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Atmospheric Chemistry and Physics 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.

D. M. Bon et al.

daniel.welshbon@noaa.gov

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Response to Anonymous Referee #1

We appreciate the comments and suggestions given by this referee. Here, we respond to specific comments listed by Referee #1:

It was pleasing to see that the measurements compared quite well from different techniques and from different platforms. The calibration standards must be good and I assume perhaps they were cross – checked against each other either during this experiment or have some time in the past. Is this true? Perhaps say something more about this. There is a hint that cross calibration was done between the PIT-MS and Aerodyne with regard to methanol and aromatics.

The NOAA PIT-MS standard and the Aerodyne PTR-MS standard were the only standards compared in the field during MILAGRO. Other standards were not compared for the purpose of this study. We have clarified in the text specifically where calibration standards were and were not compared.

It would be interesting to see if UCI used an acetylene standard for their response factor or if they assumed proportional carbon response for this species – this could possibly explain the difference in acetylene values.

The UCI group uses calibration standards for their acetylene measurements and did not simply rely on the carbon response(Baker et al., 2008). While our measurements were 26% lower than the data from UCI, in a recent inter-comparison our measurements were 30% higher than those made by the NOAA Global Monitoring Division (Gilman et al., 2010). Discrepancies between acetylene measurement techniques have also been reported in the past (Apel et al., 1994). We conclude that the 5% precision (and 10% calibration accuracy) typically quoted for acetylene measurements underestimates the uncertainty observed in the acetylene measurement. Our group is currently working with the NOAA GMD to resolve this discrepancy and we agree that further study is needed to improve the accuracy for this important species. The text has been revised to include this reference and a statement to this effect.

The differences in C8 and C9 aromatics between the UCI canisters and the NOAA PIT-MS is surprising since most of these compounds are easily identifiable and quantified with the GC-FID.

The NOAA GC-FID used in this study was not set up appropriately to quantify aromatics and no measurements were made of benzene or any higher aromatic using this instrument. In the UCI canisters NMHCs were analyzed by GC-MS and GC-FID. It is unclear why the field measurements disagree with the canister quantifications. Because calibration standards have not been compared we can only speculate on reasons for the discrepancy. Clearly further work is needed in this regard.

This is especially true for the C8 species I believe. Perhaps there are species that are interfering in the PIT-MS?

This is a possibility that in our opinion is unlikely. Benzaldehyde is generally a minor interference in PTR-MS measurements and we did not observe any non-aromatic compounds at these masses in the GC-PIT-MS measurements reported in this manuscript (Fig. 4). This agrees with previous work in the US (Warneke et al, 2003) and we added this reference to the text to strengthen this argument.

However, large differences also were observed apparently between the PIT-MS and the Aerodyne PTR-MS for these species. Combined, this may point to some unresolved issue with the PIT-MS for the measurement of these compounds. Countering this somewhat is the apparent good agreement between the PIT-MS and the G1 C8 measurements although there are few of these measurements. The agreement between the PIT-MS and the G1 PTR-MS are better than observed between the G1 and the C130 PTR-MS comparison (Ortega et al. 2006 – poster).

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.

The 20% percent uncertainty quoted for C8 and higher aromatics was an error in the manuscript. We believe a 50% uncertainty for these measurements is more consistent with previous observations. We have corrected this error in the manuscript.

We did not compare our measurements with those made by instruments on the C130 and can therefore not comment on any observed differences.

I would either not include the PIT-MS C8 measurements in the paper or add a couple caveats. It could be interesting to look at species that are detected by the PTR-MS at this mass but do not elute on the chromatogram in this area or not at all.

Because we do not know the cause of the measurement discrepancies, we think it is valuable to note them here so that they may be considered as an uncertainty in future studies using these data from MILAGRO.

We have previously compared on-line measurements of C8- and C9-aromatics by PTR-MS with the sum of compounds that elute on the chromatogram, and have found good agreement between the two (Warneke, ES&T 2003), so there is evidence to suggest that the reviewer's concern is not justified.

We have improved the discussion of these results in the manuscript to address the reviewer's concerns regarding our C8- and C9-aromatics measurements.

The Table 3 in the paper shows data for urban emission ratio estimates for non-methane hydrocarbons vs. CO. Much of the information in this table seems to be similar to data that is reported in Apel et al., 2010. There certainly is more data coverage here because the NOAA FID data are included and that is good but the question is: what is the new information here that is not already in the literature?

Apel et al., 2010 reported only daytime emission ratios of VOCs to CO for the two ground sites (from UCI canisters). There are two reasons why our in-situ GC-FID measurements are valuable. First, the GC-FID measurements are a completely separate measurement of many of the same compounds with a much higher measurement frequency (1 measurement every 15 minutes versus about 8 measurements per day). Second, we did include nighttime data for our emission ratios which rules out that chemical removal of reactive hydrocarbons influenced the results.

On a couple specific points, why is the ethane value so different from that reported in the other paper?

The emission ratios we report from the UCI canister measurements were calculated from orthogonal distance regression (ODR) fits to both day and night data. This is consistent with the method we used to calculate ERs for other species reported here. Because ethane (and propane) did not correlate well with CO, the ODR fit gave a very different result than the 1-sided regression reported by Apel et al. (2010). We have added a sentence about this to the manuscript.

Also, see above for a comment about the sum of the C8's. It is stated in the paper P 23247 line 26 that "LPG species emission ratios have substantially larger uncertainties than other VOCs due to much lower correlation with CO". Let me suggest that it is not entirely proper to call these emission ratios because the term loses its meaning in the absence of correlation with CO. However, this does not mean that the ratio is irrelevant because the lack of correlation is useful information and can be used to derive information on the sources of these species – similar to what can be derived by the more sophisticated PMF analysis. It just isn't useful in the way that true emission ratios can be in helping to evaluate bottom-up emissions inventories using a top-down approach.

We agree with the referee and have changed the text to say: "Because of the poor correlation of ethane and propane with CO, their ratios versus CO have a limited value and a very large uncertainty. We are including them here for the sake of completeness."

Table 4 (and Fig 8) give urban "emission ratio" estimated for OVOCs. Once again, I am not sure what the value is in going through this exercise. Emission ratios to CO

have value in fire emissions and anthropogenic emissions when sources emit both CO and the species of interest concomitantly. The case discussed above with LPG pointed out that there is an additional source for the species of interest that does not have any significant correlation with CO except perhaps co-location of the LPG with other CO sources. In the case of oxygenates the correlation is expected only for primary emissions from auto exhaust or fires. There are sources of many of the OVOCs in the MCMA that are not associated with primary emissions including biogenic, industrial, and secondary photochemical sources. Determining the ratios at 4-7 AM does not help too much either because here you are sampling a combination of fresh emissions and chemically processed species that are left over from the previous day that are trapped in the nocturnal boundary layer.

By only using the 4-7 AM data, we minimize the effects of photochemical formation of oxygenated VOCs, but the Reviewer is correct that we cannot rule out secondary sources completely. Separating primary emissions from rapid secondary formation of oxygenated VOCs is a general problem in the interpretation of oxygenated VOC data, and the current analysis represents an attempt to do this much closer to emission sources than we have tried in the past (de Gouw et al., JGR 2005). Our previous work has shown that acetone, MEK and acetaldehyde correlate quite well with CO in urban air, but that the ratio with CO varies with the degree of processing (de Gouw, JGR 2005, ACP 2009). In accordance, our PMF analysis did not yield results that would suggest an obvious contribution from biomass burning, industrial or biogenic sources of OVOCs at this site.

Minor: What does it mean that the GC column was divided in half? Does this mean that it is actually a 25 m column?

The NOAA GC-FID uses a split column to enable the back-flushing of the first half of the column while the sample is still eluting from the second half of the column. This is done to increase the sampling frequency. A clarification was added to the text.

Isoprene mixing ratios from UCI canisters peak at night? What is the explanation for this? We point out that the UCI canister isoprene measurements did not peak during the day as expected for a biogenic source. We have clarified this statement in the text. Anthropogenic sources of isoprene have been inferred from measurements (Borbon et al., 2001), but we have not explored this in detail for the MILAGRO data set. The discussion that the referee refers to was only about an analytical chemistry issue.

P 23257 line 11: "in conjunction with a GC separation method, the ion trap provided speciation not possible with the quad PTR-MS." Is it not true that using the GC in conjunction with the PTR-MS would yield the same specificity? – rewrite if this is the case. 23258 line 1: PMF analysis was performed. . .

In this case, we were referring to the fact that the PIT-MS provides a full spectrum while the quadrupole PTR-MS is typically operated by selecting a few masses for quantification. We have rephrased this in the newer version for clarity and thank the referee for pointing out that this was unclear. We have also revised the text to correct for the error in line 1 of page 23258.

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.

References

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