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***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.**

Anonymous Referee #1

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This paper describes a comparison of aromatic hydrocarbon measurements from a polluted urban atmosphere, Mexico City, made by three instrumental techniques, PTR-MS, DOAS and GC/FID. The results reported for the PTR-MS and the GC/FID are directly comparable as these measurements were taken from the sample line. The comparison with the DOAS is complicated because it is an open path measurement as reflects a potentially different air mass than that sampled by the PTR-MS and GC/FID which are point measurements. The measurement results reported within this manuscript are valuable and of interest to atmospheric community and their publication are ACP is warranted. The discussion of these results however fails to address previously published work on the use of the PTR-MS for the measurement of volatile organic compounds

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in the Mexico City atmosphere by Rogers et al. *Int. J. Mass Spectrom.*, 252, 26-37, 2006. Rogers et al. describe that the PTR-MS measurement of benzene is influenced by the fragmentation of ethylbenzene and propylbenzene and provide an algorithm to correct the benzene response to these spectral interferences. Rogers et al. also provide a comparison of PTR-MS and GC/FID measurements of benzene, toluene, C2-benzenes and C3-benzenes. The authors need to integrate and discuss the results from the Rogers et al. study into their current manuscript before it can be considered for publication. Beyond this major omission, the manuscript is well presented and serves to illustrate how challenging it is to make and understand trace VOC measurements in the complex urban atmosphere.

I have some concerns regarding the interpretation of the measurements attributed to the minor aromatic compounds. This manuscript seeks to examine the fidelity of the PTR-MS response at m/z 95 (phenol), m/z 105 (styrene), m/z 109 (cresols) and m/z 129 (naphthalene) through comparison with the DOAS results. An independent laboratory study demonstrates that under well controlled conditions that both the PTR-MS and the DOAS techniques provide similar quantitative results. This is a useful result but it does not demonstrate that either technique is capable of quantifying these components in the ambient atmosphere. Additional information regarding the uniqueness of the responses is required before any conclusion can be made. For instance, are there other compounds in the polluted urban environment that can produce ions in the PTR-MS at these masses? While proton transfer to styrene only produces m/z 105 there may be other potential sources of m/z 105 in the PTR-MS. O_2^+ a common impurity ion in the PTR-MS reacts with the trimethylbenzenes to form an ion at m/z 105 (Spanel and Smith, *Int. J. Mass Spectrom.* 181, 1-10, 1998). Similar concerns may exist in the DOAS measurements. Some discussion regarding the validity of these measurements should be provided.

Specific Comments:

Line 3 page 19644 – the last part of the sentence “ as high as few 10m above roof

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level” is not complete.

Line 23 page 19649 – In addition to the reference of Su and Chesnavich considering including the reference Zhao and Zheng Atmos. Environ. 38, 2177-2185, 2004, which provides a list of calculated proton transfer reaction rate coefficients for all of the compounds under discussion in your manuscript.

Line 27 page 19650 – The use of zero air to determine the backgrounds in the PTR-MS can be problematic unless great care is taken to define the humidity dependence of the PTR-MS response and can lead to systematic errors. In general zero air provides smaller instrumental background count rates which translates into higher reported concentrations. This effect is most apparent at low mixing ratios. How is the humidity dependence of the PTR-MS response handled in this study? Are both H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ included in the quantification scheme? Are the reactivities of the different reagent ions assumed to be same?

Equation 1 page 19652 – This equation assumes a fixed distribution of different isomers. Photochemical processing will shift the isomer distribution in favor of ethylbenzene and so this algorithm will only be valid when sampling “fresh” emissions.

Line 27 page 19654 – I suspect part of the larger variability in the benzene response at low mixing ratios results from the humidity dependence of the PTR-MS measurement. Benzene does not react with $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ and if this is not accounted for variations in the calculated benzene concentration can change with ambient humidity.

Line 16 page 19655 – C2-alkylbenzene is misspelled.

Section 3.3.2 Comparison of PTR-MS vs DOAS – Can any conclusions be made about the validity of the styrene, phenol, cresols and naphthalene measurements be made? Are the differences in “phenol” and “cresols” justifiable because of different source profiles or the result of spectral interferences?

Line 26 page 19658 – You refer the benzene result as being anomalous. Apparently

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this is because the PTR-MS benzene result was not corrected for fragmentation. Would the corrected signal still be high?

Figure 7 - For consistency please color the DOAS trace as blue. The DOAS trace was blue in Figure 1.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 19641, 2009.

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