

Interactive
Comment

***Interactive comment on* “Comparison of aromatic hydrocarbon measurements made by PTR-MS, DOAS and GC-FID in Mexico City during the MCMA 2003 field experiment” by B. T. Jobson et al.**

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Response to Reviewer #2

Thank you for your comments and suggestions.

General Comments:

1. Paper principally about PTR-MS / DOAS comparison.

We added a sentence in the abstract that stated this:

“The principle focus was on the comparison between PTR-MS and DOAS data.”

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2. Viability of phenol, cresols, naphthalene, PTR-MS data and need for more discussion on observed differences between DOAS and PTR-MS.

We agree it is difficult to draw strong conclusions about the fidelity of phenol, cresol, styrene, and naphthalene measurements by PTR-MS, especially since the DOAS styrene and naphthalene measurements are novel, and there may be basic issues of sampling bias due to spatial gradients driven by inhomogeneous VOC source distribution. For toluene we are of the opinion that the PTR-MS and DOAS measure this reasonably well, and that the measured differences are real and not analytical problems. As you suggest, spatial inhomogeneities in VOC sources are likely contributing to differences between DOAS and PTR-MS measurements but this is hard to prove. It's not hard to imagine that differences in toluene might be due to emissions of toluene along the DOAS beam from solvent use from small paint shops or business that use solvents.

We added another paragraph to section 3.3.1 to qualify that these measurements of phenol, cresol, naphthalene, and styrene by PTR-MS are exploratory to better understand their viability. The following text was added:

“While the lab experiment with test mixtures demonstrated consistency in the calibrations of the two techniques it does not identify potential problems with ambient sampling where there may be interferences. This is a particular concern with the PTR-MS measurements which can suffer mass interferences from fragmentation of larger organics and we note the fidelity of PTR-MS measurements of phenol, cresols, naphthalene, and styrene in urban atmospheres has not been demonstrated. One general potential problem for these species could be reactions between O₂⁺ and higher concentration organics producing fragment ions at these masses. For example, Spanel and Smith (1998) have shown that O₂⁺ reactions with trimethylbenzenes produce C₈H₉⁺ ions in 5-15% product yields which would be a mass interference for styrene at m/z =105. Given a 15% yield and the abundance O₂⁺ ion in our system of 1.5%, we calculate that the O₂⁺ + trimethylbenzene reactions yield an ion signal at m/z=105 that is only 0.2%

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of the $m/z=121$ ion signal. This reaction was not a significant interference for styrene.”

In section 3.3.2 we added the following text at the end of the section to note the issue of spatial inhomogeneities in source distributions, and that the larger DOAS mixing ratios for toluene and C2-alkylbenzenes may be driven by emissions of solvents from businesses along the DOAS beam:

“The fidelity of phenol, cresol, and naphthalene measurements by PTR-MS is not well established and this is the first reported comparison with another technique. It is difficult to draw conclusions about the analytical fidelity for these species by either technique since there is such a large amount of scatter in the data and it is not clear whether this scatter is driven by spatial gradients or analytical problems or a combination of both. Given that the corrected benzene data displayed a mean PTR-MS / DOAS ratio of 0.99, it is somewhat surprising that the toluene and C2-alkylbenzene ratios were so much lower. All these species have significant roadway sources but it’s possible that additional sources of toluene and xylenes from paint shops or other businesses using solvents may be important in the sector through which the DOAS beam passes.”

Since the PTR-MS are now corrected for the ethylbenzene interference there is better agreement on average between PTR-MS and DOAS data as reflected in Figure 10 (old figure 9) and Table 5. Given this level of benzene agreement we re-framed the toluene – wind direction discussion to note that if benzene agrees reasonably well why don’t toluene and C2-alkylbenzenes. In section 3.3 at the end of the first paragraph we added the following text to again emphasize the point that spatial inhomogeneities in VOC sources may cause differences between the techniques:

“Since wind direction played only a small role in the level of agreement, we conclude the DOAS measurements yielded higher toluene mixing ratios than point measurements from the top of the flux tower because the DOAS beam traversed a major toluene emissions area and was closer to the surface. Spatial inhomogeneities in VOC sources may have likewise contributed to the generally discrepancy between PTR-MS and DOAS

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data for C2-alkylbenzenes, naphthalene, styrene, and cresols.”

In the Conclusion we’ve re-stated the toluene discrepancy: “Given this modest dependence on wind direction, and that the benzene data displayed good agreement, we conclude that non-roadway emissions of toluene, such as solvent use, were important in the sector through which the DOAS beam passed. PTR-MS data for C2-alkylbenzenes were on average a factor of 0.50 lower than the DOAS data, consistent with the toluene data, again suggesting that non-roadway emissions were important. The DOAS data likely observed higher mixing ratios due to the difference in sampling height above roof-level and that the light path traversed an area where VOC emissions from non-roadway sources were important for these species.”

3. Humidity dependence We added the following text after line 15 on page 19649 and a new figure (Figure 1). “Instrument normalized sensitivities (Hz / ppbV per MHz H₃O⁺) were not dependent on water vapor concentrations. As an example, Figure 1 displays normalized sensitivities for acetonitrile, acetaldehyde, and benzene versus H₊(H₂O)₂ count rates normalized to MHz H₃O⁺. Depending on the operating conditions, the PTR-MS instrument can display a humidity dependent sensitivity because H₊(H₂O)₂ can act as a reagent ion. For this particular PTR-MS instrument there was no discernable humidity dependence for the 145 Td and 2.1 mbar drift pressure operating condition. Interestingly, for similar drift tube conditions (145 Td, 1.9 mbar), Roger’s et al. (2006) reported significant humidity dependent sensitivities over a similar humidity range. This difference in PTR-MS instrument behavior reinforces the need to calibrate PTR-MS instruments across a range of ambient humidity levels to document the humidity dependence.”

Specific Comments: 1. page 19645. line 19. Corrected to “FIS”. Added “that” to sentence.

2. page 19646 line 25. Added comma

3. page 19646 paragraph at line 24. Rewrote paragraph to more effectively convey

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the key points: “More recently Velasco et al. (2007) have reported intercomparison results from a PTR-MS, GC-FID, and a commercial DOAS instrument for several days of measurements from an auxiliary monitoring site in Mexico City during the MCMA 2003 field experiment. The comparison showed good agreement, with the exception of benzene measurements by the commercial DOAS, which were greater than the PTR-MS and GC-FID measurements in the early afternoon when ozone levels were high. The ozone interference can be corrected for in the DOAS technique, as was demonstrated in that work from the research grade DOAS data, which did not show the high benzene offset during afternoons, and showed excellent correlation between benzene, toluene, m-xylene and p-xylene. This paper presents results from a more detailed comparison of PTR-MS, GC-FID, and research-grade DOAS measurements of VOCs at the CENICA supersite during MCMA-2003. These techniques measured several aromatic species in common over a period of 4 weeks, and provide a much larger data set for a statistically robust analysis.”

4. page 19647 Corrected, now reads “VOCs”

5. page 19648 line 8. We note here that the PTR-MS is “sensitive” to larger alkanes (c.f. Jobson et al., 2004). Changed sentence to incorporate PTR-MS insensitivity to compounds with PA less than that of water:

“The technique identifies VOCs by molecular weight and can measure those compounds with a proton affinity greater than that of water. The technique is insensitive to C2-C7 alkanes, ethene, and acetylene, common constituents of urban atmospheres.”

6. 19649 line 23. Added period.

7. page 19649 line 24. Added “the” as suggested.

8. page 19650 line 13. Changed to “e.g. Jobson et al. 2004”

9. page 19651 line 15. Inserted semicolon in place of comma.

10. page 19652 line 20. Changed to read as suggested “Since the PTR-MS is not

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isomer specific...”

11. page 19654 line 10. Corrected.

12. page 19658 line 12. Corrected.

13. page 19660 line 2. Corrected.

14. page 19661 line 17. Corrected, change “when” to “wind”

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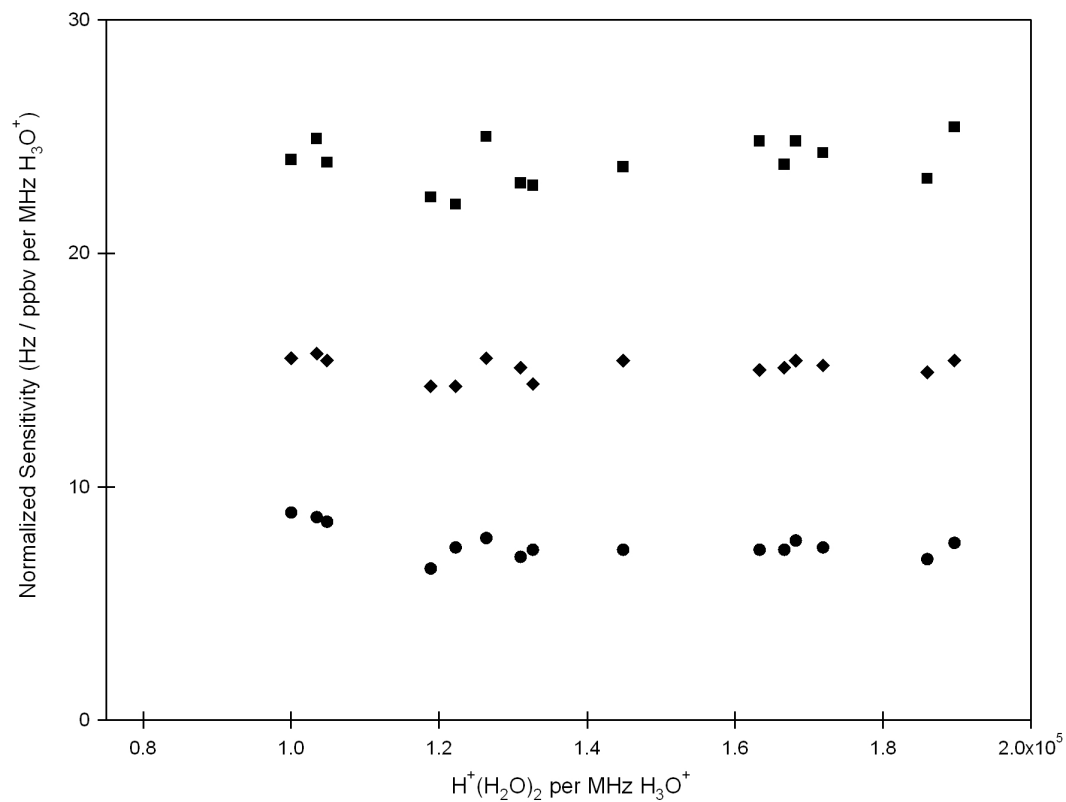


Fig. 1. PTR-MS normalized sensitivities for acetonitrile (squares), acetaldehyde (diamonds), and benzene (circles) versus water cluster count rates.

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