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Atmospheric
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Discussions

Interactive comment on "Measurements of volatile organic compounds at a suburban ground site (T1) in Mexico City during the MILAGRO 2006 campaign: measurement comparison, emission ratios, and source attribution" *by* D. M. Bon et al.

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Response to Anonymous Referee #2

We would like to thank this referee for the helpful suggestions and comments. We will address specific points below:

(1)Abstract: In the latter part of Abstract, I think that it is not well organized. For examples, the two sentences starting from “Positive matrix factorization analysis....” and “Three PMF factors. . ..” are better to put before the sentence starting from “VOC diurnal cycles. . ..”. Please recheck the abstract.

The latter portion of the abstract has been rewritten for clarity.

(2)Page 23241, Lines 16-18: As the authors mentioned, the PIT-MS measurements for Σ C8 and Σ C9 aromatics were significantly higher than the UCI canister measurements. How did the authors determine concentrations of Σ C8 and Σ C9 aromatics by PIT-MS? Did they determine detection sensitivities for all isomers? In addition, did the authors compare UCI canister with NOAA GC-FID for Σ C8 and Σ C9 aromatics?

NOAA PIT-MS mixing ratios for C8 and C9 aromatics were calculated using p-xylene and 1,2,4-trimethyl benzene in a calibration standard. Sensitivities for isomers generally vary by ∼20% based on our experience and understanding of the ion chemistry involved. The NOAA GC-FID was not configured to measure aromatic species.

(3)Page 23242, Lines 9-10: If the difference was not caused by the calibration standards for aromatics, do the authors think what possible reasons of the difference are?

Both Anonymous Referees commented on the discrepancies between measurements of the C8 and higher aromatics and this is a very valid concern. While we do not know the reason for these discrepancies we can say two things. First, the GC-PIT-MS results show no evidence for interfering compounds on these masses. Second, the disagreement between PIT-MS and other measurements of higher aromatic VOCs is in the range of what has previously been reported as shown in the PTR-MS review paper referred to in the text (de Gouw and Warneke, 2007). The measurement accuracy for these compounds appears to be not as high as for other species measured by PTR-MS. We have improved the discussion of these discrepancies in the text.

(4)Page 23255, Lines 2-6: I think that the comments here are also necessary in Sec. 4.2.1 and 4.2.2, where Figures 7f and 8 are shown but there is no discussion about 1-4 pm data.

We have added a line referring to the contrast between morning and afternoon measurements to the sections you suggest.

(5)Table 2: Is an annotation “d” necessary in Table 2?

We have corrected this and slightly modified Table 2 for clarity.

(6)Figure 6: How did the authors derive the mixing ratio from unidentified signal? Did they derive it from the calculation?

Mixing ratios for unidentified compounds are calculated using an average sensitivity and have an uncertainty of ∼50%. We have revised the text to clarify.

(7)Figure 9 bottom panel: In the mass spectrum at right column, it seems that m76 is largely contributed to PMF Factor Attribution compared with m75. Am I right? If so, what species is contributed to m76?

This observation is correct. We did not see any compounds on this mass using the GC-PIT-MS technique. The signal at m/z 76 is most likely the result of the much larger acetone-water cluster observed at m/z 77. Water clusters are often not resolved at unit mass resolution with PIT-MS under the operating conditions used during this study.

Technical corrections: We have corrected the typographical errors you refer to in our revised manuscript.

Other Changes made: We have added a column to Tables 3 and 4 showing the calibration accuracy. The error in the emission ratio reflects the uncertainty from the ODR fit. When the degree of correlation is high, this error can be very small, in which case the calibration uncertainty is important to consider when comparing against other data sets.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 23229, 2010.

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