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Interactive comment on "Non-methane hydrocarbons source apportionment at different sites in Mexico City during 2002–2003" *by* E. Vega et al.

Anonymous Referee #2

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This paper presents the results of a measurement program to characterize NMHC levels and source attributions at six sampling locations in the Mexico City Metropolitan Area. The validity of the source contribution estimates of ambient NMHC derived by the CMB receptor model depends upon a number of factors. The most important among these is typically the inclusion of all major source categories contributing to ambient NMHC, the appropriateness of source composition profiles and associated uncertainties, consistency in measurement and definition of NMHC in the source and ambient datasets, and the effect of photochemical reactions on conservation of mass between source and receptor.

A total of 33 source profiles were grouped into six source categories to aid in the interpretation of results: 1) LPG; 2) degreasing; 3) solvent in surface coatings; 4) gasoline vehicle exhaust; 5) diesel vehicle exhaust; and 6) others or unidentified. It is not clear from this description whether the 33 profiles were combined in some fashion into five composite profiles prior to the CMB analysis or whether all or some of the 33 profiles were used as individual profiles and the apportionments combined into the six categories. It would be appropriate to describe how the profiles were combined into composites if the former is the case. There would be substantial collinearity among similar profiles if individual profiles were used. In this case, the basis for the choice of specific profiles among alternatives within a category should be given as well as the variations that resulted in the source contribution estimates (SCEs) among the alternative profiles. In any case, this sort of sensitivity analysis would be necessary to evaluate the uncertainties in the SCE rather than rely on the propagated uncertainties obtained from the CMB model output alone.

Most of the vehicle related profiles appear to be from tunnel or roadway measurements. If source-dominated ambient samples are the basis for profiles, it seems necessary to account for (or subtract) the contributions of the surrounding urban NMHC and potential commingling of diesel and gasoline vehicle exhaust. What was the traffic mix and how was this considered in deriving the profile? It is a common practice in tunnel measurements to regress pollutant concentrations with fraction of gasoline and diesel traffic. Pure diesel and gasoline are extrapolated to the two extremes in the traffic mix (100% gasoline and 100% diesel). Hot soak measurements in parking lots were mentioned among the source samples. Was a gasoline evaporative emissions profile derived? Was it background subtracted? Was this profile evaluated and excluded from the final CMB fits for a particular reason? More detailed explanation is necessary to understand what the profiles actual represent and how they were derived.

The appropriateness of the source composition profiles applies not only to how the source composition profiles were obtained but also what species are included in the

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profiles. Although 200 C2 to C12 compounds were quantified, only 49 were reported and only 12 were used as fitting species. What total NMHC was used to normalize the abundances of individual hydrocarbons in the source profile (200 or 49 compounds)? What was the rationale for selecting the 12 fitting species? The paper mentions (P 13570, line 1) that the 12 species are tracers of specific emission sources. But it does not mention which sources are associated with which of these species. I would not expect that these 12 species alone would be sufficient to distinguish among the five source categories mentioned. The MPIN matrix in the CMB output should be examined to verify which species have the most influence on the fit. In addition, there should be some mention of the abundances of the twelve species in the profiles and whether they are present in the profiles in characteristic ratios. The large difference in the relative apportionment of diesel and gasoline exhaust between the 2002 and 2003 samples are puzzling. Why is there so much more diesel contribution in 2003? The SCEs should be summarized in a table with uncertainties rather than stack bar charts with no uncertainties.

The ratios of toluene to benzene were used as an indicator of the extent of photochemical reactions. This approach is useful, but it would have been preferable to use xylenes to benzene ratios as xylenes are considerably more reactive than toluene.

In summary, the paper provides valuable information on the levels and composition of NMHC in Mexico City and evidence of substantial reductions in NMHC levels since 1997. However, there is insufficient detail in the paper regarding the development and evaluations of the source composition profiles and to assess the validity of the source attributions.

Specific Comments

Abstract, line 7. (59%) must be in reference to alkanes rather than alkenes since olefins account for 9%.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13561, 2007.