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Atmospheric
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Interactive comment on “Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 and 2003 field campaigns” *by* E. Velasco et al.

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Interactive comments on “Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 & 2003 field campaigns” by E. Velasco et al.

Referee #4

2) Page 7565 lines 23-27: Only by comparison of ambient lumped VOC classes and lumped emissions, it would be not convincing enough to conclude that VOC classes are underestimated in the emissions inventory by factors of 1.1 to 3. VOC profiles

in the atmosphere evolves in favor of stable species, thus highly reactive VOCs often share a less part in the ambient samples than in emission sources. That is an important reason why the authors found an underestimate of alkanes emission and an overestimate of olefins and aromatics emission. Even this approach is sound, why the authors only reported the underestimation? This would be somewhat misleading. It is not consistent with the statements in the results and discussion part (page 7591 lines 6-8) “the emissions inventory appears to underestimate the contribution of alkanes and overestimates the contributions of olefins and aromatics.” Much care should be taken to use this approach to check the emission inventory. Imagine that VOCs from plant leaf (isoprene and monoterpenes) are typically less than 10% in total VOCs, yet they may contribute more that 50% in global NMHC inventory. Also there are other aspects that make the discussion not so strong, please see the comments No.11.

The manuscript points out that the comparison between ambient samples collected in urban sites during the morning period and the emissions reported in the inventory is a relatively simplistic analysis that does not fully account for the spatial and temporal distribution of emissions, the small number of monitoring sites, or for any early morning chemistry that might affect the ambient levels. Nevertheless, a complete evaluation of an emissions inventory for an urban area such as Mexico City with no uncertainties is impossible. Analysis such as this provides valuable insight to evaluate emission inventories.

The authors agree that the VOC profile in the atmosphere evolves in favor of stable species, and it could contribute to the observed underestimate of alkanes emissions and to the overestimate of olefins and aromatics emissions. However, no reductions were observed in the ambient concentrations of aromatics and alkenes in the 6-9 am period. In contrast, even though the evolution of the boundary layer and the morning photochemistry, the ambient concentrations of these reactive VOCs increased by a factor of 5 during this period considering as baseline the nocturnal background (see Figures 2, 3, 4 and 5 of the manuscript). For these reasons we consider that morning concentrations are mainly due to fresh emissions in the urban core of Mexico City. As part of the MCMA-2003 campaign, direct flux measurements of reactive species, such as olefins, toluene and C2-benzenes were made at the urban site of CENICA. These flux measurements showed that emissions start at 6 am and increase during the next 3 hours (Velasco et al., 2005). A comparison of the diurnal patterns of the measured fluxes of these species with the emissions reported in the inventory showed that both the magnitude and the diurnal profile are essentially equal, suggesting that the actual emissions inventory is correct.

It is true that different sources may have different diurnal pattern of VOC emissions. To avoid this issue we limited our comparison to urban sites. Samples collected at industrial and rural sites were not considered. Regarding the biogenic contribution see the answer to comment 3 of referee #2.

4) Page 7569 Line 20-21: Better list the dates/periods of both campaigns in the Table 1. Also better include the numbers of canister samples in the “method” column.

Table 1 of the revised manuscript includes the number of samples collected in canisters per site, and the number of monitored days per instrument and site. We have included also the dates of the MCMA-2002 and 2003 field campaigns.

5) What is “minimum detection limit” referring to? What is “pptC”? How about the method detection limits?

The authors thank the referee for suggesting to eliminate the word “minimum” in the term “minimum detection limit”. In the revised manuscript we changed that term to “detection limit”. However, we refer “minimum detection limit” or “detection limit” to the minimum concentration of a substance that can be measured with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte. This is the definition of the “Method Detection Limit” which is described in the Code of Federal Regulations (40 CFR 136 Appendix B). pptC = parts per trillion carbon (1Œ10-12).

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6) Page 7571 Line 2-10: The analysis by IMP seems to be not as good as that by WSU. Firstly, the detection limit of 1 ppbC might be too high for this study. If this detection limit is for propane, the detection limits for halocarbons would be much lower since FID is not a good detector for halogenated hydrocarbons. Another problem is that, if the detection limits are as high as 1 ppbC, the reported data much lower than 1 ppbC would not be regarded as valid ones. I think the detection limit of 20pptC for the WSU system is quite believable, but why the IMP system had so high a detection limit? How about sample volumes used for the analysis by the two GC-FID systems? What is the phase designation of the Quadrex capillary column? 007-01? PLT-5A? In page 7580 Lines 2-3 you reported a m-xylene to p-xylene ratio of 3.5, but DB-1 column used by WSU can not get m-xylene and p-xylene separated in the GC analysis. The GC column used by IMP can get the two xylenes separated? For the halogenated hydrocarbons, also see comments No.9.

The detection limit of WSU was better than the IMP. The referee is correct saying that the reported data by IMP lower than 1 ppbC would not be regarded as valid ones. For these reason we have fixed the ambient concentrations of the halogenated VOCs reported by IMP in Table 5 according to the detection limit of 1ppbC.

The IMP conducted their analysis using a Hewlett-Packard 5890 Series II chromatograph containing a 60-m Quadrex fused silica glass capillary column with a phase designation 007 series methyl-silicone (0.32 mm i.d. and coated with a 1 μm film thickness) at a flow of 2 ml min-1. This information was included in the revised manuscript.

Regarding the separation of m-xylene and p-xylene by GC-FID the referee is correct. However the manuscript indicates clearly that both isomers discussed at the end of Section 5.1 were measured by DOAS (page 7579, lines 25-26 of the original manuscript). That paragraph makes reference to Figure 5, which also indicates that the depicted diurnal profiles of m-xylene and p-xylene were measure by DOAS.

8) Page 7582 lines 15-16: Are there any proof that biomass or trash burning contributes to styrene? Styrene seems to be not a significantly important species in biomass burning (Andreae and Merlet, 2001).

The main styrene emissions to the atmosphere come from automobile exhaust and industries. Styrene emissions are also due to vaporization of paints, varnishes, adhesives, metal cleaners and other solvents. All these sources are common in urban environments, but not in rural sites. Therefore, we suggest that the high styrene concentrations observed at rural sites were due to trash and biomass burning. Although styrene emission rates reported by Andreae and Merlet (2001) for biomass burning are not very high compared to rates for other species, the burning of agriculture debris can be a significant contributor for the monitored rural sites together with the emissions from trash burning, which is composed in part of plastic or foam containers made of polystyrene. From personal experience of the authors, large amount of styrene have been observed from burning of tires and polymeric substances, such as insulation on wires, during Mexican trash fire events.

9) Page 7585 lines 6-22 and Table 5 in page 7608: For the detection of halocarbons, FID is not a sensitive detector as ECD. If the detection limit was as high as 1 ppbC, it is not necessary to list the data with two digits in Table 5. In this case a level like 0.52 would be regarded as analytically unreliable. Other questions/problems that need to be clarified: 1) As a long-lived halocarbon species, Freon 113 has a global troposphere mean mixing ratio of about 85 pptv and a life time of about 85 years (IPCC 2001). In the manuscript, the Freon 113 was surprisingly very high in the morning rush hours but not detected in the industrial site between 12:00 and 15:00. 2) There are other halocarbons, like CFC-11, CFC-12, HCFC-22 and chloromethane, that would typically have comparable or higher mixing ratios than Freon 113, why these compounds were not detected if the authors did use the cryogenic pre-concentration technique? 3) If the analytical aspects about the halogenated hydrocarbons are not so sure, better delete this paragraph about halogenated hydrocarbons and Table 5.

As it is indicated in comment 6, the referee is correct saying that the ambient concentrations of halogenated VOCs lower than 1 ppbC would not be regarded as valid ones. The ambient concentrations of the halogenated VOCs reported in Table 5 were fixed according to the detection limit of 1 ppbC. With the correction of the halogenated VOCs concentrations in Table 5, the resulting afternoon concentrations of Freon 113 measured at the industrial site were below the detection limit. It is difficult to say if they were different to those concentrations measured in the morning or at other sites, since all of them were just above the detection limit of 1 ppbC.

The manuscript indicates that the GC-FID technique is not the best method to identify halogenated VOCs, since these species contain other atoms besides carbon and hydrogen. The GC-FID technique can be used to identify halogenated VOCs, but not to precisely quantify their concentration. However, the obtained concentrations provide valuable information of their presence and give us an idea of their contribution to the total VOC burden.

10) Pages 7588 lines 1-8: It is not convincing enough to tell which one is an important source only by ratios, though the ratios of i-butane to butane for ambient (0.38 industrial and 0.37 urban) and vehicle exhaust (0.36) are essentially equal, though Mugica et al. (2001) reported exhaust emission ratios of 0.32 and 0.48 for gasoline and diesel vehicles in Mexico. LPG related emission may have similar ratios. There is no doubt that vehicle emission contributes to butane and i-butane. Blake and Rowland (1995) concluded that urban leakage of LPG was very important then; it would be very interesting if the authors can tell something about the relative importance of LPG leakage and vehicle emission, or if they can say vehicle emission is much more important than LPG leakage based on their study. Since the major components of LPG are propane, butane and i-butane, as mentioned by the authors, acetylene is a good marker for vehicle fuel combustion, we can calculate the ratios of propane, butane and i-butane to acetylene both in ambient samples and in vehicle exhaust. If the two batches of ratios match quite well, we would say that vehicle emission is more important; but if large

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gaps exist, the contribution of LPG leakage would depends on how big the gaps are.

The analysis suggested by the referee was already presented in the original manuscript (page 7589 line 29, page 7590 lines 1-4 and, Figure 8). However, the following table shows the ratios of propane, butane and i-butane to acetylene, both in urban ambient samples and in vehicle exhaust. Urban ambient Vehicle exhaust propane / acetylene 15.7 7.1 i-butane / acetylene 2.9 1.6 n-butane / acetylene 8.1 4.3

The ratios for urban sites were approximately twice the ratios for vehicle exhaust. This indicates that other anthropogenic sources contribute to the emissions of these low molecular weight alkenes.

To avoid confusions, the paragraph indicated by the referee was modified in the revised manuscript, specifying that vehicular emissions are also important sources of n-butane and i-butane in addition to LPG leakage, but not more important.

11a) Part 5.4 there are two aspects that might be taken into consideration: a) vehicle chase measurements is a good approach to characterize pollutant emissions, but in this manuscript the urban background was in fact the on-road background, which is strongly influenced by traffic emission. Take this on-road background as urban background would overestimate the influence of vehicle emission and underestimate the contribution of other sources. Also how many vehicles have been measured? In what routes did the selected vehicles travel? What kinds of vehicles were selected for the chase measurement? Are they representative vehicles in Mexico?

Section 5.4 describes how the vehicle exhaust measurements were made using a mobile lab during on-road conditions (page 7586 lines 2-12 of the original manuscript). As it is described, two canisters were collected per vehicle; one canister sampled the vehicle exhaust plume and the other the on-road background. We thank the referee for suggesting to change the term “urban background” to “on-road background” in page 7586 lines 11-12 to avoid any confusion in the explanation of the method to measure the vehicle exhaust plumes. For a detailed description of these on-road measurements see Herndon et al. (2005) and Zavala et al. (2006). For this study 60 vehicle exhausts were analyzed. The routes and vehicles were selected to be representative of Mexico.

11b. The comparison of ambient VOC concentrations to the emissions inventory, though it was limited to the morning period between 06:00 and 09:00 h, can not be used as a check of emissions. Firstly, we can not say that 06:00-09:00 morning period samples are totally fresh because concentrations in this period are strongly related to anthropogenic emissions before the photochemistry occurs. From the diurnal patterns or time series, we know that before 06:00 there were “background” VOCs, relatively higher for relatively stable species. Even during this morning period, very reactive species (like isoprene) may in ambient air may also decay and thus present in a much lower mixing ratios. Secondly, different sources may have different diurnal pattern of their VOC emission. This morning rush hour may have peak emission of vehicle exhaust, but may have less emission from other sources. Industrial emission, for example, may peak in the working hours. Biogenic emission may have strong dependence on light (isoprene) or temperature (monoterpenes). So this approach for checking emission inventory is useful but scientifically might be not sound enough.

See answer to comment 2 of referee #4.

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