumed for the sensitivity and its uncertainty". Interesting, so you suggest that uncertainty of sensitivity is the same directly following the calibration and in a few days after the calibration? Again, I think frequent calibrations can be the key to achieving high accuracy.

31) Which sensitivities (MCM or ACM?) were used to derive concentrations for PTRMS1 and PTRMS2 in Figure 2 and 3?

32) Figure 4. Why did you remove the outliers? How did this operation affect the mean? Can you add the mean values to the box plots?

33) Conclusions: "Thus, it can be easily estimated that e.g. any emission measurement of methanol has an uncertainty of 50–100 % due to the sensitivity of the instrument used. The results of this study show that when doing long-term measurements of ambient air, occasional comparison measurements are needed to validate the measured concentrations, even if the instrument is calibrated regularly. ". I agree with the recommendation of occasional cross-calibration exercises when conducting long-term measurements, but it is surprising that the authors generalize about so high uncertainty in methanol measurements. This probably could be linked to metal (and/or Viton) surfaces of a particular MFC and/or equilibration time, and I think more discussion of these issues could be interesting for readers.

Technical:

34) P3755 L9: Duplicated sentence: "This paper presents correlations….".
35) Multiple places: "PTR-MSs" or "GC-MSs". Might consider "PTR-MS instruments" or "GC-MS instruments/machines/systems/etc.".
36) P3760 L4 "pumped" should be "drawn".
37) P3760 L24 remove dot.
38) Figure 2, the traces look in many places unclear – the markers are big and obscure the lines. You could consider all lines (e.g. color-coded) instead of markers and lines.
39) Figure 5, can you add goodness of fit and slopes?

References:

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