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Atmospheric
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Discussions

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.

Anonymous Referee #4

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General comments: The authors measured a wide range of VOCs in the valley of Mexico with simultaneous use of different techniques for their concentrations, spatial distributions, diurnal patterns, origins, and reactivity. The study offers a good example to study VOC-related aspects in urban areas or in a mega-city with air pollution problems. The results and findings in the submitted manuscript are also very useful to support effective emission control strategies. Since emissions, chemistry and dispersion conditions all influence the occurrence and evolution of VOCs in ambient air, some discussion and statements should be cautious when observed data were used to interpret the emission. Also there are some problems or uncertainties concerning the data quality especially for VOC data from GC-FID. Please see the specific comments.

Specific comments [pages and lines refer to those in the online version (PDF, 3173 KB)]: 1 Page 7565 line 8: “Five distinct analytical techniques” should be “Four distinct analytical techniques”. I can only find GC-FID, PTR-MS, FOS and DOAS.

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

3 Page 7566 Line 14: Add “,” between “efficient” and “leading”?

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.

5 Page 7570 Line 27: What is “minimum detection limit” referring to? What is “pptC”? How about the method detection limits?

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.

7 Page 7580 lines 2-3: See the above comments about the separation of m-xylene and p-xylene.

8 Page 7582 lines 15-16: Are there any proof that biomass or trash burning contributes to styrene? Styrene seem to be not a significantly important species in biomass burning (Andreae and Merlet, 2001, Global Biogeochemical Cycles, pages 955-966)

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.

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

11. Part 5.4 and Part 5.5: 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? b) 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 isoprene0 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7563, 2006.