

## ***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 #1

Thanks very much for the comments and suggestions.

General Comments: 1. Inclusion of Rogers et al. 2006 results. This was an oversight and we have made reference to this paper where appropriate. The following changes have been made to include the results from that work.

Page 19646 line 11. Added text: “Rogers et al. (2006) compared PTR-MS measurements of aromatic compounds against air samples collected into canisters and ana-

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lyzed by GC-FID and found good agreement for benzene and toluene but significant differences for C2-alkylbenzenes and C3-alkylbenzenes.”

Page 19650. Rewrote paragraph to include reference to Rogers et al. (2006) fragmentation algorithm: “Partial fragmentation of mono-alkyl aromatics such as ethylbenzene occurs under the ion drift conditions used here. Mass scans of ethylbenzene show a dominant M+1 ion but also a significant ion at  $m/z = 79$  (40%). This fragmentation produces a positive artifact for PTR-MS benzene measurements and causes the PTR-MS to underestimate C2-benzenes. Rogers et al. (2006) provided an algorithm to correct the PTR-MS benzene measurements due to fragmentation of ethylbenzene and propylbenzene. The magnitude of this interference can be calculated from known abundances of C2 and C3-alkylbenzenes isomers. The GC-FID measurements at CENICA, other sites in Mexico City (Rogers et al., 2006), and in US urban environments (e.g. Jobson et al., 2004) indicate that ethylbenzene comprises about 20% of the C2-alkylbenzenes abundance and propylbenzene about 7% of the C3-alkylbenzene abundance. Given the fragmentation of ethylbenzene and its relative abundance, the PTR-MS measurements underestimated C2-alkylbenzenes abundance by ~8%. Using the Rogers et al. (2006) algorithm and the molar abundance of C2 and C3-alkylbenzenes measured at CENNICA, we estimate that the PTR-MS benzene measurements were over estimated by ~ 16%, primarily due to fragmentation of ethylbenzene.”

Page 19654, Section 3.1. Added text to note Rogers et al. (2006) comparison between PTR-MS and GC-FID. “Rogers et al. (2006) have shown a similar comparison between PTR-MS and GC-FID measurements of benzene, toluene, C2-alkylbenzenes, and C3-alkylbenzenes made at auxiliary ground sites in Mexico City during MCMA 2003. Their data displayed less scatter and showed better agreement for benzene and toluene than the CENICA data, but the PTR-MS data for C2-alkylbenzenes and C3-alkylbenzenes was significantly greater than GC-FID data (by 31% and 52% respectively).”

Page 19658. In the PTR-MS DOAS comparison we corrected the benzene data using

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the Rogers et al. (2006) algorithm and show corrected benzene data in what is now Figure 10 (Figure 9 in original manuscript) and updated Table 5. The log-histogram mean for the PTR-MS / DOAS benzene ratio is now 0.99. The following text was added: "In this analysis the PTR-MS benzene data were corrected for contributions from fragmenting alkylbenzenes using the Rogers et al. (2006) algorithm."

2. Known interferences on phenol, cresols, naphthalane, styrene ions and O<sub>2</sub><sup>+</sup> + trimethylbenzene

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 O<sub>2</sub><sup>+</sup> and higher concentration organics producing fragment ions at these masses. For example Spanel and Smith (1998) have shown that O<sub>2</sub><sup>+</sup> reactions with trimethylbenzenes produce C<sub>8</sub>H<sub>9</sub><sup>+</sup> 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 O<sub>2</sub><sup>+</sup> ion in our system of 1.5%, we calculate that the O<sub>2</sub><sup>+</sup> + trimethylbenzene reactions yield an ion signal at m/z=105 that is only 0.2% of the m/z=121 ion signal. This reaction was not a significant interference for styrene."

Specific Comments: 1. Line 3 page 19644 Corrected : "... as high as few 10's of meters above roof level."

2. page 19649, line 23. Added Zhao and Zhang, 2004 reference

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3. page 19650, zero air and humidity dependent sensitivities

Zero air was generated from ambient air and so has the same water vapor content as ambient air. Our backgrounds displayed no humidity dependence. Our normalized sensitivities displayed no humidity dependence either. We have added a new figure to show the correlation between normalized sensitivity and m37 count rates normalized to MHz H<sub>3</sub>O<sup>+</sup>. The figure shows the normalized sensitivity for acetonitrile, acetaldehyde, and benzene for the different calibrations performed over the month of April. The lack of a water vapor dependence with this particular PTR-MS instrument at 145 Td is in contrast to our newer PTR-MS instrument operated at 120 Td where we observe a significant humidity dependence for acetonitrile and acetaldehyde but essentially none for benzene (c.f. Jobson and McCoskey, APCD, 9, 19845-19877, 2009). Interestingly, this is also in contrast to the Rogers et al. (2006) instrument that operated under similar drift conditions (145 Td, 1.9 mbar). We added the following text after line 15 on page 19649:

"Instrument normalized sensitivities (Hz / ppbV per MHz H<sub>3</sub>O<sup>+</sup>) were not dependent on water vapor concentrations. As an example, Figure 1 displays normalized sensitivities for acetonitrile, acetaldehyde, and benzene versus H<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> count rates normalized to MHz H<sub>3</sub>O<sup>+</sup>. Depending on the operating conditions, the PTR-MS instrument can display a humidity dependent sensitivity because H<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> 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."

4. page 19652 equation 1

Yes this equation was developed for fresh unprocessed emissions at CENICA. We

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added a sentence to state this: "The relationship is valid for fresh emissions."

5. page 19654 line 27 : benzene variability and humidity dependence

Benzene did not have a humidity dependent sensitivity (as shown in the new Figure 1) and so humidity dependent sensitivities can't be a contributor to mixing ratio variability.

6. page 19655 line 16. Corrected spelling.

7. Section 3.3.2 Conclusions regarding styrene, phenol, cresols, naphthalene measurements.

It is difficult to draw conclusions regarding the fidelity of these measurements by PTR-MS. Styrene and naphthalene measurements by DOAS were also something new so it is difficult to conclude much given 2 unproven techniques and lots of data scatter. In section 3.3.2 we added the following text at the end of the section to note this issue and the general issue of spatial inhomogeneities in source distributions contributing to differences.:

"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."

8. page 19658 line 26 anomalous benzene. Yes there was better agreement if the alkylbenzene fragmentation was accounted for. In the PTR-MS DOAS ratio comparison we corrected the benzene data using the Rogers algorithm and show corrected benzene data in what is now Figure 10 (Figure 9 in original manuscript) and updated

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Table 5. The log-histogram mean for the PTR-MS / DOAS benzene ratio is now 0.99.

We removed the following sentence from this section: "The anomalous results appear to be those for benzene and phenol which yielded mean ratios larger than 1." and the last 3 sentences from section 3.3.2 since we are now using corrected benzene data.

The following text was added was added to this section: "In this analysis the PTR-MS benzene data were corrected for contributions from fragmenting alkylbenzenes using the Rogers et al. (2006) algorithm."

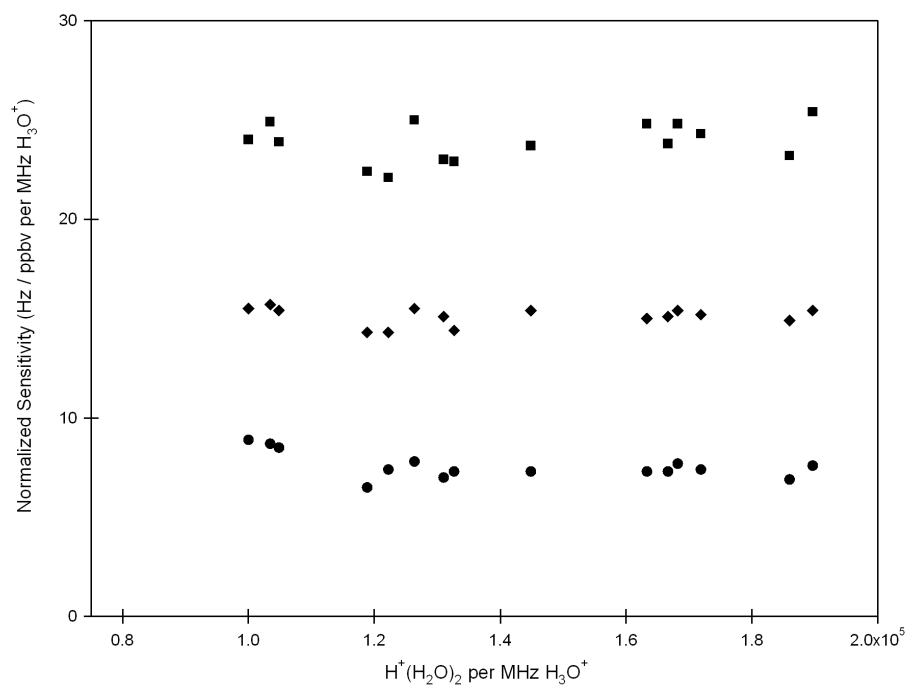
"For benzene, the histogram fit yielded a mean ratio of 0.99, suggesting that the fragmentation of ethylbenzene and propylbenzene was properly accounted for in the PTR-MS data by the Rogers et al. (2006) algorithm."

9. Figure 7 color DOAS trace blue. Corrected.

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