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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.

Anonymous Referee #1

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This paper is about measurements and interpretation of VOCs at the T1 Mexico City suburban site.

This is good contribution to the growing body of knowledge for the Mexico City and the current state of affairs with respect to emissions and photochemical processing leading to degraded air quality in the basin. MCMA has been much studied and as a result much of the new information, including that reported in this paper, is incremental

but in this case still valuable.

The paper is very well written and well organized.

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

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

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.

The PMF analysis was done very well and the authors did a good job of pointing out the limitations of the PMF analysis method.

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

Isoprene mixing ratios from UCI canisters peak at night? What is the explanation for this?

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. . .

Summary: With some relatively minor changes which could possibly serve to shorten the paper while not taking away from its primary emphasis, this could be an overall good contribution to the literature. The data reported in the paper are very solid – top notch. The PMF analysis was done well and even though not a great deal of new information is gained by it in this case I believe it is still a useful exercise. The authors did a good job of pointing out the limitations of the PMF analysis method.

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