Atmos. Chem. Phys. Discuss., 7, S9749–S9755, 2008
www.atmos-chem-phys-discuss.net/7/S9749/2008/

Atmospheric Chemistry and Physics Discussions

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

E. Vega et al.

Received and published: 2 April 2008

General comments

In regards to diesel emissions of NMHC in Mexico city:

This result has aroused serious comments. We have done more analysis for both ambient data and CMB results. As mentioned above (Answers to referee 2), in general, the higher contribution of diesel was related to both conditions in ambient air, high concentration of toluene and low concentration of n-pentane.

Another aspect we further investigated was the difference of emissions on holidays versus normal days and the effect on the CMB simulations. The MCMA 2003 field cam-

paign included school vacations as well as Holy Week and Easter (from 14/04/2003 to 25/04/2003 inclusive) when traffic is greatly reduced in the whole city, providing a natural experiment for the impact of emissions reductions. Good Friday (18/04/2003) had CO concentrations around 50% lower than normal and O3 around 20% lower. In addition, it followed a day with emissions estimated to be 30% lower (de Foy et al, 2005). The NMHC samples were taken from 14/04/2003 to 02/05/2003 (at PED site) and from 21/04/2003 to 02/05/2003 (at MER, XAL and CEN sites). This database allows comparing observations during holydays (14/04/2003 to 25/04/2003) with working (normal) days (from 26/04/2003, Saturday, to 02/05/2003). Although the reduction is not evident for the total NMHC concentrations, it was observed that when a higher contribution of diesel was determined by CMB modelling, there was also a higher concentration of toluene and lower concentration of pentanes in ambient air. Table 3 contains the average percentage of toluene, pentanes and other NMHC for holidays and normal days.

3) NMCH definition

The chemical analysis of C2-C12 compounds for the 1997, 2002 and 2003 samples followed the TO-14 EPA method. At least 186 chemical species (in some cases 258) were quantified and their mass was added to obtain the NMHC total mass concentration (ppbC), which was used to calculate the fraction of each species on the profile. In general, 62 species were used for the application of the CMB model (Vega et al. 2000 and 2001) which on average account for 85-90% of the total NMHC mass concentration.

4) toluene/benzene ratio

As stated in the manuscript, there is a trend of increment on the toluene/benzene ratio with continuous wind flow (i.e., the ratios were higher on the north or south of the city depending on the wind flow pattern). We also noted a weekly cycle on VOCs concentrations and differences on weekday and weekend days, as emissions are stronger

ACPD

7, S9749–S9755, 2008

during weekdays. However, no categorical conclusions could be drawn as the number of data is not enough for statistical purposes. We are aware of the limitations of such method and the results presented in the manuscript are a first approximation of the relationship between wind flow and the toluene/benzene ratio on the urban scale.

We agree with the referee about the toluene/benzene ratio that it should be used in a larger scale rather that an urban scale, however, as we have the data for two rural sites (at northern and southern part of the city) and also a well detailed meteorology data, we took the chance to have a first approximation. The main objective was to evaluate if there was a photochemical aging of air masses, although, once again, we agree that the ratio is highly dependent on source mixtures, the ratio showed a relationship with air circulation, i.e. the ratio at the northern sites increased when a north circulation pattern was observed.

5) how industrial sources affect XAL site

This is something that should be taking into account for future work. We feel that the fuel used at the industry (in Mexico is mainly diesel and some other heavy oil residuals) at the moment could not be differentiated from the one used by motor vehicles, which could bias the CMB results.

6) CMB results apparently not very robust

We agree with the referee about the CMB limitations, but the analysis of the ambient data also showed a spatial and temporal variability which is also reflected on the CMB results. Sensitivity analysis was performed prior each CMB run.

7) number of samples per site/year

Year Site Sampling time N (06:00-09:00) 1997 XAL 12 MER 13 PED 11

2002 XAL 7 MER 7 PED 7

2003 XAL 8 MER 9 PED 10 CEN 9

ACPD

7, S9749–S9755, 2008

8) diesel profile heavily impacted by ambient species

When the diesel profiles were determined, ambient data was not subtracted as it was considered negligible. Samples were collected at isolated places, or where the contribution of other sources was minimal.

9) demonstrate that source samples are representative

See comments for referee 2 (first answers)

Specific comments

1) Abstract - Are the differences between weekday and weekend concentrations statistically different? What statistical test was used for this assessment? Answer: the differences between week and weekend levels were analyzed by a Wilcoxon test, showing statistical significance for Saturday against Wednesday and Thursday. The number of data for Monday and Sunday was insufficient for running a statistical method. The abstract was modified.

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

Indeed, one of the limitations of the CMB model is the use of non-reactive species for the simulations, specifically for the selection of ‘fitting species’. Regarding this important requirement of the model, we selected those species with the lowest reactivity.

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?

All the field campaigns were carried out following the same sampling and analysis techniques; same sampling period (0600-0900) and same season (early spring).

4) Page 13566, line 10 – The model number and company location for the

ACPD

7, S9749–S9755, 2008

Andersen sampler needs to be provided

Information was added.

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 if is really true, the vehicle representiveness and its distributions of control technologies as well as driving cycle are very important in obtaining representative profiles.

The source profiles for diesel and gasoline exhaust hydrocarbons were obtained in May-November 1997 (Vega et al., 2000). Indeed, between 1997 and 2002 changes occurred in both the vehicle fleet and in fuel composition in MCMA, which introduce uncertainty in the source profile. However, a study comparing emissions from Magna and Premium conducted by Shifter et al. (1999) and Diaz et al. (2002) clearly stated that there are no significant differences on nitrogen oxides, total hydrocarbons and carbon monoxide emissions. The reduction on aromatic and toxic compounds using Premium instead of Magna gasoline has no significant effect on CMB results, as species such as benzene, 1,3-butadiene, formaldehyde and acetaldehyde were not used as fitting species. Shifter et al. (1999) also concluded that exhaust emissions from both types of gasoline (Magna and Premium) were alike since they have similar olefins, aromatics, oxygenated contents and volatility. The main difference is the octane index. However, the results showed that the most important control to reduce these emissions is related to the improvement in the vehicle technology and its maintenance.

Diaz, L., Schifter I., Vera, M., Castillo, M., Rodríguez, R., Larios, P., Avalos S., López-Salinas, E., and Gamas, E. Fuel reformulation in the Metropolitan Area of Mexico City. Journal of Environment and pollution, Vol. 17 No. 4 pp 367-389, 2002.

Schifter, I., Díaz, L., and Guzman, E.: La tecnología en los vehículos y las gasolinas PEMEX Magna y PEMEX Premium, Octanaje 25, 1999. Available at: http://www.ref.pemex.com/octanaje/octxe25.htm.

ACPD

7, S9749–S9755, 2008

6) Page 13576, lines 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?

ibutane is the third most abundant species on the LPG source profile with a percentage of approximately 30% (Vega et al., 2000).

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

The detailed meteorological information (i. e. wind flow type) is only available for the 2003 campaign.

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

Figure 1 has been modified.

9) Are the trends discussed in figures 2, 3 and 5 statistically significant? Regression uncertainties should be presented for the regression in figure 5.

Data of figure 2 (not included in the text). A first test of correlation coefficient (R2) was applied to the 1997, 2002 and 2003 0600-0900 concentrations to determine trend. Although the slope is negative, the number of data for the analysis is very small to draw any conclusion.

The Wilcoxon test was also applied to the data. Even though the results indicate statistical differences from 1997 to 2002 and 2003, the uncertainty is high due to the small number of data and no categorical conclusion can be made.

Results for Wilcoxon Test N T Z p-level 1997 & 2002 3 0.000000 1.603567 .108819 1997 & 2003 3 1.000000 1.069045 .285057 2002 & 1997 3 0.000000 1.603567 .108819 2002 & 2003 3 1.000000 1.069045 .285057 2003 & 1997 3 1.000000 1.069045 .285057 2003 & 2002 3 1.000000 1.069045 .285057

data of figure 3. The same problem (i. e., small number of data) is found when trying

ACPD

7, S9749–S9755, 2008

to determine trend for the individual concentrations of chemical species. Most of the calculated slopes are negative, but the uncertainty is high.

XAL MER PED Species equation R2 eq R2 eq R2 ethene propane y = -20.39x + 573.31 R2 = 0.03 y = -105.44x + 700.05 R2 = 0.71 y = 32.38x + 172.61 R2 = 0.99 n-butane y = 4.66x + 263.8 R2 = 0.01 y = -60.76x + 391.91 R2 = 0.63 y = 14.12x + 92.49 R2 = 0.83 m,p-xylene y = -24.17x + 157.24 R2 = 0.80 y = -42.87x + 177.26 R2 = 0.81 y = -28.49x + 99.04 R2 = 0.80 i-butene 2mbutene y = 5.28x + 1.56 R2 = 0.34 y = -1.69x + 14.32 R2 = 0.09 y = -0.53x + 4.18 R2 = 0.23 toluene y = 17.92x + 182.79 R2 = 0.18 y = -67.81x + 320.9 R2 = 0.74 y = -12.25x + 79.43 R2 = 0.95 2m2butene y = -0.11x + 8.36 R2 = 0.00 y = -4.81x + 20.53 R2 = 0.65 y = -0.30x + 3.68 R2 = 0.24 t-2,butene y = 1.40x + 8.98 R2 = 0.13 y = -1.64x + 14.13 R2 = 0.18 y = 0.39x + 2.56 R2 = 0.05

all sites Species eq R2 ethene propane y = -31.149x + 481.99 R2 = 0.2193 n-butane y = -13.99x + 249.41 R2 = 0.1213 m,p-xylene y = -31.847x + 144.52 R2 = 0.8046 i-butene 2mbutene y = 1.0179x + 6.69 R2 = 0.0474 toluene y = -20.713x + 194.37 R2 = 0.9918 2m2butene y = -1.7468x + 10.861 R2 = 0.4144 t-2,butene y = 0.0513x + 8.5614 R2 = 0.0003

Data of figure 5 These figures were removed from the text as the section of photochemistry was also removed as suggested.

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