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> Interactive Comment

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

## Anonymous Referee #3

Received and published: 6 November 2007

The subject manuscript presents an analysis of Non-Methane Hydrocarbon (NMHC) data from Mexico City from spring periods in 1997, 2002, and 2003. The analysis includes the presentation of descriptive statistics, concentration ratios and chemical mass balance (CMB) modeling. The manuscript largely uses existing data analysis tools but the interest in pollution in mega-cities, like Mexico City, makes the focus of the manuscript of interest to the readership of ACP. The manuscript contains a lot of information that is not very well organized. The manuscript should be better organized to help the reader in understanding the motivation, results, and implications of the subject study. In addition, the following issues need to be addressed before the manuscript if suitable for publication:



## **General Comments**

1) The manuscript needs to be better organized. Much of the Introduction is presents methods. The Introduction should be re-written to provide context for the work in reference to past efforts to apportion NMHC, the uniqueness of NMHC composition and sources in Mexico City, and the importance of quantifying the sources of NMHC in Mexico City.

2) I find it very difficult to understand how diesel emissions can be the dominate source of NMHC in Mexico City. Although diesel engines have high NOX and PM emissions, they have relatively low NMHC emissions. Is it reasonable that diesel vehicles make up one third of the NMHC emissions in Mexico City? I am not aware of any urban atmosphere where diesel emissions have such a significant contribution to NMHC concentrations.

3) Throughout the paper it is very difficult to understand exactly what is included in NMHCs. It appears that this is a sum of quantified NHMC and not an integrated measure such at EPA method TO-12. In difference locations in the manuscript different lists of NMHC are presented but it is included in the NMHC quantity. This needs to be clarified as the definition of the NMHC has implication to the results.

4) The use of toluene/benzene ratios to understand atmospheric aging is very confusing and not convincing. The fact that the ratio changes with meteorology (i.e. wind direction) and NMHC concentration suggests that this ratio is largely changing due to different source mixtures and not atmospheric aging. The use o the toluene/benzene ratio to assess aging is largely used to look at the aging of an air parcel and cannot really be used in the urban environment where the relative source strengths are changing. I recommend that this discussion and presentation be removed or substantially revised.

5) As described in the manuscript, XAL is impacted by industrial sources but the CMB analysis does not include industrial emissions. The authors need to assess how this is

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biasing the analysis.

6) The CMB results do not appear to be very robust as they change significantly across sites and samples. Some sensitivity analysis is needed to be better asses the robust-ness of the results. The use of CMB output statistics is not sufficient to assure good CMB results.

7) The number of samples used for each site in each year should be presented. It is unclear if the number of samples is sufficient to draw the conclusions about trends across the sites and across years. If the meteorology is different for a majority of the samples in different years and there are many local industrial sources, then the comparison across years needs to be qualified.

8) In the context of comment 2 above, the diesel profile shown in Figure 1 does not seem typical of diesel emissions. It looks like this profile is heavily impacted by ambient NMHC levels. If this profile is from roadway or near source sampling then efforts need to be presented that the background is properly subtracted from the sample to generate a representative diesel profile.

9) The details of the source samples are very confusing and the authors provide little information to demonstrate that these are representative. I do not believe that samples of vehicle emissions are representative of the average driving cycle of mobile sources. Likewise, it looks like the other source tests were spot samples that used fast fill times (Page 13566). Averaging over many source profiles helps with representativeness but the base measurements still need to be reasonable.

## **Specific Comments**

1) Abstract - Are the differences between weekday and weekend concentrations statistically different? What statistical test was used for this assessment?

2) Page 13564, line 18 - CMB does not only require that the chemical species do not react with each other but it also requires that they do not react at all.

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3) Page 13565, Methods - When were the 1997 samples collected. I find no reference to the time of day, season, and methods used for these samples. Is this data really comparable to the 2002 and 2003 data?

4) Page 13566, Line 10 - The model number and company location for the "ANDER-SEN" sampler needs to be provided.

5) Page 13568, Lines 8-10 - Fuel is not the only factor impacting source profiles from mobile sources. Even if fuel has not changed, which I am not sure is really true, the vehicle representiveness and its distributions of control technologies as well as driving cycle are very important in obtaining representative profiles.

6) Page 13576, line 24-26 - I am not familiar with the details of gasoline in Mexico City but iso-butane is specifically produced in refineries around the world as an excellent gasoline additive. Is it really reasonable to state the iso-butane is largely from LPG in Mexico City?

7) Why is only 2003 data shown in Table 2?

8) What are the units in Figure 1 and what is represented by the symbols and bars?

9) Are the trends discussed in Figures 2, 3, and 5 statistically significant? Regression uncertainties should be presented for the regressions in Figure 5.

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