Atmos. Chem. Phys. Discuss., 7, S6197–S6204, 2007
www.atmos-chem-phys-discuss.net/7/S6197/2007/

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. Velasco

he_velasco2003@yahoo.com

Received and published: 19 October 2007

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.

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). MCMA-2002 was an exploratory campaign performed in February 2002, in which the Laboratory for Atmospheric Research of Washington State University (WSU) collected 46 instantaneous whole air canister samples and analyzed them by Gas Chromatography separation and Flame Ionization Detection (GC-FID). 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). MCMA-2003 was an intensive five-week field study during April and May 2003, in which a wide array of VOC measurements were conducted in the Valley of Mexico, including locations in the urban core, in a heavily industrial area and at boundary sites in rural landscapes. A mobile-laboratory-based conditional sampling method was used also to collect samples dominated by fresh on-road vehicle exhaust. In addition to the whole air canister samples with GC-FID, online ionization using Proton Transfer Reaction Mass Spectroscopy (PTR-MS), continuous real-time detection of olefins using a Fast Isoprene Sensor (FIS), long path measurements using UV Differential Optical Absorption Spectroscopy (DOAS) and Fourier Transform Infrared Spectroscopy (FTIR) were used during MCMA-2003. A detailed description of these measurements is provided in Velasco et al. (2007), as well as a detailed and visual description of the position of the monitored sites in Table 1 and Fig. 1, respectively, in the same article. In 2003, WSU collected and analyzed 133 canister samples and IMP collected 51. IMP collected 3-hour samples during two periods, 6-9 and 12-15 h, at four sites: Pedregal, La Merced, CENICA and Xalostoc, while WSU col-

ACPD

7, S6197–S6204, 2007

lected samples at 5 sites: Pedregal, La Merced, CENICA, La Reforma and Santa Ana Tlacotenco in periods of 30 min, 1 and 3 hours during the morning and early afternoon.

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". In February and March 1997 the IMADA project was carried out by the IMP and the U.S. Department of Energy (Doran et al., 1998). If the 1997 VOC data used for this work correspond to measurements made as part of the IMADA project, the authors need to indicate it. The same IMP group has reported VOC measurements made in March 1997 in previous articles (Mugica et al., 2003; Mugica et al., 2002a, 2002b), which we believe are the same presented in this manuscript. However, the authors do not make any reference to those articles. 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).

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, 51% of gasoline consumption in Mexico City corresponded to unleaded MAGNA gasoline, 48% to leaded NOVA and 1% to the recently introduced unleaded PREMIUM.

ACPD

7, S6197–S6204, 2007

In 2002, however, NOVA gasoline was no longer on the market, MAGNA represented 87% of the total consumption, and PREMIUM the remaining 13%. 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 gasoline 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 18% with the use of PREMIUM gasoline, instead of MAGNA (Schifter et al., 1999). If the authors considered 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.

The changes experienced in the vehicle fleet from 1996 to 2002 and 2003, were significant enough to modify the emission profiles. In 2002, 56% of the gasoline powered vehicles were 1993 models and older, fitted with catalytic converter systems and other antipollution devices, while in 1996, only 26% had catalytic converters. In regard to diesel vehicles, in 1996 6% were using EPA94 technology. This increased to 13% in 2002, and 27% were using EPA98 technology (SMAGDF, 2002; SMAGDF, 2004). In addition to these changes in vehicle technology, the total fleet increased 27% 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% respectively is difficult to understand, since in 2002 the diesel fleet represented only 4% of the total fleet, while the gasoline fleet 95%. This is not consistent with the emissions reported in the local emissions inventory (SMAGDF, 2004), where the gasoline

ACPD
7, S6197–S6204, 2007

EGU

fleet contributed 33% and the diesel 5% to the total VOC emissions. Moreover, there are further inconsistencies in the diesel and gasoline apportionments 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.

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.

Gasoline consumption in Mexico City measured in daily barrels (Information provided by the "Centro Mario Molina para Estudios Estrategicos sobre Energía y Medio Ambiente, A.C.". Source: PEMEX-Refinación

MAGNA: 55,105 (1996); 92,778 (1997); 101,934 (2002); 100,808 (2003)

NOVA: 52,387 (1996); 14,082 (1997); — (2002); — (2003)

PREMIUM: 86 (1996); 3,314 (1997); 14,953 (2002); 16,760 (2003)

References

ACPD

7, S6197–S6204, 2007

Doran, J. C., Abbott, S., Archuleta, J., Bian, X., Chow, J., et al.: The IMADA-AVER boundary layer experiment in the Mexico City area, Bull. Amer. Meteorol. Soc., 79, 2497-2508, 1998.

Molina, L. T., Kolb, C. E., de Foy, B., Lamb B. K., Brune, W. H., Jiménez, 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 the MCMA-2003 campaign, Atmos. Chem. Phys, 7, 2447-2473, 2007.

Mugica, V., Ruiz, M. E., Watson, J., and Chow, J.: Volatile aromatic compounds in Mexico City atmosphere: levels and source apportionment, Atmosfera, 16, 15-27, 2003.

Mugica, V., Vega, E., Ruiz, H., Sanchez, G., Reyes, E., and Cervantes, A.: Photochemical reactivity and sources of individual VOCs in Mexico City, in: Air pollution X, edited by: Brebbia, C. A. and Martin-Duque, J. F., WIT Press, UK, 2002a.

Mugica, V., Watson, J., Vega, E., Reyes, E., Ruiz, M. E., and Chow, J.: Receptor model source apportionment of nonmethane hydrocarbons in Mexico City, The Scientific World Journal, 2, 844-860, 2002b.

Mugica, V., Vega, E., Sanchez, G., Reyes, E., Arriaga, J. L., Chow, J., Watson, J., and Arriaga, J. L.: Volatile organic compounds emissions from gasoline and diesel powered vehicle, Atmosfera 14, 29-37, 2001.

Mugica, V., Vega, E., Arriaga, J. L., and Ruiz, M. E.: Determination of motor vehicle profiles for non-methane organic compounds in the Mexico City Metropolitan Area, J. Air & Waste Manage. Assoc., 48, 1060-1068, 1998.

Sanchez, G., Vega, E., Reyes, E. Mugica, V., Chow, J., Watson, J., and Arriaga, J. L.: Importance of Determining Volatile Organic Compounds Source Profiles to Diminish Ozone Concentrations in Mexico City Metropolitan Area, 94TH Annual Conference and exhibition of the Air and Waste Management Association, Orlando, Florida, 2001.

Schifter, I., Díaz, L., and Guzman, E.: La tecnología en los vehículos y las

ACPD

7, S6197–S6204, 2007

gasolinas PEMEX Magna y PEMEX Premium, Octanaje 25, 1999. Available at: http://www.ref.pemex.com/octanaje/octxe25.htm

Shirley, T. R., Brune, W. H., Ren, X., Mao, J., Cardenas, B., Volkamer, R., Molina, L. T., Molina, M. J., Lamb, B., Velasco, E., Jobson, T., and Alexander, M.: Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003, Atmos. Chem. Phys. 6, 2753-2765, 2006.

SMAGDF: Inventario de Emisiones a la Atmósfera, Zona Metropolitana del Valle de México 2000, Dirección General de Gestión Ambiental del Aire, México D. F., 2002.

SMAGDF: Inventario de Emisiones de la Zona Metropolitana del Valle de México 2002, Dirección General de Gestión Ambiental del Aire, México D. F., 2004.

Vega, E., Mugica, V., Carmona, R., and Valencia, E.: Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model, Atmos. Environ, 34, 4121-4129, 2000.

Velasco, E., Lamb, B., Westeberg, H., Allwine, E., Sosa, G., Arriaga-Colina, J. L., Jonson, 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.

Volkamer, R., Molina, L. T., Molina, M. J., Shirley, T., and Brune, W. H.: DOAS measurement of glyoxal as an indicator for fast VOC chemistry in urban air, Geophys. Res. Lett., 32, L08806, doi:10.1029/2005GL022616, 2005.

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

ACPD

7, S6197–S6204, 2007

MCMA-2003 Field Campaign, Atmos. Chem. Phys., 6, 5129-5142, 2006.

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