Atmos. Chem. Phys. Discuss., 7, S6614–S6623, 2007
www.atmos-chem-phys-discuss.net/7/S6614/2007/


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: 6 November 2007

Authors' response to interactive comments by E. Velasco

We thank E. Velasco for taking the time to put together an extensive and thoughtful set of comments on our ACPD paper by Vega et al. The comment makes a number of important points that we have addressed in our revised version of the paper; we have also clarified some of the specific comments below.

General Comment: The manuscript presented by E. Vega et al. provides additional and valuable information on the characteristics and origin of the volatile organic compounds (VOCs) in Mexico City's atmosphere. The VOCs data were obtained from three field campaigns carried out in 1997, 2002 and 2003. Overall, the authors confirmed

some of the observations reported by Velasco et al. (2007) from the MCMA-2002 2003 field campaigns, such as the morning VOCs distribution dominated by alkanes followed by aromatics and olefins, and the result that motor-vehicles are the main VOC source in Mexico City. However, the manuscript contains a number of inaccuracies on the description of the measurements made during the 2002 and 2003 field campaigns, and none information is provided for the 1997 measurements. Also, the manuscript presents inconsistencies on the vehicular emission profiles used to run a receptor model to identify the VOC contribution from different emission sources, which could make flawed the final results.

Response: We have modified the first paragraph under sect. 2.1 and we have also added a reference (Edgerton, 1999), which describes the measurements, data analysis and results of the 1997 field campaign. The 2002 is a sampling campaign carried out by IMP as part of an internal project, so there are no inaccuracies in describing our sampling campaign. We have added a reference to clarify this.

"The Mexican Petroleum Institute (IMP) in collaboration with a number of national and international institutions, conducted the project Investigación sobre Materia Particulada y Deterioro Atmosférico-Aerosol and Visibility Evaluation Research (IMADA-AVER) in 1997 (Edgerton et al., 1999) to determined NMHC at three sites (XAL, MER, and PED). Additionally, two sampling campaigns were carried out to obtain the ambient data during March 2002 (see Vega et al., 2004 for location and sampling period) and April-May 2003 as a part of the MCMA-2003 campaign (Molina et al., 2007; Velasco et al., 2007) at different sites. The sampling sites encompass residential, industrial and mixed settings, and all of them classified as urban sites. The Northeast site, Xalostoc (XAL), is under the influence of heavily travelled paved and unpaved roads with old and new gasoline and diesel vehicles and historically has shown the highest concentrations of NMHC in Mexico City with major industrial activities. La Merced (MER) site is located in the administrative district in Central city, under the influence of commercial activities, residential and heavily traveled paved roads with light-duty vehicles and modern



ACPD
7, S6614–S6623, 2007





EGU

heavy-duty diesel buses. The southwest site is located in Pedregal (PED), in a residential area, with paved roads lightly travelled. The southeast site CENICA (CEN) is located near stone-cutting operations and heavily travelled paved and unpaved roads with old and new gasoline and diesel vehicles."

In the following sections, we respond to the specific comments about measurements and source profiles used in the CMB receptor model. Excerpts are taken from the comments; our responses are given after each comment.

Comment: The MCMA-2002 2003 field campaigns were extensive and collaborative scientific efforts to update and improve the emissions inventory, and to gain a better understating of the chemistry and transport processes driving atmospheric pollution in Mexico City (Molina et al., 2007)..... The Mexican Petroleum Institute (IMP) participated only in MCMA-2003 and not in both field campaigns, as the authors indicate in the manuscript. If the authors used VOC samples collected by IPM in 2002 outside MCMA-2002, they need to provide a different reference to (Velasco et al., 2007).

Response: As explained above, the MCMA-2002 data base was not used in this paper.

Comment: With regard to the 1997 samples, the authors provide an erroneous reference. Molina et al. (2007) present a summary of the VOC measurements made during the 2002 and 2003 field campaigns, but none of the 1997 VOC measurements, as the authors indicate in the section titled "1.1 Background".

Response: For clarification, two references were included, in addition to the article by Molina et al. (2007), which in fact provides an overview of the MCMA-2002/2003 Campaign and also refers to the 1997 IMADA Campaign (with several citations) as well as other earlier field studies conducted in Mexico City.

"The first part of this article presents the spatial and temporal analysis of the ambient concentrations of the most abundant NMHC which were measured during three field campaigns: 1997 (Edgerton et al., 1999), 2002 (Vega et al., 2004) and 2003 (Molina



ACPD
7, S6614–S6623, 2007





EGU

et al., 2007, Velasco et al., 2007) at several monitoring sites within the MCMA."

Comment: In the aforesaid articles the Chemical Mass Balance (CMB) receptor model version 8 was applied to the 1997 VOC data, as it was applied also to the 2002 and 2003 VOC data. Although the authors clearly indicate in the abstract that the 1997 measurements were used as input for the CMB model to determine the source contribution of VOCs, they do not present any results of those measurements, nor they describe the results presented previously by Mugica et al. (2002a, 2002b).

Response: The Abstract has been modified as follows: "The atmospheric concentrations of a variety of non-methane hydrocarbons (NMHC) collected at different sites within Mexico City Metropolitan Area (MCMA) during 1997, 2002 and 2003 field campaigns were compared. Additionally, the 2002 and 2003 data bases were used as an input for the Chemical Mass Balance (CMB) receptor model to determine the source contribution of NMHC to the atmosphere."

Comment: The authors indicate correctly that one of the basic assumptions made for the CMB receptor model is that the composition of source emissions and fuels are constant over the period of ambient and source sampling. However, the authors use motor-vehicle emission profiles that are not consistent with this assumption. In the article given by the authors as reference for the source emission profiles, Vega et al. (2000), they mention the vehicle emission profiles determined by Mugica et al. (1998) from a tunnel and parking garage studies conducted in 1996. They failed to consider that from 1996 to 2002 gasoline composition and vehicle technology suffered drastic changes. In 1996, 51percent of gasoline consumption in Mexico City corresponded to unleaded MAGNA gasoline, 48 percent to leaded NOVA and 1 percent to the recently introduced unleaded PREMIUM. In 2002, however, NOVA gasoline was no longer on the market, MAGNA represented 87 percent of the total consumption, and PREMIUM the remaining 13 percent. At the end of this document the fuel consumption in Mexico City is tabulated by type of gasoline in the period of time related to this study. Vega et al. (2000) also analyzed in 1996 the chemical composition of MAGNA and NOVA gaso-



ACPD

7, S6614–S6623, 2007

line as part of profile determination, but one must consider the possibility of change in the composition and quality of MAGNA gasoline during a 6 year period. Furthermore, there is no mention to the PREMIUM gasoline composition. It has been reported that the olefin and aromatic content in the MAGNA and PREMIUM gasoline is similar, and that the main differences are the octane number and sulfur content. However, the same IMP and the Mexican Petroleum Company (PEMEX) reported that the vehicle exhaust emission of toxic VOCs, such as benzene, 1,3-butadiene, formaldehyde and acetaldehyde is reduced 8considered the same emission profile for both, MAGNA and PREMIUM, they need to explain how these differences could modify the vehicle emission profiles used in this manuscript.

Response: The use of source profiles previously determined as input for the CMB model combined with 2002 and 2003 ambient data certainly may raised some questions about the validity of such profiles. The vehicular source profiles used in this study were determined from dozens of samples obtained in tunnels and cross-roads which ensured that emissions from thousands of vehicles were collected and also represented a real fleet in comparison to dynamometer measurements (Vega et al., 2000).

The references mentioned in the comment were not included as the source profiles reported were determined by our institution (IMP) and described in the other references cited in the article.

The source profiles for diesel and gasoline exhaust hydrocarbons were obtained in May-November 1997 (Vega et al. 2000). Between 1997 and 2002 changes occurred in both the vehicle fleet and in fuel composition, which introduce uncertainty in the source profile. As is discussed below, the changes in fuel composition should not have had a significant effect on the source profiles due to the fitting species used. However, the vehicle fleet change could have had a significant effect because of the increase in the proportion of gasoline fueled vehicles with improved emissions control equipment. Since vehicle emissions are important contributors to the hydrocarbon inventory, work to revise these profiles would be justified.



ACPD

7, S6614–S6623, 2007

When the assumption "composition of source emission are constant over the period of ambient and source sampling" it should be noted that there are no important changes in fuel composition (Magna) since that study took place. On the other hand, a new fuel (Premium) was introduced in 2002 but 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.

Moreover, the results from the chase mode studies using mobile lab are not comparable since Zavala et al. (2006) reported specific species using a different technique than the one used for ambient and source profile reported in this paper.

Finally, the Premium source profile is still not easy to determine because it is difficult to know which vehicles are using this fuel. On the other hand, if dynamometer or chase mode studies are conducted to determine the profile, this will not represent the real fleet and still the uncertainty will be high, as the use of Premium gasoline is not compulsory for a specific model of vehicle. 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.

Comment: The changes experienced in the vehicle fleet from 1996 to 2002 and 2003, were significant enough to modify the emission profiles. In 2002, 56 percent of the gasoline powered vehicles were 1993 models and older, fitted with catalytic converter systems and other antipollution devices, while in 1996, only 26diesel vehicles, in 1996 62002, and 27 percent were using EPA98 technology (SMAGDF, 2002; SMAGDF,



ACPD
7, S6614–S6623, 2007

2004). In addition to these changes in vehicle technology, the total fleet increased 27 percent from 1996 to 2002, going from 2,883,858 to 3,588,290 vehicles in a 6 year period. The conclusion that gasoline and diesel powered vehicles contribute 19.7 and 35.4 percnet respectively is difficult to understand, since in 2002 the diesel fleet represented only 4 percent of the total fleet, while the gasoline fleet 95 percent.This is not consistent with the emissions reported in the local emissions inventory (SMAGDF, 2004), where the gasoline fleet contributed 33 percent and the diesel 5 percent to the total VOC emissions.

Response: The high contribution of hydrocarbons from diesel vehicle exhaust to gasoline vehicle exhaust is indeed surprising. According to an article reviewing VOC source apportionment using chemical mass balance by Watson, Chow, and Fujita (2001), "Vehicle exhaust is invariably the major contributor (frequently more than 50 percent) to NMHC in urban/suburban areas. The gasoline exhaust contribution is typically four times the diesel exhaust contribution. Evaporated gasoline and liquid gasoline are the next most abundant contributors in most areas."

One of the applications of the source apportionment studies is to validate emission inventories. The fact that CMB results and Emission inventory (EI) estimates do not totally agree opens an opportunity to review the estimates of the EI, as CMB model is based on field measurements, although with source profiles from a few years earlier.

Another possible validation technique for vehicle exhaust in the emissions inventory would be to conduct remote sensing studies for both gasoline and diesel vehicles. The remote sensing results are expressed in grams of emissions per gallon of fuel. These could be multiplied by the gallons of diesel and gasoline fuel used in the area. The use of remote sensing results multiplied by fuel sales has been successfully demonstrated in a number of published studies. This technique would bypass the uncertainty associated with gasoline and diesel exhaust source profiles.

Comment: Moreover, there are further inconsistencies in the diesel and gasoline ap-



ACPD

7, S6614–S6623, 2007

portionments reported for the two-year period analyzed. While in 2002 gasoline contribution was higher than diesel, the opposite was true for 2003. These inconsistencies could be due to the uncertainties in the motor-vehicle emission profiles discussed above. In order to substantiate the results presented in this article, the authors need to demonstrate the validity of applying the CMB receptor model with motor-vehicle emissions profiles measured in 1996 to ambient samples collected 6 and 7 years later. Also, the authors need to explain why they did not use the vehicular emission characterization, which they carried out in 1998 (Mugica et al., 2001; Sanchez et al., 2001), nor the on-road vehicle exhaust measurements in chase mode carried out during the 2003 field campaign (Zavala et al., 2006) to update, in as much area as possible, the 1996 profiles used here.

Response: PTR-MS system was applied for measuring vehicle emissions during on-road chase measurements by Zavala et al. (2006). The species reported in this article are NOx, NOy, NH3, H2CO, CH3CHO, and other selected VOCs. Although some of the VOCs reported by Zavala et al. are indeed species used for source profile determination, their number is not enough for determining or even modifying our profiles, which are composed of 65 species indicating both concentration and uncertainty.

Comment: The final comment is about the application of a receptor model to samples collected early afternoon, when the photochemical activity is intense and the fresh emitted VOCs are efficiently oxidized as consequence of the high OH reactivity and strong solar radiation (Volkamer et al., 2005; Shirley et al., 2006). The authors need to explain how the model considers the photochemical loss on the VOC source contributions; otherwise their results from the early afternoon samples could be suspicious.

Response: As stated in the article, the main fitting species used for the CMB modelling were: propane, butane, i-butane, acetylene, pentane, hexane, toluene, xylenes, MTBE, 2,2,4-trimethylpentane, 2-methylpentane and 3-methylpentane, because they are usually above minimum detectable limits (MDLs) and also because they are tracers of specific emission sources. It is important to note that the CMB model, as a



ACPD
7, S6614–S6623, 2007





EGU

source apportionment technique, does not take into account the photochemistry. We are planning to include a photochemistry module on the CMB to improve the simulations.

Regarding the model results for early afternoon samples, the simulations generally gave higher contribution to LP gas emissions, such results agree with the ambient measurements which are characterized by higher concentrations of propane and i-butane during the early afternoon.

References:

Edgerton SA, Bian X, Doran JC, Fast JD, Hubbe JM, Malone EL, Shaw WJ, Whiteman CD, Zhong S, Arriaga JL, Ortíz E, Ruiz M, Sosa G, Vega E, Limón T, Guzmán F, Archuleta J, Bossert JE, Elliot SM, Lee JT, McNair LA, Chow JC, Watson JG, Coulter RL, Doskey PV, Gaffney JS, Marley NA, Neff W, Petty R. Particulate air pollution in Mexico City: A collaborative research project. J. Air Waste Manage. Assoc. 49: 1221-1229, 1999.

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.

Molina, L. T., Kolb, C. E., de Foy, B., Lamb, B. K., Brune, W. H., Jimeacute;nez, J. L., Ramos-Villegas,R., Sarmiento, J., Paramo-Figueroa, V. H., Cardenas, B., Gutierrez-Avedoy, V., and Molina, M.J.: Air quality in North America's most populous city: Overview of MCMA-2003 campaign, Atmos. Chem. Phys., 7, 2447-2473, 2007.

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.

Vega, R.E., Mugica, A.V., Diaz, G.L., Ramos, L.F. Estudio comparativo de perfiles de emisiones vehiculares en túnel y dinamómetro. Revista Internacional de Contami-



ACPD

7, S6614–S6623, 2007

nación Ambiental. 16, (2), 55-60, 2000.

Vega, E., Reyes, E., Ruiz, H., García, J., Sánchez, G., Martínez-Villa, G., González, U., Chow, J.C. and Watson J.G.: Analysis of PM2.5 and PM10 in Mexico City atmosphere during 2000-2002. J. Air Waste Manag. Assoc. 54, 786-798, 2004.

Velasco, E., Lamb, B., Westberg, H., Allwine, E., Sosa, G., Arriaga-Colina, J. L., Jobson, B. T., Alexander, M. L., Prazeller, P., Knighton, W. B., Rogers, T. M., Grutter, M., Herndon, S. C., Kolb, C. E., Zavala, M., de Foy, B., Volkamer, R., Molina, L. T., and Molina, M. J.: Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 2003 field campaigns, Atmos. Chem. Phys., 7, 329-353, 2007.

Watson,J.G., J.C. Chow and E.M. Fujita Review of volatile organic compound source apportionment by chemical mass balance, Atmos. Environ., 35, 1567-1584, 2001.

Zavala, M., Herndon, S. C., Slott, R. S., Dunlea, E. J., Marr, L. C., Shorter, J. H., Zahniser, M., Knighton, W. B., Rogers, T. M., Kolb, C. E., Molina, L. T., and Molina, M., J.: Characterization of on-road vehicle emissions in the Mexico City Metropolitan Area using a mobile laboratory in chase and fleet average measurement modes during the MCMA-2003 Field Campaign, Atmos. Chem. Phys., 6, 5129-5142, 2006.

---

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