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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.

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Referee #2

1) As the authors pointed out that the FOS responded to several olefin species with different sensitivity, but it could not specify the olefin species. If the FOS signal was treated as the response from propylene, how would this affect the estimation of the

olefin budget? Was it possible to use the canister data to identify the olefin peaks?

The FOS is a Fast Isoprene Sensor calibrated with propylene instead of isoprene. Detection is based on chemiluminescent reaction between alkenes and ozone, and the detector responds with different sensitivity to a variety of olefins, and possibly to other trace gases that could be potential interferences. Instrument response factors for a number of compounds have been previously reported (Guenther and Hills, 1998). To analyze the FOS response in the atmosphere of Mexico City, the sensitivities of 5 olefins and nitric oxide were analyzed. Sensitivities for those species are shown in Table 2 of the manuscript with their corresponding relative sensitivities to propylene and FOS responses to average concentrations measured during selected days throughout the campaign between 6 an 10 am by a canister sampling system. The next figure compares the FOS response to the sum of olefins as measured simultaneously with the canister sampling system. Results suggest that generally the total olefins level detected by the FOS is larger than the sum of identified olefins from canister samples. In only 3 of the 21 sampling periods compared was the FOS response less than the sum of olefins measured in canister samples. With these periods removed, the ratio between the sum of olefins measured by canisters and the FOS signal shows a median of 48%. This indicates that 52% of olefins detected by the FOS remain unknown. Additional analysis is needed to identify these unknown species.

Figure A2. Comparison of identified olefins weighted by their corresponding FOS sensitivities from GC-FID measurements versus FOS measurements for 21 samples during selected days throughout the campaign between 6 and 10 am.

2) The long-path could improve instrumental sensitivity, but it also made the inter-comparison with other point measurement techniques difficult. This issue should be discussed.

This statement was considered for the discussion on the inter-comparison between GC-FID, PTR-MS and DOAS measurements (Section 4). Some differences between

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concentration levels measured by DOAS and the other two methods are expected. The DOAS signal represents average concentrations over a long open path distance, while the PTR-MS and GC data are from measurements at a specific location.

To emphasize this point, the summary and conclusions in Section 6 of the revised manuscript point out these differences.

3) The author claimed that the isoprene more likely had an origin from vehicle exhaust. Can the author provide some reference of the chemistry to support this statement?

Different studies have reveled that the isoprene has a strong anthropogenic origin in urban and suburban sites, mainly due to traffic emissions (Borbon et al., 2001; Reinmann et al., 2000; Mclaren et al., 1996). During the MCMA-2003 campaign flux measurements of olefins were collected and no insights of biogenic contributions were observed (Velasco et al., 2005), as described in the manuscript. In addition, with the knowledge that 1,3-butadiene is a good tracer of vehicle exhaust, we compared the morning ambient concentrations of isoprene and 1,3-butadiene measured at urban sites. The regression between these two species was nearly linear, suggesting that they share the same emission source (see Figure A3). Using the on-road samples collected by the Aerodyne mobile-laboratory, we found an isoprene:1,3-butadiene ratio of 0.27, comparable to the ratio of 0.30 obtained for the ambient samples. These ratios are similar to those reported for other urban and suburban sites (Borbon et al., 2001; Reinmann et al., 2000).

Figure 3A. Scatter plot of isoprene versus 1,3-butadiene for the morning (6-9 am) ambient samples collected at the 4 different urban sites (Pedregal, La Merced, Constituyentes and CENICA).

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