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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 #1

1) This paper is 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

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can clearly understand where this paper fits with others, and find references if desired.

This article will be part of the ACP special issue “Mexico City Metropolitan Area Field Campaign 2003 (MCMA-2003)” edited by L.T. Molina, C.E. Kolb and U. Pöschl. In this special issue there will be an overview article describing the entire MCMA-2003 campaign and the resulting publications. The introduction of our article includes a brief description of the MCMA-2002 and 2003 field campaigns with the aim to put in context the VOC measurements discussed here. In the course of the article the reader will find references to diverse articles related to both campaigns. Among these articles are: Zavala et al. (2006), Volkamer et al. (2005) and Velasco et al. (2005), etc.

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.

The abstract of the revised manuscript mentioned that the VOCs diurnal patterns also depend on meteorological processes. These meteorological processes are described in Section 5.1.

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.

The abstract of the revised manuscript states that the examination of the VOC data in terms of lumped modeling VOC classes and its comparison to the VOC lumped emissions reported in other photochemical air quality modeling studies suggests that some alkanes are underestimated in the emissions inventory, in contrast to some olefins and

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aromatics that are overestimated.

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.

The problem is that a large fraction of the Mexican fleet is relatively old and do not have adequate maintenance. These two factors in addition to the lower concentration of oxygen in the air compared to sea level because of the high altitude of the Valley of Mexico (2240 m) make combustion process less efficient, leading to enhanced VOC emissions due to higher fuel consumption.

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 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.

The manuscript points out clearly the differences between each technique: GC-FID, FOS and PTR-MS data are from measurements at a specific location, while DOAS data represents average concentrations over a long open path distance. Besides the difference in the spatial scales, the temporal scales are also different. Because of these differences, the data obtained from each technique are not mixed for the different analysis presented in the article. However the combination of the results obtained with each technique is used to reach the objectives of this study. For this reason the authors

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consider the importance of the comparison presented in Section 4.

Jobson et al. will present a more detailed inter-comparison of the VOCs measurements performed with PTR-MS, GC-FID and DOAS at the CENICA site. They will focus only in the measurements at the CENICA site and not at the La Merced site. For this reason the authors consider it is necessary to maintain Section 4.

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. Since Jobson et al. will present figures of time series for the VOCs measured by PTR-MS, GC-FID and DOAS at the CENICA site, similar to the time series presented in Figure 2 of this article, the authors do not consider necessary to duplicate those figures.

Figure 3 shows time series of the PTR-MS and GC-FID measurements of C2-benzenes and C3-benzenes for three different sites instead of scatter plots of the full data set, because the objective is to illustrate at the same time the differences in the diurnal patterns and the correlations between PTR-MS and GC-FID as function of the time and site. However, next figures show the scatter plots suggested by the referee. They show the correlation between these two techniques for ambient concentrations of C2-benzenes and C3-benzenes measured at the Santa Ana, Pedregal, CENICA and La Merced sites. The correlation between GC-FID and PTR-MS for C2-benzene was good and followed closely the dashed line that indicates the 1:1 correlation. The exception was the CENICA site, where the PTR-MS concentrations were overestimated compared to the GC-FID concentrations. For C3-benzenes the PTR-MS overestimated the concentrations at all sites, except at Santa Ana. This discrepancy is due to the fact that not all species detected as mass 121 (C3-benzenes) by the PTR-MS were determined by GC-FID.

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Figure A1. Correlations between ambient concentrations of C2-benzenes and C3-benzenes measured at 4 different sites by GC-FID and PTR-MS. The dashed line indicates the correlation 1:1, and the solid line, the linear regression. Regarding the comment on the discrepancy between the FOS and the sum of the alkenes from canisters may also indicate that alkenes are destroyed in the canisters, the canister samples were analyzed within 24-hour period after the sample was taken with the aim to avoid the destruction of alkenes and other reactive species.

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.

This statement was considered in the revised manuscript, indicating that olefins concentrations are lower in the afternoon compared to the morning because of the evolution of the boundary layer, the photochemical processes and a decrease in the emissions.

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.

The reactions of oxygen-containing organics with OH are reasonably fast, ranging from ˜10-13 cm3 molecule-1 s-1 with acetone to more than 10-11 cm3 molecule-1 s-1 with the aldehydes, furan, and, in general, compounds having an alkyl group larger than -CH3. Compared to olefins and aromatics, the oxygenated VOCs and carbonyls have lower OH reactivity rates, but compared to alkanes, their OH reactivity rates are similar or slightly higher. Since all unidentified VOCs, including these oxygen-containing VOCs represent 20% of the total VOC burden, we can conclude that their contribution to the total OH reactivity is not very significant as the contribution of aromatics and olefins, as well of alkanes, which have low reactivities rates, but high ambient concentrations.

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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.

The manuscript indicates that emissions of low molecular alkanes, particularly of propane, n-butane and i-butane are in large part due to LPG leakage. LPG is the main fuel for cooking and water heating in Mexican households, and Mexicans use to bath in the morning before go to work, therefore a higher consumption and leakage of LPG could be expected in the period between 6 and 9 am.

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 discussion.

The MTBE average concentrations are presented in Table 4. The revised manuscript stated that ETBE concentrations were 96% lower than MTBE concentrations in both urban and industrial sites.

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?

The VOC data used for Table 4 were measured in two campaigns: MCMA-2002 and MCMA-2003. Five species were identified in 2002 and not in 2003 (1-hexene, propyne, 2-methylheptane, 1,2,4-trimethyl cyclohexane and p-propylbenzene); while in 2003, twelve species were identified and not in 2002 (ethylene, acetylene, ethane, cyclopentane, 2,3-dimethylpentane, 2,5-dimethylhexane, 2,4-dimethylhexane, nonane, n-decane, p-ethyltoluene, MTBE and ethyl acetate). In 2002 all samples were filled

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instantaneously, while in 2003 samples were collected with averaged intervals of 30 min, 1 and 3 hours using automated samplers, because of the different sampling objectives at each site. For these reasons there was none or only one available data for 9 and 2 VOC species reported in Table 4 for the industrial and rural sites, respectively. For example, in 2002 at the industrial site, samples were collected during the morning period only in one day, and although several samples were collected between 6 and 9 am, only the average of those samples was used. Therefore, for species that were identified only in 2002, such as 1-hexene and propyne, there was only one available data to be presented. The reader needs to be cautious with those species. Table 4 indicates for which species there was only one data.

Regarding the concentrations of halogenated VOCs below the detection limit see comment 9 of referee #4.

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.)

The authors agree with the referee. Geometric means are more appropriate than arithmetic means to evaluate ratios as those presented in Table 6. It is recommended to use the geometric mean when the largest value is at least 3 times the smallest value. The arithmetic means in Table 6 were changed to geometric means in the revised manuscript, but the results and conclusions remain unchanged.

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?

The introduction describes briefly the topography of the Valley of Mexico and its

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metropolitan area. The shadow in Figure 1 represents the so called “Mexico City Metropolitan Area (MCMA)”, which identify the expansion of historical Mexico City to the neighboring areas. In fact, MCMA is not only composed of urban districts, it is composed of a mix of urban, suburban, industrial, rural and forested districts. Points 1, 2, 3 and 5 in Figure 1 indicate the monitored urban sites and give an idea where the urban area is located in the Valley.

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.

Section 5.6 indicates that the VOC emissions used to run the CIT model were multiplied by a factor of three. However, to avoid any confusion, Figure 11 of the revised manuscript also indicates that the presented results of the CIT model considered the increment factor of 3 in VOC emissions.

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.

The objectives of the MCMA-2003 field campaign were to gain a better understanding of the emissions patterns and sources of pollutant species, as well as the chemistry and transport processes driving atmospheric pollution in the Valley of Mexico. These objectives were determined to provide scientific information to design efficient strategies to reduce emissions of pollutants threatening the health of Mexico City inhabitants. Therefore, any good policy focused to reduce pollution needs to be acknowledge by the experts on the field, especially if that policy was based on the scientific information provided by studies such as MCMA-2003. In this case the recently initiated system of confined buses to isolated lanes on main avenues is a good example of a strategy to reduce emissions pollutants, in particular of VOCs due to transportation. It is also important for investigators to know the policies that may reduce the emissions in order to

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understand the changes in the emissions inventory as well as ambient concentrations of pollutants.

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