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Atmospheric Chemistry and Physics 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 #1

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General Comments:

The paper addresses an important topic: the characterization of the ambient concentrations and emissions of VOC in a megacity - the Mexico City Metro area. Much work has been done in urban areas of highly industrialized countries, but investigations in other urban areas are expected to give new insights into the sources and photochemical roles of VOC. The measurements and analysis presented in this paper are generally sound; they provide a reasonably comprehensive picture of VOC in Mexico City. However, I suggest that the discussion be strengthened in places. Specific suggestions for

revisions are given below.

Major Specific Comments:

1) This paper is evidently one of a series of papers that describe various aspects of VOC measurements collected in Mexico City in 2002 and 2003. One hopes that these papers are reasonably well coordinated; this coordination should be described so that the reader can clearly understand where this paper fits with others, and find references if desired.

2) In the abstract the authors state “vehicle exhaust is the main source of VOCs in Mexico City and that diurnal patterns depend on vehicular traffic.” Vehicle exhaust as the main source of VOC in Mexico City is well established in this paper, but the critical role of PBL evolution and other transport patterns in driving diurnal patterns should be acknowledged.

3) The last sentence of the abstract concludes that “suggests that some, but not all, VOC classes are underestimated in the emissions inventory by factors of 1.1 to 3.” This gives the impression that the emissions inventory tends to underestimate VOC emissions, but in fact the paper shows that the VOC most important from the point of view of reactivity are apparently overestimated rather than underestimated in the emission inventory. This impression should be corrected.

4) Pg. 7566, lines 13-15 state that combustion processes are less efficient at high altitude. This contention needs more discussion. If motor vehicles are the major source of VOC, then the combustion processes of interest are internal combustion engines, and it is my understanding that emission from these engines (if properly tuned for the altitude) are not a strong function of altitude.

5) The measurement comparison presented in Section 4 of this paper is important, but the discussion in this paper is inadequate. Some comparisons are made and discrepancies are identified, but I could not see where these discrepancies were taken

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into account in the following analysis. Evidently there is a paper by Jobson et al. in preparation that discusses the comparisons in more detail. If this comparison paper will indeed be completed, then perhaps this Section 4 should be eliminated, and reference made to Jobson et al. paper. However, if the Jobson et al. paper is unlikely to be finished, then section 4 should be expanded. In either case, these comparisons should be clearly considered in the following analysis.

6) If Section 4 is retained, specific needs include a figure similar to Fig. 2 for the CENICA site. The comparison in Figure 3 should rely on scatter plots of the full data set with derived slopes, intercepts and correlation coefficients rather than time series for a selected two-day period. The discrepancy between the FOS and sum of the alkenes from canisters (Pg. 7577, lines 11-13) may also indicate that alkenes are destroyed in the canisters.

7) Pg. 7579, lines 15-18 - Certainly the reaction of alkenes during the photochemical active part of the day contribute to the diurnal cycle of the alkenes.

8) Pg. 7581, lines 17-20 - The authors rightly point out that their analysis omits important VOC species. However, the authors should give the reader some idea of the likely importance of the reactivity of “many oxygenated VOCs and carbonyls” that are omitted. It is my impression that it is likely to be small, with the possible exception of some aldehydes.

9) Pg. 7583, lines 12-14 - To explain the larger proportional loss of alkanes, the authors conclude, “Emission rates must be a factor, as well, with a large decrease in alkane emissions relative to aromatics and olefins.” How can this be? The authors conclude that vehicle emissions dominate the VOC emissions, and it seems unlikely that vehicle emissions are particularly depleted in alkanes later in the day. Clearer discussion is required here.

10) Pg. 7584 - Two ethers (MBTE and ETBE) are discussed, yet only the concentration of the latter is discussed. The concentrations of both should be compared in the

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discussion.

11) In Tables 4 and 5 average concentrations and OH reactivity are tabulated. It is not clear how data below the detection limit are treated. Is this an important consideration? Are many data below the detection limit? Were they counted in the average? If so, why is there only one available measurement in some cases?

12) In Table 6 average ratios are tabulated. Arithmetic averages of ratios with relatively large variability can be misleading, because large outliers are over emphasized. This appears to possibly be the case here because the median is usually smaller than the average. Geometric means of ratios avoid this problem and should be used rather than arithmetic means. (This can be demonstrated by seeing if the mean of the inverse ratios is equal to the inverse of the mean ratio; it is for the geometric, but not the arithmetic mean.)

13) Figure 1 needs more explanation. What is the color code? If white represents high altitude mountains, how can the Metropolitan Area extend into these regions?

14) Section 5.6 needs to be clarified. It is not clear if the CIT model used in Figure 11 had VOC increased by a factor of 3. This should be clear from the beginning of this section.

15) Pg. 7595 - The last half of the final paragraph before the acknowledgements should be removed. It moves from science to policy recommendations, which are not directly discussed in the paper.

Minor Comments and Technical Corrections:

1) Pg. 7569, line 2 - “data” is plural, not singular.

2) Pg. 7575, lines 20-22 - A reference should be given for what is “well-known”

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