Atmos. Chem. Phys. Discuss., 10, 3319–3346, 2010
www.atmos-chem-phys-discuss.net/10/3319/2010/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Measurements and receptor modeling of volatile organic compounds in south-eastern Mexico City, 2000–2007

H. Wöhrnschimmel[1,2], M. Magaña[1], W. A. Stahel[3], S. Blanco[1], S. Acuña[4], J. M. Pérez[1], S. González[1], V. Gutiérrez[1], S. Wakamatsu[5], and B. Cárdenas[1]

[1]Instituto Nacional de Ecología, Mexico City, Mexico
[2]Institute for Chemical and Bioengineering, ETH Zurich, Switzerland
[3]Seminar for Statistics, ETH Zurich, Switzerland
[4]Instituto Politécnico Nacional, Mexico City, Mexico
[5]Ehime University, Matsuyama, Japan

Received: 19 January 2010 – Accepted: 21 January 2010 – Published: 8 February 2010

Correspondence to: H. Wöhrnschimmel (henry.woehrnschimmel@chem.ethz.ch)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Ambient samples of volatile organic compounds (VOCs) were measured between 2000 and 2007 in south-eastern Mexico City, quantifying 13 species (ethane, propane, propylene, butane, acetylene, pentane, hexane, heptane, benzene, octane, toluene, nonane, o-xylene). These time series were analyzed for long-term trends, using linear regression models. A main finding was that the concentrations for several of the quantified VOC species were decreasing during this period. A receptor model was applied to identify possible VOC sources, as well as temporal patterns in their respective activities. Domestic use of liquefied petroleum gas and vehicle exhaust are suggested to be the principal emission sources, contributing together between 70% and 80% to total VOC. Both diurnal and seasonal patterns, as well as a weekend effect were recognized in the modelled source activities. Furthermore, vehicle exhaust emissions showed a decreasing trend over time, with a reduction of about 8% per year.

1 Introduction

1.1 The air pollution problem in Mexico City

The Mexico City Metropolitan Area (MCMA) is an example of the rapidly expanding Megacities in developing countries. Its population has grown from 1.6 million in 1940 and 13.3 million in 1980, to approximately 18.1 million in 2005 (Anzaldo and Barrón, 2009). Along with the number of inhabitants, the air pollution problem has also increased. Athough control measures over the last decade have led to decreasing trends in some air pollutants, both suspended particles and ozone still frequently exceed the national standards in many regions of the MCMA. Sulfur dioxide (SO_2) has also become a local problem in the northern parts of the City (SMA, 2007; De Foy et al., 2007).

ACPD

10, 3319–3346, 2010

Volatile Organic Compounds (VOCs) are a crucial determinant of air quality in Mexico City. Together with nitrogen oxides (NO_x) they are responsible for the formation of ozone, which peaks over 200 ppb within the MCMA, and exceeds the national air quality standard (110 ppb for 1-h average), on over half of the days of a year (SMA, 2007). Ozone is thought to cause restricted activity days, and has even been identified as a likely contributor to mortality (Evans et al., 2002). In addition, some VOCs are air toxics, such as benzene and toluene, among others. Benzene has been recognized as a human carcinogen (WHO, 2000), and air quality standards have been established for this compound in several countries. For example, the European Community has set a limit of 5 µg/m^3 (9.4 ppbC) as an annual mean in order to protect public health (EC, 2000), while Japan set its air quality standard to 3 µg/m^3 (5.6 ppbC, Japanese Ministry of Environment, 1997).

1.2 Previous VOC measurements

Although VOCs are not yet routinely measured by the Mexico City air quality monitoring network, they have been addressed in several measurement campaigns carried out in Mexico City. One of the longest time series has been determined at three sites over 9 years (1992–2001), measuring 55 VOCs in the morning hours, and in selected months of the year. A decreasing trend has been reported for one of the sites, Xalostoc, an industrial site in north-eastern Mexico City. Two other sites, Merced, in the city center with prevailing vehicle emissions, and Pedregal, an affluent residential area in southern Mexico City, did not show any trends. It is thought that VOC concentrations did not increase – in spite of an augmenting vehicle fleet – due to better fuel efficiency and cleaner vehicle technology (Arriaga et al., 2004).

The composition of VOCs has been characterized in some of the studies, finding that alkanes contribute most to the total VOCs (54–60%), followed by aromatics (15–26%) and alkenes (5–18%) (INE/SMA/UAM, 2006; Apel et al., 2009; Velasco et al., 2007; and references therein). From these groups, aromatics and alkenes are especially important for ozone formation due to their high reactivity, in spite of their lower con-

centration in ambient air. Also formaldehyde and other oxygenated VOCs have been determined in specific campaigns (Grutter et al., 2005; Volkamer et al., 2005; Apel et al., 2009; Fortner et al., 2009).

In the context of ozone formation, VOC vs. NO_x sensitivity of the Mexico City air has been discussed as a crucial parameter (Molina et al., 2002) and was subject of several recent studies (Lei et al., 2007, 2008; Tie et al., 2007; Song et al., 2009). Chemical transport model simulations indicated that ozone formation was VOC limited during the MCMA-2003 campaign (Lei et al., 2007, 2008). Sensitivity analyses of ozone production to precursor emissions under different meteorological conditions during the MCMA-2006/MILAGRO campaign demonstrate that the MCMA urban core region is VOC-limited for all meteorological episodes, while the surrounding areas with relatively low-NO_x emissions can be either NO_x- or VOC-limited regime depending on the episode (Song et al., 2009). The analysis of the weekend effect by Stephens et al. (2008) also provided direct empirical evidence for VOC limitation. These results suggest that the controls on VOC emissions would be a more effective way to reduce ozone levels in the urban area, which is consistent with previous results from the MCMA-2003 campaign (Lei et al., 2007, 2008). However, the degree of VOC-limitation increased for MCMA-2006 due to reduced VOC/NO_x ratio and VOC reactivity in the estimated emissions. Furthermore, meteorological conditions led to large variations in regime for the relatively low-NO_x emitting area, implying that emission controls would depend on location and meteorology (Song et al., 2009).

As part of VOC reactivity, the contribution of compounds associated to liquefied petroleum gas (LPG) has been an issue of debate. Although they have low reactivity, they are emitted in huge amounts, so their contribution has been discussed in several works. The conclusions range from a relatively small effect (Gasca et al., 2004; Jaimes-López et al., 2003; Gamas et al., 2000) to a significant contribution (Blake and Rowland, 1995; Wöhrnschimmel et al., 2006), depending on where in the MCMA the experimental data were obtained, and on the methodological approach.

The debate about LPG's contribution to total VOC concentrations and ozone formation leads almost instantly to the question of other VOC sources' contribution to the total VOC burden. Source apportionment studies have been carried out in the MCMA (Mugica et al., 2002; Sosa et al., 2008; Wöhrnschimmel et al., 2006) using source profiles measured in Mexico City (Mugica et al., 2002; Zavala et al., 2006). The general finding was that vehicle exhaust and the domestic use of LPG are the principal sources, along with the use of solvents.

These findings, however, are in contrast with the most recent official emission inventory, where mobile sources (gasoline- and diesel-powered) are estimated to contribute 34% to the total VOC burden, whereas leaking and unburnt LPG only contributes about 11% (SMA, 2008). Several studies suggest that this and previous inventories underestimate VOC emissions by a factor or 2 or 3, or that at least alkanes, aromatics and aldehydes are underestimated (West et al., 2004; Arriaga et al., 2004; Lei et al, 2007; 2008; Zavala et al., 2009). Flux measurements at fixed urban sites within the MCMA conclude that the emission inventory actually overestimates the emissions of aromatic VOC species (Velasco et al., 2005; Velasco et al., 2009).

Finally, the toxicity of some VOC species has been addressed in particular by measurements of benzene and toluene. Bravo et al. (2002) report benzene concentrations from grab samples at a condominium and a university campus site of 18.7 and 22.0 ppbC, respectively, which is two times higher than the EC limit value. The authors suggest that an air quality standard for benzene is needed in Mexico, followed by control strategies like assuring proper functioning of catalytic converters and vapor recovery systems at gas stations.

1.3 Objective of this study

The present study provides a unique updated time series of VOC measurements between 2000 and 2007 at one site in southeastern Mexico City. It not only continues previous measurements, but also covers different seasons of the year and times of the day. The specific objectives of this paper are to analyze the trends in VOC con-

centrations applying regression analysis, and assess the importance of potential VOC sources over time using a receptor model.

2 Methods

2.1 Sampling and analytical procedure

VOC grab samples were taken during a 7-year period from July 2000 to June 2007 at different times of the day at the Mexican National Center for Environmental Research and Training (CENICA). This site is located in south-eastern Mexico City, in a low-income residential area with some small industries and mechanical workshops (coordinates: 19°21′29″ N, 99°04′19″ W, 2240 m above mean sea level). The sample inlet was located on the CENICA rooftop at a height of 12.7 m above ground level. A stainless steel line transferred the air sample to a concentrator, then to a gas chromatograph with flame ionization detector (GC-FID, Hewlett-Packard 6890 Series plus) coupled to a concentrator, where the following 13 species were quantified: ethane, propane, propylene, butane, acetylene, pentane, hexane, heptane, benzene, octane, toluene, nonane and o-xylene. More details on the measurements and analytical procedure are given in Bravo et al. (2002).

The sum of the 13 quantified compounds (from now on denoted as Σ_{13}VOC) makes up a major part of all VOC species in the Mexico City air. Compared with other measurements of 55 VOC species at the same sampling site (INE/SMA/UAM, 2006), Σ_{13}VOC constituted an average fraction of 50% when concentrations are expressed as ppbC (such fractions will from now on be denoted as ppbC %).

2.2 Data analysis

Descriptive statistics and graphical data analysis, as well as the regression and receptor modeling described in the following subsections, were carried out with the the statistical package R version 2.10.0 (R Development Core Team, 2009).

2.2.1 Regression model

Regression models were fitted to VOC data, in order to estimate the long-term trend of the different species. As explanatory variables for the linear regression models we used time and month, as shown in Eq. (1):

$$\log(C_j) = \alpha_j + \beta_j * t + \gamma_{j,m} + \varepsilon_j \quad (1)$$

where C_j are the monthly average concentrations of VOC species j (in ppbC), t is the time in years since 2000, γ_m is the effect of month m that is introduced to improve the precision of the results, and ε is the error term, modeled as an autoregressive time series of order 5. α is the intercept of the regression equation, whereas the trend is given by β and translates to a yearly rate of change by the formula $e^{\beta}-1$. The assumption of linearity was verified by testing the significance of a quadratic term $\beta_2 * t^2$, which turned out to be insignificant in most cases.

Since trends might vary for different times of the day, an analysis with the hour of the day and its interaction with time included in the model was also performed.

More models were tested that are not shown here, using hourly measurements instead of monthly averages, and including the temperature, the wind speed, and the daily and weekly cycle as explanatory variables. This led to rather complex models giving information about the dependence of the VOC concentrations on meteorology and cyclic patterns. However, no additional benefit was gained for the interpretation of the long-term trends, so these results will be reported elsewhere.

2.2.2 Receptor model

A Chemical Mass Balance (CMB) model was used to analyze the activity of different potential emission sources. The CMB model correlates previously determined source profiles to measured receptor concentrations, solving the multiple regression equation

$$\mathbf{C}_t = \mathbf{F} \times \mathbf{S}_t + \varepsilon_t \quad (2)$$

where $\mathbf{C}_t$ is the vector of the VOC species' concentrations quantified in one sample taken at time t, $\mathbf{F}$ is the source profile matrix, $\mathbf{S}_t$ is the source activity vector, and ε_t is the error vector. The source profile matrix $\mathbf{F}$ is composed of previously measured source profile vectors, with each vector describing the relative contents of VOC species (in ppbC %) from the respective source. The source activity vector, which is the unknown of this equation, is the absolute contribution of each source to the total measured ambient VOC concentrations (in ppbC). For each observation, this multiple linear regression problem is solved for $\mathbf{S}_t$ by minimizing the sum of squares of the error vector.

Some essential assumptions of the CMB model are that the source profiles are constant in time, that there is negligible chemical transformation during the transport from the emission source to the receptor site, and that no unknown emission source contributes significantly to the concentrations at the receptor site.

The above described CMB algorithm, which is also used in US-EPA's CMB8 model (US-EPA, 2001) has been implemented in *R*, together with a criteria based algorithm to select the ideal combination of sources and species. This step makes it possible to automatically analyze large data sets, and avoids the need to combine sources and species for each sample in a process of trial and error.

The emission profiles used in our analysis covered emissions related to LPG usage (like evaporative losses or LPG that remains unburnt during incomplete combustion), vehicle exhaust (EXHAUST), vaporized hot soak from the heat of motor engines (HOTSOAK), solvent use (SOLVENT), and emissions from food preparations (FOOD). For each category, between 1 and 4 different profiles were used. Most of them were measured in Mexico City between 1996 and 1998 (Vega et al., 2000; Mugica et al., 2002). Also some newer profiles for vehicle exhaust that were determined during 2008 in a tunnel study in the city of Guanajuato, Mexico (INE, personal communication), were included in the EXHAUST category, in order to account for recent changes in the vehicle technology and fuel characteristics. These source profiles are provided in the supplementary information (http://www.atmos-chem-phys-discuss.net/10/3319/

2010/acpd-10-3319-2010-supplement.pdf).

The resulting model fits were evaluated by means of the model performance parameters R^2, the reduced χ^2 (the weighted sum of squares of the differences between the calculated and measured fitting species concentrations), as well as the ratio of modeled to measured mass. A model fit was considered acceptable when its R^2 >0.8, χ^2 <3, and the proportion of modeled to measured mass was between 80% and 120%. For the final results, only model fits that complied with the above criteria were selected, which made up about 78% of all model fits. Also, the data were grouped into night averages (all samples from 01:00 to 04:00 for each day without missing observations in this time window), morning averages (06:00 to 09:00), and evening averages (18:00 to 21:00).

The results of the CMB model were used to describe the relative importance of the potential sources, and to identify temporal patterns in absolute source activities. Long-term trends were examined in analogy to the regression analysis for individual VOCs.

3 Results and discussion

3.1 VOC concentrations

In Table 1, descriptive statistics are given for each of the quantified VOCs for the whole measurement period from 2000 to 2007. The relative composition for all data and during selected time intervals is shown in Fig. 1. It becomes clear that propane and butane constitute the major components of the VOC mixture at all times of the day, with mean concentrations of 241.5 ppbC and 108.6 ppbC, respectively, followed by toluene, with 70.3 ppbC. The average annual benzene concentration of 7.9 ppbC is close to the European limit value of 9.4 ppbC. These results are similar to previous measurements carried out at different sites of the MCMA (INE/SMA/UAM, 2006; Velasco et al., 2007; Apel et al., 2009). In particular, there is very good agreement with 24-h samples taken at the same site during 2005 and 2006 (INE/SMA/UAM, 2006).

In Fig. 2, time series of all samples from 2000 to 2007, as well as monthly mean concentrations, are shown for Σ_{13}VOC, benzene and toluene. Although there is a huge variability in the data, spanning several orders of magnitude, a cyclic annual pattern can be inferred, and will be discussed later in this section. Longer gaps in the data exist in 2002 for reasons of maintenance of the GC-FID, and in 2006, when the analytical method was certified. Figure 3 shows the diurnal cycle of Σ_{13}VOC, benzene and toluene. Highest concentrations appear between 06:00 and 09:00 and to a lesser extent after 21:00. The average benzene peak reaches 10 ppbC in the morning, with high concentrations over several hours. These peaks can also be observed in the other quantified species (provided in the supplementary information http://www.atmos-chem-phys-discuss.net/10/3319/2010/acpd-10-3319-2010-supplement.pdf), indicating a general pattern of increased emission related activities in the morning and in the evening, like the traffic rush hours and domestic water heating. In addition, the reduced vertical mixing of the atmosphere at these times contributes to increased concentrations. Solvent related compounds (like hexane, but also toluene) show less pronounced peaks, since their emissions are more uniformly distributed along the day, with higher evaporation around midday. These general characteristics of the diurnal VOC cycles have been measured also at different urban sites during the MCMA-2003 and MILAGRO-2006 campaigns (Velasco et al., 2007; Fortner et al., 2009).

Linear regression models were applied to determine possible long-term trends of ambient VOC concentrations, according to Eq. (1). The resulting regression parameters, together with their standard errors and significance are shown in Table 2, and the modeled curves are added to Fig. 2. Over the 7-years measurement period, several species showed significant negative trends, namely butane, acetylene, hexane, nonane and oxylene. Other species had negative regression coefficients, although they were not significant. For example, toluene decreased by about 7.4% annually (p=0.052), whereas benzene showed no trend. These results compare to Arriaga et al. (2004), who found significantly decreasing concentrations of total VOC (defined as the sum

of 55 measured species) between 1992 and 2001 at one out of three sampling sites, whereas at the other two sites no significant change was evident.

The modeled curves in Fig. 2 also indicate the cyclic annual pattern of VOC concentrations: highest concentrations occur between November and February, which in Mexico City corresponds to the dry-cold season, characterized by thermal inversions and high pressure systems. During the dry-warm season (March to May) and the rainy season (June to October), concentrations are lower. This tendency is the same for most of the other quantified species.

Trends have been analyzed also in function of the time of the day. The results are added to Fig. 3, showing the modeled average concentration for each hour for mid 2000 and mid 2007, respectively. Reductions did not occur homogeneously over the day or for each VOC species in the same way. For toluene, the largest reductions were around noon, whereas its decrease during the morning hours was not significant. Similar figures for all species are given in the supplementary information (http://www.atmos-chem-phys-discuss.net/10/3319/2010/acpd-10-3319-2010-supplement.pdf).

3.2 Source apportionment

Table 3 provides information on the receptor model fits that complied with the criteria of satisfactory model performance. The number of acceptable model fits was sufficient to derive a representative image of source activities over the 7 years period.

Figure 4 illustrates the modelled importance of different emission sources in terms of their relative contribution to the measured VOC concentrations at different times of the day. It becomes clear that LPG and vehicle exhaust are the principal sources. At night, LPG is dominant with a median contribution of 68 %, whereas vehicle exhaust adds just 12% to the total VOC concentration. During the day, the relative contribution of LPG decreases, down to a median share of 42% in the evening, whereas vehicle exhaust becomes more important, increasing up to 28%. Solvent use, food preparation and hot soak emissions contribute together between 12% and 25% to the quantified species during the course of the day. These findings confirm previous receptor mod-

elling studies in the MCMA, which have identified LPG and vehicle exhaust as the dominant sources: Sosa et al. (2008) report an LPG and vehicle exhaust contribution of 52% and 25%, respectively, at a University campus site. Mugica et al. (2002) find vehicle exhaust contribution to be higher than LPG at three sites (industrial, commercial and high-income neighbourhood, respectively), which shows that source activities within the MCMA are not spatially homogeneous. The latest emission inventory (SMA, 2008) takes this fact into consideration, presenting gridded emissions over the MCMA area. However, this emission inventory still fails to recognize the high contribution of LPG to total VOC concentrations.

In Fig. 5 the inter-annual variations of absolute source activities of LPG and vehicle exhaust are shown. The modelled trend according to the regressions analysis is also added, and the corresponding numerical results are given in Table 4, along with results for the other sources.

There was a significant trend for both LPG and vehicle exhaust, with annual decrease rates of 5.4% and 8.1%, respectively. The recent literature confirms such a trend for vehicle emissions: Zavala et al. (2009) report measurements of on-road emission factors in 2003 and 2006, where for cruising conditions and selected aldehydes and aromatics an average decrease between 25% and 58% was found over the three years span. For stop-and-go conditions and heavy traffic, the reductions were found to be smaller.

Also an intra-annual cycle is evident from the linear model curve in Fig. 5, with higher absolute source contributions during the dry-cold season. This is in analogy to the higher VOC concentrations observed at this time of the year (Fig. 2). LPG contribution is about 70% higher from November to February than in the period from July to October; vehicle exhaust is about 37% higher (for both comparisons $p \leq 0.01$; paired Wilcoxon signed ranked test on monthly averaged source activities). If we assume, as a first approximation, that LPG increases due to both the reduced mixing layer height and higher LPG usage for heating purposes, whereas vehicle exhaust increases only due to meteorological effects, we can estimate that during the dry-cold season the usage of LPG increases by about 24%. This can be compared to national sales data

for LPG (SENER, 2009), which over the last decade have been about 15% higher in the months from September to January than in the 4 previous months. The difference might be explained by the fact that the national sales numbers include regions where due to the climate conditions no or just little extra demand for LPG is expected in the colder season.

Finally, also a weekend effect becomes evident in the vehicle exhaust activity: during the morning hours, we find less vehicle exhaust emissions on Saturdays and Sundays in comparison with working days, by about 17% and 35%, respectively (for both comparisons $p < 0.001$; paired Wilcoxon signed ranked test, using averaged source activities from Monday to Friday of each week). Velasco et al. (2009) report similar values for weekend decreases in alkene and C_2-benzene fluxes. The reason is that for most people economic activities and related vehicle use start later in the day or are suspended on weekends. During the night hours from 01:00 to 04:00, however, vehicle exhaust activity is higher on Saturdays ($p < 0.05$) and Sundays ($p < 0.001$), by about 40% and 41%, respectively. This effect has been observed also for VOC fluxes (Velasco et al., 2009) and criteria air pollutants (Stephens et al., 2008) in Mexico City and it has been described as the "party-effect", since higher vehicle emissions derive from abundant social and economic activities during Friday and Saturday nights.

4 Conclusions

In this paper, a time series of 7 years of VOC measurements in ambient air in Mexico City has been analyzed. The average composition of the 13 quantified VOC species was in agreement with previous measurements, and indicated a strong presence of emissions from vehicle exhaust and LPG. A receptor model used for source apportionment formally showed that these two sources are the dominant ones, with LPG having a higher source activity at all times of the day. Trend analyses indicated a significant decrease in some of the VOC species, which correspond to a reduction of 5.4% and 8.1% annually for LPG and vehicle exhaust, respectively. The receptor model was also

ACPD
10, 3319–3346, 2010

able to detect seasonal and weekend effects in the modelled source activities.

These results confirm a positive effect of the efforts that have been placed into improving vehicle technology and fuel quality in Mexico City, as well as a stricter exhaust monitoring program. Nevertheless, neither benzene nor total VOC decreased significantly, which implies that additional measures are necessary to head towards a healthier environment for Mexico City's inhabitants. This is true especially in the context of a growing demand for private mobility and a developing market for low-cost vehicles. Among other strategies, the public transport needs to be further developed in quality and coverage. Regarding the still high emissions of LPG, we encourage a maintenance program for domestic equipment.

Further research is also necessary in order to detect future potential changes in the observed trends, and provide new input for developing air quality management strategies. Measurements at the CENICA site should be continued, and also the establishment of additional long-term monitoring sites would be desirable. A re-analysis of the data presented by Arriaga et al. (2004), where trends have been discussed only on a basis of the total concentration of 55 VOC species, could give additional insight into how measures implemented in the past affected the concentrations of different VOC species. Finally, the results of the source apportionment presented in this paper provide an opportunity to revise and improve the official emission inventory of the MCMA.

Acknowledgements. The authors acknowledge Emma Bueno for the continuous operation of the gas chromatograph. Toshiyuki Tanaka from Teikyo University of Science and Technology gave essential advice in the part of VOC analytics. Furthermore, we thank Luisa Molina, Matthew MacLeod and Sasha Madronich for their valuable comments on the manuscript.

References

Apel, E. C., Emmons, L. K., Karl, T., Flocke, F., Hills, A. J., Madronich, S., Lee-Taylor, J., Fried, A., Weibring, P., Walega, J., Richter, D., Tie, X., Mauldin, L., Campos, T., Sive, B.,

Kleinman, L., Springston, S., Zaveri, R., Ortega, J., Voss, P., Blake, D., Baker, A., Warneke, C., Welsh-Bon, D., de Gouw, J., Zheng, J., Zhang, R., Rudolph, J., Junkermann, W., and Riemer, D. D.: Chemical evolution of volatile organic compounds in the outflow of the Mexico City Metropolitan area, Atmos. Chem. Phys. Discuss., 9, 24085–24143, 2009, http://www.atmos-chem-phys-discuss.net/9/24085/2009/.

Anzaldo, C. and Barrón, E. A.: La transicin urbana de México, 1900–2005, in: Consejo Nacional de Población: La situación demográfica de México, http://www.conapo.gob.mx/publicaciones/sdm/sdm2009/04.pdf, 2009.

Arriaga-Colina, J. L., West, J. J., Sosa, G., Escalona, S. S., Ordúñez, R. M., and Cervantes, A. D. M.: Measurements of VOCs in Mexico City (1992–2001) and evaluation of VOCs and CO in the emissions inventory, Atmos. Environ., 38, 2523–2533, 2004.

Blake, D. R. and Rowland, S. F.: Urban leakage of liquefied petroleum gas and its impact on Mexico City Air Quality, Science, 269, 953–956, 1995.

Bravo, H., Sosa, R., Sánchez, P., Bueno, E., and González, L.: Concentrations of benzene and toluene in the atmosphere of the southwestern area at the Mexico City Metropolitan Zone, Atmos. Environ., 36, 3843–3849, 2002.

de Foy, B., Lei, W., Zavala, M., Volkamer, R., Samuelsson, J., Mellqvist, J., Galle, B., Martínez, A.-P., Grutter, M., Retama, A., and Molina, L. T.: Modelling constraints on the emission inventory and on vertical dispersion for CO and SO_2 in the Mexico City Metropolitan Area using Solar FTIR and zenith sky UV spectroscopy, Atmos. Chem. Phys., 7, 781–801, 2007, http://www.atmos-chem-phys.net/7/781/2007/.

EC: Directive 2000/69/EC of the European Parliament and of the Council Relating to Limit Values for Benzene and Carbon MoNO_xide in Ambient Air. European Community, Official Journal of the European Communities, 2000.

Evans, J., Levy, J., Hammit, J., Santos Burgoa, C., and Castillejos, M.: Health benefits of air pollution control. In: Molina, M. J., and Molina, L. T.: Air Quality in the Mexico Megacity - An Integrated Assessment. Kluwer Academic Publishers, Dordrecht/Boston/London, 2002.

Fortner, E. C., Zheng, J., Zhang, R., Berk Knighton, W., Volkamer, R. M., Sheehy, P., Molina, L., and André, M.: Measurements of Volatile Organic Compounds Using Proton Transfer Reaction – Mass Spectrometry during the MILAGRO 2006 Campaign, Atmos. Chem. Phys., 9, 467–481, 2009, http://www.atmos-chem-phys.net/9/467/2009/.

Gamas, E. D., Magdaleno, M., Díaz, L., Schifter, I., Ontiveros, L., and Álvarez-Cansino, G.:

Contribution of Liquefied Petroleum Gas to Air Pollution in the Metropolitan Area of Mexico City, J. Air Waste Manage., 50, 188–198, 2000.
Gasca, J., Ortiz, E., Castillo, H., Jaimes, J. L., and González, U.: The impact of liquefied petroleum gas usage on air quality in Mexico City, Atmos. Environ., 38, 3517–3527, 2004.
Grutter, M., Flores, E., Andraca-Azala, G., and Báez, A.: Formaldehyde levels in downtown Mexico City during 2003, Atmos. Environ., 39, 1027–1034, 2005.
INE/SMA/UAM: Monitoreo y Evaluación de las Concentraciones de Compuestos Orgánicos Volátiles en la Zona Metropolitana de la Ciudad de México. Informe final. Instituto Nacional de Ecología, Secretaría de Medio Ambiente del Gobierno del Distrito Federal, Universidad Autónoma Metropolitana, Mexico City, 2006.
Jaimes-López, J. L., Sandoval-Fernández, J., González-Macías, U., and González-Ortiz, E.: Liquefied petroleum gas effect on ozone formation in Mexico City, Atmos. Environ., 37, 2327–2335, 2003.
Japanese Ministry of Environment: Environmental Quality Standards for Benzene, Trichloroethylene, Tetrachloroethylene and Dichloromethane, Notification on February 4th, 1997, Website: www.env.go.jp/en/air/aq/aq.html.
Karl, T., Apel, E., Hodzic, A., Riemer, D. D., Blake, D. R., and Wiedinmyer, C.: Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity, Atmos. Chem. Phys., 9, 271–285, 2009, http://www.atmos-chem-phys.net/9/271/2009/.
Lei, W., de Foy, B., Zavala, M., Volkamer, R., and Molina, L. T.: Characterizing ozone production in the Mexico City Metropolitan Area: a case study using a chemical transport model, Atmos. Chem. Phys., 7, 1347–1366, 2007, http://www.atmos-chem-phys.net/7/1347/2007/.
Lei, W., Zavala, M., de Foy, B., Volkamer, R., and Molina, L. T.: Characterizing ozone production and response under different meteorological conditions in Mexico City, Atmos. Chem. Phys., 8, 7571—7581, 2008, http://www.atmos-chem-phys.net/8/7571/2008/.
Molina, M. J., Molina, L. T., West, J., Sosa, G., Sheinbaum Pardo, C., San Martini, F., Zavala, M. A., and McRae, G.: Air Pollution Science in the MCMA: Understanding Source-Receptor Relationships through emissions inventories, measurements, and modeling, in: Air Quality in the Mexico Megacity – An Integrated Assessment, edited by: Molina, M. J. and Molina, L. T., Kluwer Academic Publishers, Dordrecht/Boston/London, 2002.

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, 2, 844–860, 2002.

R Development Core Team: R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, http://www.R-project.org, 2009.

SENER (Secretaría de Energía): Sistema de Información Energética, http://sie.energia.gob.mx, 2009.

SMA (Secretaría de Medio Ambiente del Gobierno del Distrito Federal): La calidad del aire en la Zona Metropolitana del Valle de México, 1986–2006, 2007.

SMA (Secretaría de Medio Ambiente del Gobierno del Distrito Federal): Inventario de emisiones de contaminantes criterio de la Zona Metropolitana del Valle de México 2006, http://www.sma.df.gob.mx/sma/index.php?opcion=26&id=501, 2008.

Song, J., Lei, W., Bei, N., Zavala, M., de Foy, B., Volkamer, R., Cardenas, B., Zheng, J., Zhang, R., and Molina, L. T.: Ozone response to emission changes: a modeling study during the MCMA-2006/MILAGRO campaign, Atmos. Chem. Phys. Discuss., 9, 23419–23463, 2009, http://www.atmos-chem-phys-discuss.net/9/23419/2009/.

Sosa, E. R., Bravo, A. H., Mugica, A. V., Sanchez, A. P., Bueno, L. E., and Krupa, S.: Levels and source apportionment of volatile organic compounds in southwestern area of Mexico City, Environ. Pollut., 157, 1038–1044, 2009.

Stephens, S., Madronich, S., Wu, F., Olson, J. B., Ramos, R., Retama, A., and Muñoz, R.: Weekly patterns of Mxico City's surface concentrations of CO, NO_x, PM_{10} and O_3 during 1986–2007, Atmos. Chem. Phys., 8, 5313–5325, 2008, http://www.atmos-chem-phys.net/8/5313/2008/.

Tie, X., Madronich, S., Li, G., Ying, Z., Zhang, R., Garcia, A., Lee-Taylor, J., and Liu, Y.: Characterization of chemical oxidants in Mexico City: A regional chemical dynamical model (WRFChem) study, Atmos. Environ., 41, 1989–2008, 2007.

US-EPA: CMB8 user's manual. US Environmental Protection Agency, Research Triangle Park, 2001.

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, Pressley, S, Allwine, E., Westberg, H., Jobson, T., Alexander, M.,

Prazeller, P., Molina, L., and Molina, M.: Flux measurements of volatile organic compounds from an urban landscape, Geophys. Res. Lett., 32, L20802, doi:10.1029/2005GL023356, 2005.

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, http://www.atmos-chem-phys.net/7/329/2007/.

Velasco, E., Pressley, S., Grivicke, R., Allwine, E., Coons, T., Foster, W., Jobson, B. T., Westberg, H., Ramos, R., Hernández, F., Molina, L. T., and Lamb, B.: Eddy covariance flux measurements of pollutant gases in urban Mexico City, Atmos. Chem. Phys., 9, 7325–7342, 2009, http://www.atmos-chem-phys.net/9/7325/2009/.

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.

West, J. J., Zavala, M. A., Molina, L. T., Molina, M. J., San Martín, F., McRae, G. J., Sosa-Iglesias, G., and Arriaga-Colina, J. L.: Modeling ozone photochemistry and evaluation of hydrocarbon emissions in the Mexico City metropolitan area, J. Geophys. Res., 109, D19312, doi:10.1029/2004JD004614, 2004.

WHO: Air quality guidelines for Europe, second edition. World Health Organization, Copenhagen, 2000.

Wöhrnschimmel, H., Márquez, C., Mugica, V., Stahel, W. A., Staehelin, J., Cárdenas, B., and Blanco, S.: Vertical profiles and receptor modeling of volatile organic compounds over Southeastern Mexico City, Atmos. Environ., 40, 5125–5136, 2006.

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, http://www.atmos-chem-phys.net/6/5129/2006/.

Zavala, M., Herndon, S. C., Wood, E. C., Onasch, T. B., Knighton, W. B., Marr, L. C., Kolb, C. E., and Molina, L. T.: Evaluation of mobile emissions contributions to Mexico City's emissions inventory using on-road and cross-road emission measurements and ambient data, Atmos. Chem. Phys., 9, 6305–6317, 2009, http://www.atmos-chem-phys.net/9/6305/2009/.

Table 1. Descriptive statistics of VOC measurements from 2000 to 2007 for each of the quantified species. Concentrations in ppbC.

	n	Mean	Median	Standard Dev.	Percentile .05	Percentile .95
Ethane	20251	10.8	8.5	8.0	2.4	26.3
Propane	21 188	241.5	157.2	243.4	34.3	734.3
Propylene	19 356	18.1	11.7	25.5	2.1	53.0
Butane	21 138	108.6	72.4	105.7	16.1	324.8
Acetylene	20 973	26.6	18.2	26.2	4.2	77.2
Pentane	21 127	25.2	16.5	31.8	4.5	70.9
Hexane	20 765	17.5	10.7	23.1	2.0	55.3
Heptane	20 700	3.9	2.5	5.8	0.6	11.3
Benzene	20 950	7.9	5.8	7.4	1.3	21.6
Octane	19 495	2.6	1.7	5.5	0.6	6.3
Toluene	20 848	70.3	50.3	74.9	11.2	188.1
Nonane	19 507	3.8	2.4	6.9	0.6	9.7
o-X ylene	19 545	12.0	8.0	17.3	1.7	33.3
Σ_{13}VOC	15 777	575.9	428.1	472.3	131.2	1531.3

ACPD
10, 3319–3346, 2010

Table 2. Results for linear regression for all VOC species.

	Intercept		Time		Month
	α	β	SE	p	p
Ethane	2.43	−0.005	0.023	0.843	0.010**
Propane	5.90	−0.048	0.025	0.058	0.029*
Propylene	3.33	0.014	0.053	0.791	0.427
Butane	4.99	−0.041	0.020	0.047*	0.068
Acetylene	3.74	−0.067	0.016	0.000***	0.011*
Pentane	3.32	−0.063	0.051	0.220	0.024*
Hexane	3.21	−0.135	0.055	0.017*	0.340
Heptane	1.82	−0.028	0.027	0.299	0.145
Benzene	2.32	−0.024	0.027	0.377	0.215
Octane	1.42	−0.052	0.031	0.093	0.519
Toluene	4.62	−0.077	0.038	0.052	0.219
Nonane	1.69	−0.100	0.047	0.037*	0.669
o-Xylene	2.88	−0.123	0.056	0.034*	0.061
Σ_{13}VOC	6.69	−0.030	0.020	0.144	0.029*

α , β=regression coefficients, SE=standard error, p=level of significance of coefficients. The p-value is represented as follows: p <.001***, p <.01**, p <.05*.

ACPD
10, 3319–3346, 2010

Table 3. Descriptive statistics on CMB model performance parameters.

	n	R^2	χ^2	Mass%
Night	679	0.96±0.02	1.5±0.7	105.0±7.6
Morning	667	0.97±0.02	1.4±0.7	103.9±6.3
Evening	733	0.97±0.02	1.2±0.7	100.3±7.0
Total	2079	0.97±0.02	1.4±0.7	103.0±7.3

n=number of fits, including averages of the samples of one day within the respective time interval. Mean R^2, χ^2, Mass%, with their respective standard deviations: see explanations in the text.

Table 4. Results for linear regression for all source activities.

	Intercept		Time		Month
	α	β	SE	p	p
LPG	6.52	−0.055	0.027	0.043*	0.145
EXHAUST	5.60	−0.085	0.026	0.002**	0.0633
HOTSOAK	2.87	−0.016	0.018	0.379	0.058
SOLVENT	3.92	0.006	0.061	0.927	0.708
FOODR	1.73	0.223	0.044	0.000***	0.290

α, β=regression coefficients, SE=standard error, p=level of significance of coefficients. The p-value is represented as follows: $p < .001$***, $p < .01$**, $p < .05$*.

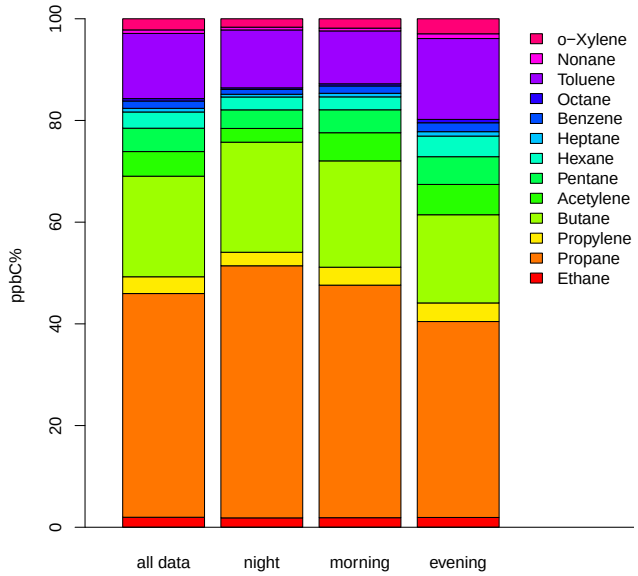

Fig. 1. Relative composition of VOC species in ppbC for all data (00:00–24:00) and during selected time intervals (night: 01:00–04:00; morning: 06:00–09:00; evening: 18:00–21:00).

ACPD
10, 3319–3346, 2010

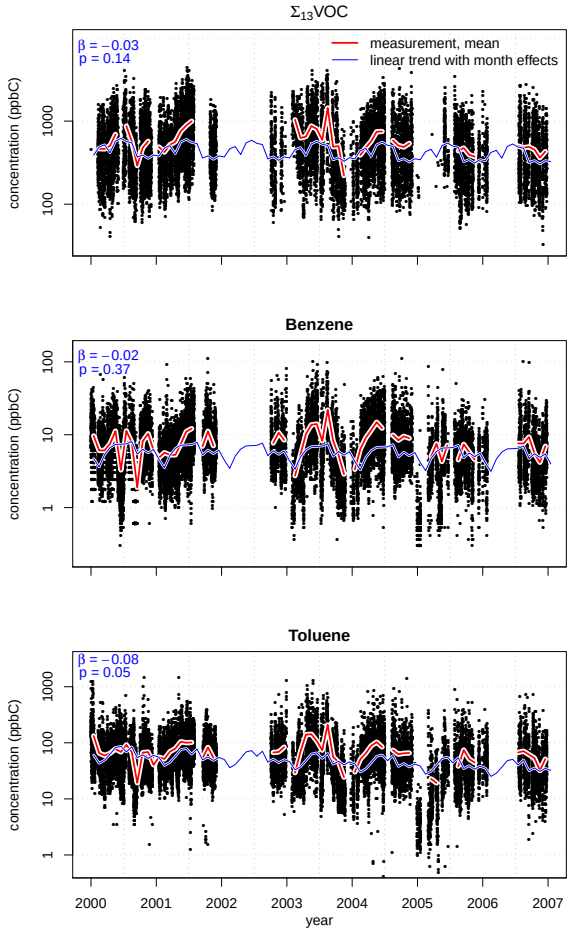

Fig. 2. Time series and monthly mean concentrations of Σ_{13}VOC, benzene and toluene from 2000 to 2007.

ACPD
10, 3319–3346, 2010

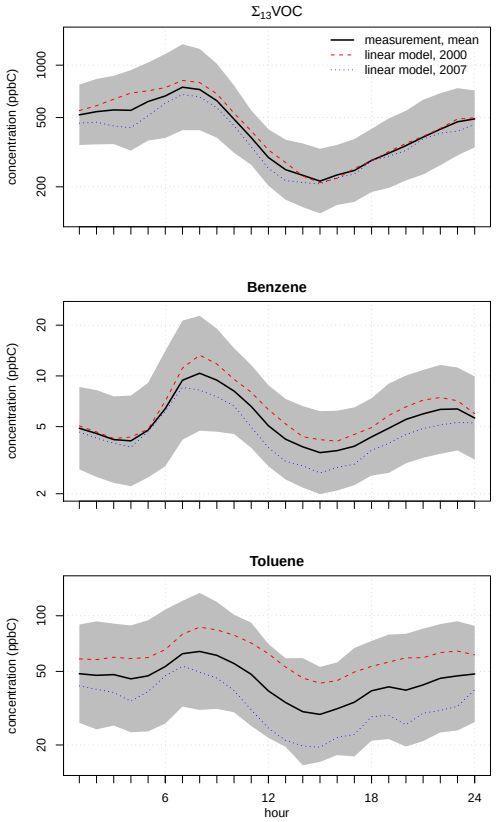

Fig. 3. Diurnal variation of Σ_{13}VOC, benzene, and toluene. Shown are concentrations with standard deviations (solid line with grey shadow), as well as the modelled values for mid 2000 and mid 2007 (dotted lines).

ACPD
10, 3319–3346, 2010

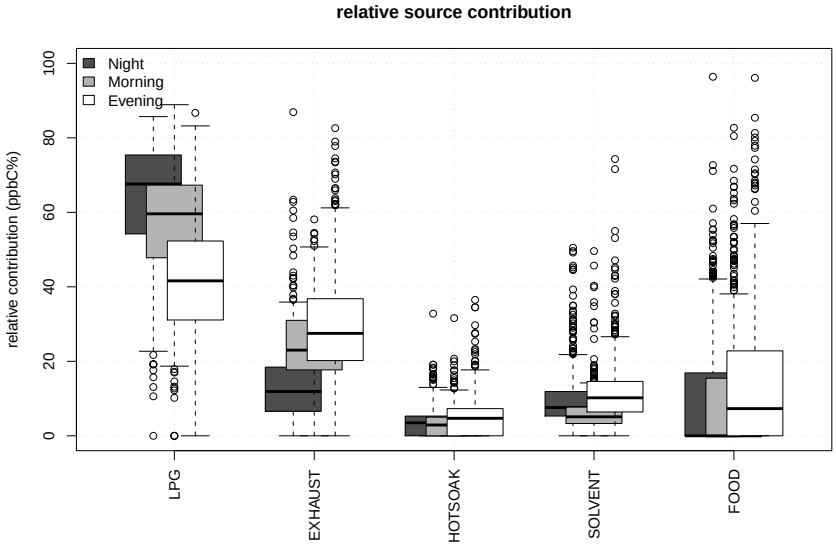

Fig. 4. Relative source contributions at night (01:00–04:00), in the morning (06:00–09:00), and in the evening (18:00–21:00).

ACPD
10, 3319–3346, 2010

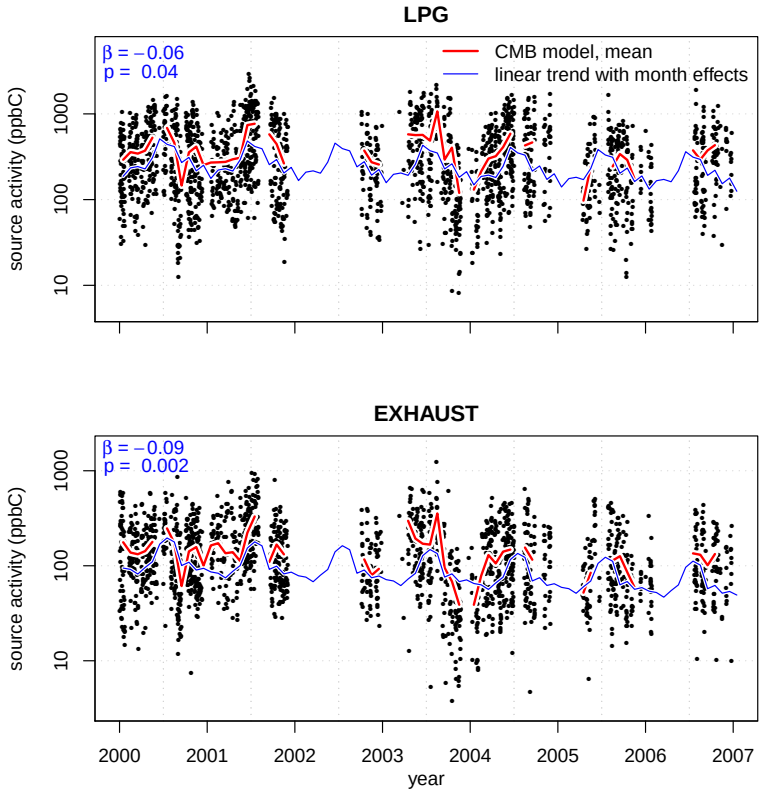

Fig. 5. Inter-annual variation of the absolute LPG and vehicle exhaust source activities.

ACPD
10, 3319–3346, 2010