

Interactive comment on “Comparison of VOC measurements made by PTR-MS, Adsorbent Tube/GC-FID-MS and DNPH-derivatization/HPLC during the Sydney Particle Study, 2012: a contribution to the assessment of uncertainty in current atmospheric VOC measurements” by Erin Dunne et al.

Anonymous Referee #3

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This paper describes an inter-comparison of PTR-MS, Adsorbent Tube analysis by GC-FID and DNPH-HPLC methods in an urban environment in Sydney Australia. Inter-comparisons between different techniques are always an important exercise and should be done whenever possible to identify potential issues that affect the data interpretation. The methods compared here are the basic standard methods; the PTR-MS is the older quadrupole version and not the newer PTR-TOF, the AT analysis is done

with a GC-FID and not with a more sophisticated GC such as a GCxGC-MS, but this means that they are widely used and available to the community. This inter-comparison reveals some known artifacts from the DNPH method and discusses some potential interferences for the PTR-MS method, although I do not fully agree with the conclusion by the authors that interfering compounds are the main reason for the general higher means or slopes for the PTR-MS compared to the other techniques. There are also a few other points or omissions that need to be addressed, before this manuscript can be accepted. I actually think some minor additional measurement tests would be appropriate to resolve some of the open issues for the disagreement between the methods. Overall a major revision to the paper is needed.

Major comments

The authors conclude that interferences from other mainly unknown compounds are the main reason for higher PTR-MS measurements compared to the other techniques, even though they take all the known interferences into account. The amount of work that has been done on PTR-MS and recently on PTR-TOF-MS, including work on measurements of coupled GCs with PTR-MS, give us a very good understanding of the compounds that can interfere, especially for benzene, toluene, the C8-aromatics and acetaldehyde. All this published work has not revealed any interferences that can make up an additional ~20% bias in PTR-MS in addition to what has been taken into account in this work already. I suggest revising the conclusion and various places in the text accordingly or show proof or possibilities for other interferences. One possibility for benzene would be the acetic acid cluster (propionic acid for toluene), which could be significant under the configuration of the PTR-MS used here. The E/N seemed to have been around 100 Td, which is pretty low and could favor cluster ions. These potential interferences need to be also added in the discussion.

It is also clear that in the presented literature summary of intercomparisons presented in Figure 2, the current study is always at the high end. This also could be an indication for a more systematic overestimation of PTR-MS or underestimation of the AT and

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DNPH methods. I would like to see that pointed out in the text and conclusion more clearly. Here I should mention that I like Figure 2 a lot and would like to see this expanded a little by adding a Table with all the data and references included.

Formaldehyde and acetone do seem to have significant interferences in PTR-MS, some of which have not been discussed in the text well. Stoenner et al 2016 (DOI 10.1002/jms.3893) have described glyoxal measurements by PTR-TOF-MS and found that glyoxal is detected mostly at mass 31, which could give a significant interference for formaldehyde, and only to a small fraction on mass 59. In addition, the glyoxal reaction is not exothermic as stated in the text, just suffers from strong fragmentation. There are several places in the manuscript that have to be updated with the results from this paper.

The most obvious interference is seen for isoprene. In an urban environment or oil&gas extraction regions the largest interference likely comes from cycloalkanes, which are a significant fraction in vehicle exhaust. The detection of cycloalkanes on mass 69 was described first by Yuan et al 2014 (<http://dx.doi.org/10.1016/j.ijms.2013.11.006>). This has been overlooked in the discussion and needs to be added.

The correction of benzene and toluene has been done using literature data, but nothing has been done to confirm the interferences or fragmentations in the PTR-MS used here. The instrument settings influencing the E/N are critical for the fragmentation of larger aromatics to benzene and monoterpenes to toluene. The E/N used here is very low and fragmentation should be reduced compared to the literature data used. Most importantly, the fragmentation in the PTR-MS at a certain setting can be measured very easily by simply exposing the instrument to the pure compound. Using the measured fragmentation patterns and looking at the parent masses 121 or 137 measured during SPS2 should give a much better indication on potential contributions to benzene and toluene and can be used to properly correct mass 79 and 93 in PTR-MS.

If the PTR-MS measurements suffer from interferences, the PTR-MS should be cor-

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rected and not the AT-VOC data. You are generating not atmospherically meaningful data. Please subtract from the PTR-MS benzene and toluene signal instead. Also, it needs to be made clear in the figures and tables that corrected data were used. This means changes the formula. Text, table and figures in many places.

The same issues arise in the discussion about DNPH losses. If for example acetone is collected poorly on DNPH, especially at high water mixing ratios, a very simple test with an acetone standard should be done. It seems from the instrument description that only the HPLC was calibrated with a liquid standard, but a calibration should be done with the entire sampling setup. This means including the DNPH cartridges. You actually should cross calibrate the PTR-MS standard. From page 5 line 10 it seems that cross calibration was done only with the BTEX standard and the GC-FID PTR-MS combination and also not through the adsorbent tubes.

In addition, the DNPH measurements of acetone in Figure 3 actually go to essentially zero at high humidity. In the atmosphere, especially in urban areas, so low acetone values have never been observed and clearly point to measurement issues. This should be added as an argument for the ketone loss in the DNPH method.

The selection criteria for measurement comparison #4 of median/MDL>5 should not be used. All the data that are above the MDL should be used. That's what MDL means. If you do have a reason not to use those data, you have to change your definition of MDL. The use of these lower concentration data should decrease the R-coef, but the slopes should still be valid.

Minor comments

Page 4 line 21: Was the silcosteel inlet tube heated? If not, this is highly recommended.

Page 4 line 25: Ellis and Mayhew 2014 ref is missing from the reference list, Lindinger et al 1998 or de Gouw and Warneke 2007 could be mentioned here as well.

Page 4 line 41: How does your definition of MDL compare to the more standard $S/N=2$

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or 3?

Page 5 line4: Table 2 comes before Table 1 in the text, they should be switched.

Page 5 line 4: What do you mean with the scatter in the calibration measurements? Was this 10% around the mean for the 30 min daily measurements or are the 10% the deviation for each daily calibration around the campaign average?

Page 5 line 10: Can you add the manufacturers stated uncertainties for the calibration standards?

Table 2: The sensitivity of PTR-MS should not be given in ncps/ppb only without indicating the primary ion counts or adding cps/ppb. With ncps/ppb you still don't know the actual instrument sensitivity.

Page 5 line 18: "Each compound known to substantially contribute" How do you know which compounds contribute, I guess from literature studies? Please add.

Page 5 line 3: What is the difference between RMA and ODR, which is mostly used for instrument comparisons? In ODR the actual instrument uncertainty can be used as the error estimate for both axis. Is that also done in RMA?

Table 3: Please indicate the sampling times and PTR-MS averaging times.

Page 7 line 24: Here and elsewhere in the text: Cappellin et al 2010 is the wrong reference. This should be Cappellin 2012.

Page 8 line 33: "we correct the AT-VOC data". This should say something like: We calculate the weighted sum of the individual VOCs measured by AT-VOC that corresponds to m/z 107

Page 9 line 15: If you separate daytime data, you should also look at nighttime data, at night the interference should be the largest.

Page 9 line 33: I don't think the influence of other compounds on isoprene by PTR-MS

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is poorly understood, it is indeed a poorly quantified uncertainty, but we know pretty well what the other compounds are.

Figure 2: Indicate what the grey squares are. I guess daytime data.

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