Non-methane hydrocarbons in the atmosphere of Mexico City: results of the 2012 ozone-season campaign

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Abstract

With the aim to strengthen the verification capabilities of the local air quality management, the air quality monitoring network of Mexico City has started the monitoring of selected non-methane hydrocarbons (NMHCs). Previous information on the NMHC characterization had been obtained through individual studies and comprehensive intensive field campaigns, in both cases restricted to sampling periods of short duration. This new initiative will address the NMHC pollution problem during longer monitoring periods and provide robust information to evaluate the effectiveness of new control measures. The article introduces the design of the monitoring network and presents results from the first campaign carried out during the first six months of 2012 covering the ozone-season (Mar-May). Results show reductions during the morning rush hour (6 – 9 h) in the mixing ratios of light alkanes associated with the consumption and distribution of liquefied petroleum gas and aromatic compounds related with the evaporation of fossil fuels and solvents, in contrast to olefins from vehicular traffic. The increase in mixing ratios of reactive olefins is of relevance to understand the moderate success in the ozone and fine aerosols abatement in recent years in comparison to other criteria pollutants. In the case of

isoprene, the typical afternoon peak triggered by biogenic emissions was clearly observed for the first time within the city. The diurnal profiles of the monitored compounds are analyzed in terms of the energy balance throughout the day as a surrogate of the boundary layer evolution. Particular features of the diurnal profiles and correlation between individual NMHCs and carbon monoxide are used to investigate the influence of specific emission sources. The results discussed here highlight the importance of monitoring NMHCs to better understand the drivers and impacts of air pollution in large cities like Mexico City.

Keywords: Volatile organic compounds; Non-methane hydrocarbons; Ozone precursors; OH reactivity; Mexico City.

1. INTRODUCTION

Over the last two decades Mexico City has experienced a significant progress towards achieving cleaner air without compromising its economic growth. Its case has been used as an example for other cities of the world, especially in developing countries where rapid economic growth and environmental policies must evolve together (Parrish et al., 2011). This progress has been possible because of the concerted efforts of scientists, stakeholders and society. Mexico City has led the country in enforcing regulatory and control policies. Specific policies have included the requirement of catalytic converters in cars, distribution of cleaner unleaded fuels, substitution of natural gas for heavy oil in industry and power plants, reformulation of liquefied petroleum gas (LPG) for residential use, installation of vapor recovery systems in fuel service stations, implementation of inspection and maintenance programs for private vehicles, strengthening driving restrictions, improvement of the public transport by extending the subway infrastructure and implementing a bus rapid transport (BRT) system along confined lanes of main roads (SMA-GEM et al., 2012). These policies have responded to the integration of air quality information obtained by local authorities and scientific efforts to understand the physics and chemistry of the air pollution, as well as to evaluate the impact on human health, economic development, ecosystem sustainability and climate change. Special mention deserves the interdisciplinary studies based on intensive field campaigns that have provided a wealth of information on the emissions, dispersion and transformation of airborne pollutants within Mexico City and downwind regions (e.g., Doran et al., 1998; Molina et al., 2007; 2010).

The concentrations of all criteria pollutants in Mexico City have substantially decreased during the last 25 years, and some of them, such as sulfur dioxide (SO₂), nitrogen dioxide (NO₂), carbon monoxide (CO), total suspended particulate matter (SPT) and lead (Pb) are in compliance with the Mexican Air Quality Standards (M-AQS) for health protection; however, the concentrations of ozone (O₃) and particles with aerodynamic diameter ≤ 10 and $2.5 \mu\text{m}$ (PM₁₀ and PM_{2.5}, respectively) still exceed the standard threshold concentrations. In 2012-2014 the 1-hour O₃ concentration exceeded the M-AQS of 110 ppb on 118-126 days of each year with a maximum concentration of 185 ppb on 9 May 2014, while the 8-hour O₃ moving average concentration exceeded the M-AQS of 80 ppb on 108-120 days. For comparison, 343 and 341 days exceeded the 1-hour and 8-hour O₃ standards in 1991, when the city recorded the highest O₃ concentrations. With respect to particles, the annual PM₁₀ concentration has never met the M-AQS of $50 \mu\text{g m}^{-3}$ since the outset of the air quality monitoring in the city in 1986, while the 24-hour M-AQS of $120 \mu\text{g m}^{-3}$ was only recently met in 2013. The PM_{2.5} concentration meets the 24-hour M-AQS of $65 \mu\text{g m}^{-3}$, but does not meet the annual standard of $15 \mu\text{g m}^{-3}$; during the last three years it ranged from 26 to $28 \mu\text{g m}^{-3}$ (SMA-GDF, 2015).

The high levels of particles and O₃ are still a public health threat in Mexico City. In a recent study Riojas-Rodríguez et al. (2014) found that reductions of PM₁₀ to $20 \mu\text{g m}^{-3}$ and O₃ to 50 ppb would prevent 2300 and 400 premature annual deaths (13 and 2 deaths per 100,000 inhabitants) using population and air quality data from 2005. In a similar study based on PM_{2.5} data from 2010 López-Villegas and Pérez-Rivas (2014) estimated the prevention of 753 and 1421 premature annual deaths (4 and 7 deaths per 100,000 inhabitants) with associated costs of over 1.3 and 4 million US dollars if the annual PM_{2.5} average concentration would meet the M-AQS and the World Health Organization (WHO) guideline of $10 \mu\text{g m}^{-3}$, respectively. Note that these studies have estimated the premature deaths and economic benefits considering each pollutant separately. The savings on health-related costs would be much larger if other pollutants were included and their synergic impact considered.

The topography, meteorology, great population density (> 20 million inhabitants over $3,540 \text{ km}^2$) and magnitude of the economic activities and associated emissions enhance the photochemical formation of secondary pollutants, such as O₃, organic aerosols, carbonyls, peroxides, formaldehyde, glyoxal, nitric acid, etc. The formation of secondary aerosols contributes up to 75% of the afternoon PM_{2.5} budget (Paredes-Miranda et al., 2009). The control of such pollutants

depends on the accurate characterization of the ambient concentrations and emissions (biogenic and anthropogenic) of their precursor species: volatile organic compounds (VOCs) and nitrogen oxides (NO_x). The reactions involved in the photochemical transformations are non-linear and therefore difficult to evaluate. However, the intensive field campaigns mentioned above have provided detailed information to suggest that the formation of secondary pollutants in Mexico City, in particular of O₃, has shifted in recent years to a regime where VOC reductions would be more effective. Modeling studies and analysis of measurements indicate that O₃ production is generally VOC limited within the city (e.g., Tie et al., 2007; Lei et al., 2008; Zhang & Bubey, 2009; Song et al., 2010). This has been supported by studies of radical budgets showing significant chain termination by NO_x chemistry (Wood et al., 2009; Volkamer et al., 2010; Sheehy et al., 2010), and by the weekend effect showing large reduction in NO_x and CO but not in O₃ compared to weekday concentrations (Stephens et al., 2008).

Similar to the photochemistry, many studies have documented the distribution, diurnal pattern, magnitude, and reactivity of VOCs within and downwind of Mexico City since the nineties (e.g., Blake & Rowland, 1995; Arriaga-Colina et al., 2004; Velasco et al., 2007, 2008; de Gouw et al., 2009; Bon et al., 2011). These studies have provided valuable information, but their duration has been restricted to a few weeks since the majority have been part of intensive field campaigns. With the aim of addressing the VOC pollution problem during longer monitoring periods and evaluating O₃ and PM_{2.5} reductions according to new control measures, the environmental authorities of Mexico City through its Air Quality Monitoring Network (MC-AQMN) have developed a program to monitor continuously over 50 non-methane hydrocarbons (NMHCs) every hour in existing air quality monitoring stations inside and outside the urban area. The program started in 2012 and considers campaigns during the following 4 years in a first stage.

It is important indicate that VOCs containing oxygen, chlorine, or other elements besides carbon and hydrogen, such as aldehydes, ethers, alcohols, ketones, esters, chlorinated alkanes and alkenes, among others have not been included in this study, and therefore it is more appropriate to use the term NMHCs. The term of NMHCs is usually used for hydrocarbon of relevance in the O₃ formation with less than 12 carbons.

The NMHC monitoring program will strengthen the verification capabilities of the local air quality management providing a better insight of the atmospheric composition and chemistry of Mexico City. The program will provide data on the spatial and temporal distribution of the

NMHCs that will help to identify and characterize existing and new emission sources, and evaluate the potential of each individual species to produce O₃ and other secondary pollutants.

This article introduces the NMHC monitoring network of Mexico City and presents results from the first campaign carried out during the first six months of 2012, covering the so called “ozone season” from March to May. The data were restricted to 22 NMHCs (9 alkanes, 7 olefins, 6 aromatics) collected from two representative locations within the city. The purpose of this campaign was to obtain a first set of NMHC data during 24 continuous weeks, while evaluating the program’s feasibility and identifying potential technical and logistic shortcomings for the subsequent campaigns.

Before introducing the design of the monitoring network a brief description of the geographical, climatological and economic conditions that influence the photochemical pollution of Mexico City is provided. Then, the process followed for the selection of the monitored sites is explained, as well as the methodology of the NMHC measurements. The collected NMHC data are analyzed in terms of diurnal variations and reactivity with the hydroxyl radical (OH). Relationships between mixing ratios of individual NMHC species and CO are used to characterize both sites and determine the origin of the NMHCs, with a particular interest on vehicular traffic, LPG consumption and distribution, evaporation of fossil fuels and solvents, and vegetation.

2. Geographic setting, local meteorology and economic forces that influence the air quality of Mexico City

Mexico City lies in a nearly flat basin on the central Mexican Plateau at an elevation of 2240 m above sea level and a latitude of N19°25'. The basin is surrounded on three sides by mountain ridges, but with a broad opening to the north and a narrower gap to the south-southwest. The local meteorology and climate are strongly influenced by the surrounding terrain and by the extensive and heavily developed urbanization. The climate is highland subtropical, with a well-defined rainy season (June – October). The mean annual temperature varies from 15 to 17°C. The temperature is rarely below 3°C or above 30°C. The city receives ~800 mm of annual rain, the majority during the wet season when tropical winds bring unstable air and moist conditions that produce intense convective rains. The climate is relatively drier with little or no precipitation during the rest of the year. The dry season can be divided into a cold period and a warm period. The former spans from November to February when polar air masses bring anticyclone weather

(i.e., clear skies and calm conditions). The dry warm period also known as the ozone season extends from March to May when tropical winds again dominate but do not yet carry enough moisture for rain which produces conditions of atmospheric stability and clear skies favorable for photochemical activity. Over 60% of the O₃ episodes (i.e., exceedances to the 1-hour OMN standard) occur during this period (SMA-GDF, 2015).

Mexico City is one of the largest urban conglomerations in the world. It is the capital city and the economic, social and cultural hub of the country. At national scale, its economy contributes 25% to the gross domestic product, despite of comprising only 17% of the total population (IMCO, 2014). The city's 20.7 million inhabitants, 5 million vehicles, 5.6 million households and over 700 thousand area sources (64 thousand industries and 641 thousand commercial establishments such as fuel service stations, workshops, hotels, restaurants, dry cleaners, etc.) consume over 554 PJ of energy (47 million equivalent liters of gasoline) per year. According to the emissions inventory 633 thousand Mg of VOCs were emitted in 2012. The transport sector consumed 59% of the total energy but its emissions contributed only 32% to the total VOC burden. Similarly, industries consumed 25% and contributed 28% to the emissions, while the area sources (residences and commercial establishments) consumed 16% and contributed 37% to the VOC burden. The remaining 4% of the emissions were attributed to the biogenic component (SMA-GDF, 2015). The use of solvents for cleaning, degreasing, painting and diverse industrial processes represents also an important source of VOCs, as well as the leaks of LPG in residences and its deficient burning in stoves and boilers.

The low latitude, high altitude, meteorology and topography of the valley in which Mexico City sits facilitate the production of O₃ and secondary aerosols. Synoptic forcing is generally weak and the pollutants dispersion is strongly influenced by the mountain-valley wind pattern (Molina et al., 2007; 2010). The high altitude makes combustion processes less efficient leading to enhanced VOC emissions. And the subtropical weather and intense solar radiation accentuate the VOC evaporative emissions from a variety of sources including the use of solvents and paints, and the storage and distribution of fossil fuels.

3. METHODS

The NMHC monitoring program has been designed to monitor up to five representative locations of Mexico City based on the methodology of the Photochemical Assessment Monitoring Stations

(PAMS) program of the US Environmental Protection Agency (US-EPA, 1994). The monitoring locations include two sites where the O₃ peak concentrations are usually reported within the urban core, one representative site of the fresh urban mix of NMHCs using as reference results of previous studies and data from the emissions inventory, one site located in the predominant morning upwind direction to characterize the inflow of background NMHCs to the city, and one site located downwind from the edge of the urban sprawl to evaluate the impact of the city plume to surrounding rural areas. Figure 1 shows the location of the selected monitoring sites. At every site it is expected to monitor continuously every hour over 50 NMHC species by gas chromatography (GC) separation and photoionization detection (PID) or flame ionization detection (FID).

This section presents first a description of the methodology used for the selection of the monitoring sites. Full details are provided in (Jaimes and Retama, 2013). Then, the sampling procedures and details of the chemical analysis are introduced.

3.1 Monitoring sites

The NMHC monitoring sites were selected from the 29 stations that form the MC-AQMN through a comprehensive analysis of the VOC emissions' distribution within the city, historical records of ambient concentrations of criteria pollutants, predominant winds, land use characteristics and population density data. In brief, based on the emissions data from the emissions inventory and location of major emission sources the centroid of the city in terms of VOC emissions was defined. Then, from the wind analysis covering the ozone season a predominant pattern from north to south was identified during daytime. The black lines in the wind roses shown in Fig. 1 indicate the main wind direction during the morning and afternoon. The dominant daytime wind direction was used as reference to draw two lines at 45° intersecting at the emissions centroid as shown in the same figure. The northeast and southwest sectors delimited by these lines correspond to the upwind and downwind areas of the city. The monitoring station Acolman (ACO) within the northeast sector was selected as the upwind background station, while the station Ajusco (AJU) within the southwest sector and beyond the urban sprawl was selected as the downwind station. Both stations are located in rural environments and are not impacted by any significant local emission source. Previous studies based on observations and dispersion modelling have shown the impact of the local circulation on

the pollutants loading in the slopes of the southeast mountains of the valley (e.g., de Foy et al., 2006; 2008).

The monitoring station La Merced (MER) in a central section of the city was selected as the representative site to characterize the fresh mix of NMHCs. It is located in a district composed of a mix of residences, small and medium commerce, light industry and a busy market. Surrounding avenues are heavily travelled by private cars, light-duty vehicles and diesel buses. According to the emissions inventory this sector of the city is one of the areas with the highest VOC emissions (SMA-GDF, 2013).

The monitoring stations Pedregal (PED) and FES Acatlán (FAC) were selected to monitor the photochemical aging of the NMHCs. Both stations are located in the regions where O₃ peaks are more frequently reported. The former is in a suburban neighborhood in the prevailing downwind direction at about 25 km from the emissions centroid. The surrounding avenues are lightly travelled and there is no major emission point source (i.e. large industry). The O₃ concentration recorded by this station often exceeds the Mexican air quality standards; the 1-hour O₃ standard was exceeded in 123 days in 2014, usually in the afternoon between 15 and 17 h. Under specific meteorological conditions, which are not uncommon, winds may switch direction during the day venting masses of polluted air back to the north (de Foy et al. 2008), causing even higher O₃ peaks than in the southwest of the city. The monitoring station FAC is expected to collect NMHC data during such episodes.

For this first campaign, as mentioned above, the NMHC measurements were limited to two monitoring sites, MER (N19°25'28.596", W99°7'10.538", 2245 m) and PED (N19°19'30.5256", W99°12'14.890", 2326 m). Figure 2 shows their location over aerial photographs standing out surrounding avenues and point sources. The campaign covered the period of 1 Jan. – 30 Jun, 2012, including the complete ozone season. In the past both monitoring stations have been used to characterize the VOC pollution and investigate the photochemistry of the city (e.g., Arriaga-Colina et al., 2004; Velasco et al., 2007). Both stations are fully equipped to monitor all criteria pollutants (O₃, SO₂, CO, NO_x, PM₁₀ and PM_{2.5}) and basic meteorological parameters (temperature, relative humidity, wind direction and wind speed). The monitors use US-EPA reference of equivalent methods, for example, O₃ is measured by monitors API-T400 with detection limit of 0.1 ppb, NO_x by monitors API-200E or API-T200 with detection limit of 0.5 ppb, and CO by monitors API-300 with detection limit of 0.05 ppm.

3.2 Instrumentation

Every monitoring station meets the requirements of installation, operation and maintenance set by the official Mexican norms for air quality monitoring (NOM-156-SEMARNAT-2012; SEMARNAT, 2012). The samples for NMHC analysis are taken using a stainless steel tubing from the borosilicate glass sampling manifold that supplies air continuously to each one of the sensors for criteria pollutants. The inlet of the sampling probes of both stations, MER and PED, are free of obstacles over the urban canopy at heights of 17 and 11 m above the ground level, respectively. A sample of 0.6 L is taken during sampling cycles of 30 min, duration in which the NMHC analysis is completed. For analysis purposes, the hourly averages are only considered. If a 30-min period is not valid, the 1-hour average is discarded.

The GC analysis is performed using Syntech Spectras chromatographs GC955 611/811 (Synspec BV, Groningen, Netherlands) operated by pistons strokes of 38 cm³ every 3 min. To cover the hydrocarbons C₂-C₁₂, this instrument is designed like a double gas chromatograph, each chromatograph has a pre-concentration system. The hydrocarbons C₂-C₅ are pre-concentrated in Carbosieve SIII trap cooled at 5 °C, and then thermally desorbed and separated by a combination of two columns, a capillary film column and a capillary Al₂O₃/KCl PLOT column using nitrogen 5.0 as carrier gas with a flow of 3.2 cm³ min⁻¹. The unsaturated hydrocarbons are detected by PID and the saturated by FID. The hydrocarbons C₆-C₁₂ are pre-concentrated in Tenax GR, thermally desorbed and separated in a standard DB-1 column (30-m fused silica, 0.32 mm i.d. and 1 µm film thickness) with a 1.4 cm³ min⁻¹ carrier flow, and detected by PID.

Detectors response is calibrated with a standard mix of 51 species (Spectra Gases Company, NJ, USA) in interval concentrations of 3 to 15 ppbv. The detection limit for the different species was in the range of 0.012 ppbv for 3-methylpentane to 0.861 ppbv for ethene. Every GC system is calibrated twice during the campaign. To avoid deviations in the retention times during the individual VOC identification the temperature inside the stations is maintained at 20°C. It was found that a variation of ±3°C is enough to produce significant deviations.

Figure 3 shows good NMHC data coverage was achieved at both sites. With the exception of a few species in January, over 85% and 95% of the sampling periods recorded good data at MER and PED, respectively. The missing data did not follow any diurnal or seasonal tendency. The data gaps at the beginning of the campaign were caused by calibration issues.

4. RESULTS

As expected with the design of the NMHC monitoring network, the downtown site of MER recorded higher concentrations than the downwind urban site of PED. According to the gridded emissions inventory, MER is located in the sector with highest emissions of the city, and is therefore expected to be a representative site to characterize the fresh mix of VOCs. On average, the sum of the 22 NMHC species reported here was 41% higher at MER than at PED on a daily basis during weekdays. The individual sums of the 9 measured alkanes, 7 olefins and 6 aromatics were 41%, 38% and 49% higher, respectively. The lower concentrations of NMHCs at PED, but the 2 to 6 ppb higher concentrations of O₃ with a one-hour later peak in the afternoon are indicative of an important advection of aged air masses from other sectors of the city in agreements with the frequent “O₃-south” episodes described by de Foy et al. (2008). Figures 4 and 5 shows the diurnal profiles of selected NMHC species at both sites along with the diurnal profiles of O₃, NO_x (NO + NO₂) and CO.

Despite the differences in the concentrations, the diurnal patterns at both sites were similar. These patterns are described in the following section. Particular attention is given to the peak concentrations recorded during the morning rush hour. The influence of the major emission sources is discussed based on particular features and correlations with CO. Then, the concentrations are compared to those reported in a 9-year older study as a mean to evaluate the NMCH changes in composition and magnitude in the atmosphere of Mexico City. The observed changes are also analyzed in terms of the capacity to form O₃ through individual calculations of reactivity with the OH radical.

To explain the impact of the urban micrometeorology on the diurnal profiles of the monitored species, Fig. 6 shows the diurnal evolution of the energy balance evaluated during the same 6 months of this campaign. The energy fluxes were measured by an eddy covariance flux system deployed in the residential/commercial neighborhood of Escandón close to downtown at a distance of 6.4 km to the WSW from MER and 9.5 km to the NNE from PED. Details of the flux system are provided in Velasco et al. (2014). Despite the land-cover differences and distances between the observation sites, the energy flux profiles shed light on the role of the energy balance components as direct drivers of the boundary layer depth, and therefore of the changes in the ambient concentrations of NMHCs. Figure 6 shows also the diurnal variations of the meteorological parameters monitored at MER and PED.

4.1. Diurnal, weekly and seasonal variations

All NMHC species showed diurnal profiles similar to those of primary emitted pollutants, such as CO and NO_x. Weak winds and strong temperature inversions at night lead to high concentrations of such primary species of anthropogenic origin in a relatively shallow boundary layer at the time of the morning rush hour when the emissions of the intense traffic add up to the nighttime accumulated pollutants. The absence of an efficient chemical removal enhances the accumulation of reactive NMHCs, such as olefins and some aromatic species. However, the buildings and extended roads of the city lessen this adverse effect on the air quality. The heat stored in the built-up surfaces (ΔQ_s) during daytime is the larger component of the energy balance (Fig. 6b) and its release throughout the night is enough to maintain turbulent conditions in a ~200-m layer above the surface (Velasco et al., 2008). Without the presence of this turbulence, the same amount of pollutants would accumulate in a shallower layer causing even more deterioration in the air quality. After this period, the mixing ratios of primary species decrease quickly by dilution in a rapidly expanding boundary layer and by photochemical reactions with hydroxyl radicals (OH). Both, the expansion of the boundary layer and the vigorous photochemical activity respond to the intense solar radiation that Mexico City receives. By early afternoon, the boundary layer has grown up to heights of 2 – 4 km, when O₃ and other secondary species attain maximum concentrations, but primary emitted VOCs attain minimum concentrations. Similar diurnal patterns have been previously described for these and other locations within the city boundaries (e.g., Velasco et al., 2007; 2008; de Gouw et al., 2009; Fortner et al., 2009; Wöhrnschimmel et al., 2010).

Similar to CO, the measured NMHCs did not show variations in the diurnal pattern as a function of the day of the week. From Monday to Friday their concentrations reached similar magnitudes. On Saturdays the magnitudes were only lower during the morning rush hour compared to weekdays. An interesting feature also observed for primary emitted pollutants such as CO, NO_x and SO₂ is that the early morning (i.e., 0 – 7 h) mixing ratios on Saturdays and Sundays were consistently higher than on weekdays. The aromatic species showed the highest difference with mixing ratios between 10% and 30% higher at both sites. This is the so called “party effect” originated from the abundant social and entertainment activities during Friday and Saturday nights, which yield higher traffic levels. This effect has been also reported in eddy covariance flux measurements of CO₂ and selected VOCs (Velasco et al., 2009; 2014). In the context of a

conductive boundary layer and reactive atmosphere, the party effect emissions might have an important role on the weekend's photochemistry. On average, the mixing ratio sum of the 9 alkanes measured during the whole day at MER was 4% higher on Saturdays and 21% lower on Sundays. Similarly, the sum of the 7 olefins was 2% higher and 22% lower, and the sum of the 6 aromatics 11% higher and 17% lower on those days, respectively. The lower mixing ratios on Sundays correspond to a lower vehicular traffic during daytime compared to the other days. Mixing ratios at PED showed a similar pattern as a function of the day of the week with the exception of the aromatic species on Saturdays, which were between 0.4% and 6% lower than on weekdays.

The higher mixing ratios of NMHCs on Saturdays were accompanied by higher concentrations of O₃ and PM_{2.5}. Based on the one standard deviation range obtained from the 6 months of data, the peak concentrations of O₃ and PM_{2.5} were 6-11 ppb and 2-5 µg m⁻³ higher than on weekdays at PED, and 9-15 ppb and 0-5 µg m⁻³ higher at MER. In contrast, the lowest peak concentrations of O₃ and PM_{2.5} occurred on Sundays. The peak concentrations of O₃ at PED and MER were 1-3 and 0-7 ppb lower than on weekdays, and the peaks of PM_{2.5}, 0-2 µg m⁻³ and 3-4 µg m⁻³, respectively.

In a comprehensive statistical analysis of the criteria pollutants reported by the MC-AQMN from its outset in 1986 to 2007, Stephens et al. (2008) found a pattern somewhat similar on weekends. They found daytime mixing ratios of CO and NO_x consistently lower on Saturdays and Sundays compared to weekdays, but not for O₃. The O₃ peaks used to be as high as those on weekdays and occasionally higher. Their findings were consistent with a VOC-limited and NO_x-inhibited chemical regime for O₃ production, where any VOC reduction would be positive, but only large reductions in NO_x emissions would be effective, with smaller reductions being ineffective and possibly even detrimental.

In 2008, the environmental authorities extended the driving restrictions on weekdays to Saturdays, banning the circulation of vehicles with foreign plates or registered outside the city. This was a preventive measure against the increase of old cars after the official permit to import second-hand vehicles (>10 year old) from USA into the country in 2005. At that time, the worst pollution episodes and the major number of hospital visits due to respiratory illnesses started to occur on weekends (SMA-GDF, 2009). Flux measurements by eddy covariance of CO₂ and other species associated with vehicular traffic, such as olefins and C₂-benzenes, conducted in 2006 at

the Escandón site did not find a clear difference between weekdays and Saturdays (Velasco et al., 2009). In 2012 the same site was again instrumented to measure CO₂ fluxes, with the finding that six years later the CO₂ emissions on Saturdays were clearly smaller than on weekdays by 25% (Velasco et al., 2014).

The higher peaks of O₃ on Saturdays than on weekdays suggest that the reduction of VOC and NO_x emissions from the new vehicular restriction was not as efficient as in the case of CO₂. The traffic emissions of VOC and NO_x might have decreased, but not in the magnitude and proportion needed to reduce the O₃ production on Saturdays.

As a consequence of the subtropical location of Mexico City, no major seasonal variations on the anthropogenic emissions of VOCs within the city occur. For instance, the benign weather throughout the year, even during the dry cold season, eliminates the need of domestic heating and thereby an important emission source. Holiday periods such as the Holy Week and the *Guadalupe-Reyes* marathon (i.e. Mexican winter holiday period), in which schools and government offices close, and some private businesses reduce their activities, are associated with less anthropogenic emissions. Regional wildfires during the end of the dry season may influence the VOC burden of the city, as well as air masses rich of biogenic VOCs advected from surrounding forests during the months of major incoming solar radiation.

In general, the seasonal variations in the ambient concentrations respond to changes in the climatological parameters rather than to social behaviours. The concentrations of primary emitted pollutants such as CO, NO_x, SO₂ and PM₁₀ are larger from December to February, while O₃ from March to May when solar radiation is higher and cloudiness low. In the case of PM_{2.5}, which results from a mix of primary emissions and photochemical reactions, its maximum concentrations occur during the whole dry season from December to May. For all pollutants, the lowest concentrations occur during the rainy season as a direct consequence of convective ventilation and wet removal. The monthly variations observed for the 22 NMHCs reported here followed the same seasonal variations in contrast to the primary emitted pollutants mentioned above. The highest mixing ratios were recorded during the morning rush hour of January and February. The less intense solar radiation during these months reduced the availability of energy to produce turbulence, enhancing conditions of atmospheric stability and thereby the accumulation of pollutants in a shallower boundary layer. Based on the sum of the 9 alkanes, 7 olefins and 6 aromatic species from 6 to 9 h the peak concentrations during the winter months of

January and February were on average 35%, 26% and 19% larger at MER, and 28%, 8% and 19% larger at PED than during the ozone season from March to May.

4.2. Changes in time

Table 1 presents the average concentration of the 22 compounds measured at both sites during the morning rush hour of the ozone season. With the exception of 2,2,4-trimethylpentane, 2,4-dimethylpentane and 1-butene, Velasco et al. (2007) measured in 2003 these species at the same sites and hours. Those concentrations are included as a mean to evaluate the evolution of the NMHC pollution in Mexico City. Ten years ago, the rush hour used to span from 6 to 9 h; nowadays it starts at about 4 h and ends after 10 h as a direct consequence of the expansion of the urban sprawl. For comparison purposes, the concentrations recorded between 6 and 9 h on weekdays are only considered as those corresponding to the peak of the rush hour.

The seven alkanes and six aromatics measured in both years showed consistent reductions in both sites. Based on their average mixing ratios during the morning rush hour, the alkanes decreased by 33-44% at MER and 29-65% at PED, with mean reductions of 36% and 42%, respectively. The aromatic species showed even higher reductions. Their individual mixing ratios decreased by 50-81% at MER and 43-83% at PED, with mean reductions of 60% and 57%, respectively. At both sites, m,p-xylene showed the highest reduction followed by 2,4-trimethylbenzene. Benzene, ethylbenzene, o-xylene, toluene and i-pentane reported reductions > 50% at least in one site.

The light alkanes associated with LPG (propane, n-butane and i-butane) showed also important reductions from 33% to 45% at both sites, suggesting a reduction in the LPG leakages during distribution and storage. In contrast, none of the olefins showed a clear reduction. With the exception of ethene at both sites and trans-2-butene at MER, the mixing ratio of the other olefins has increased. The sum of the six olefins measured in both years increased between 4% and 24% at MER and between 4% and 52% at PED, with mean increases of 10% and 16%, respectively.

Although the statistical confidence of the changes in the concentrations of NMHCs cannot be assessed because of the limited number (< 10) of samples collected at each site in 2003, they provide insight on the reduction/increase of certain species despite the growth in the vehicular fleet and other activities during this period. Arriaga-Colina et al. (2004) and Velasco et al. (2007) had already reported an apparent stabilization and possible decrease in the total concentration of

over 50 species based on VOC data collected at the same two sites. Similarly, Wöhrnschimmel et al. (2010) had observed a decrease in some VOCs associated with LPG consumption and evaporative hot soak emissions from motor engines in a different sector of the city for the 2000 – 2007 period. The latter is in good agreement with the observed reductions in alkanes and aromatics, but not in alkenes, which are strongly associated with on-road vehicle exhaust emissions.

4.3. Changes in reactivity with the hydroxyl radical

A useful approach to evaluate the VOCs influence on the O₃ production is through the analysis of their reactivity with the OH radical, the inverse of the OH lifetime. The hydroxyl radical is an important oxidant that controls the lifetime and fate of most VOCs. The oxidation chemistry between VOCs and NO_x that leads to the formation of O₃ and secondary aerosols is initiated by reactions of OH with VOCs. Figure 7 shows the OH reactivity or contribution to the OH loss rate of every compound measured at both sites during the peak of the morning rush hour. The OH reactivity of those compounds measured also in 2003 by Velasco et al. (2007) are included as a mean to determine changes in their potential as O₃ precursors.

In concert with the higher concentrations recorded at MER, the OH reactivity was also higher for the three groups of NMHCs measured in 2012. The OH reactivity for the nine alkanes together at MER was twice the reactivity at PED, as well as for the seven olefins. For the aromatic species, MER showed an OH reactivity 3 times larger.

Not surprisingly, olefins were the NMHC species with the highest OH reactivity. The top three compounds at PED were olefins associated with vehicular traffic: propene, ethene and trans-2-butene. At MER, propene, ethene and isoprene were the most reactive NMHCs. Isoprene was the sixth most reactive olefin at PED. Considering only compounds measured in 2012, propene, ethene and trans-2-butene were also at the top of the list at both sites in 2003. Isoprene ranked last at both sites among the olefins measured at that time. The advance of isoprene in the ranking compared to other olefins might be the result of changes in the gasoline composition, a major biogenic contribution or changes in the atmospheric chemistry. This point will be discussed later.

In 2003, propane and n-butane ranked third and fourth at both sites. For 2012 they dropped a few positions. Propane ranked fifth and fourth at MER and PED among all the measured NMHCs,

and n-butane seventh at both sites. Adding i-butane, the contribution of the light alkanes associated with LPG consumption showed a significant decrease of 37% and 42% at MER and PED, respectively.

The seven alkanes measured in both years during the morning rush hour showed together an OH reactivity 40% and 46% lower at MER and PED in 2012; similarly, the OH reactivity of the six aromatic species decreased 67% at both sites. In contrast, the six olefins evaluated in both years reported together an increase of 38% and 63%, respectively. Isoprene, 1-3-butadiene and propene showed the highest percentage increases, while the 8- and 9- carbon aromatic showed the highest decreases. The OH reactivity of m-p-xylene and 1,2,4- trimethylbenzene decreased > 70%.

5. MAIN CONTRIBUTORS OF NMHCS IN MEXICO CITY

The main emission sources of alkanes, olefins and aromatics have apparently not changed in the last two decades. Vehicular traffic, evaporative emissions from fossil fuels and solvents, and LPG consumption are still the main emission sources of NMHCs in Mexico City. Table 2 shows the primary sources of the NMHCs reported here using as reference the emission source profiles determined by Vega et al. (2000) and Mugica et al. (2002) for Mexico City in the late nineties. The fractional amount of every compound to the total emission of NMHCs for each source type is not included because of the changes experienced in the fuel composition, control measures, technology in industrial processes and vehicular fleet in a period of over 15 years.

This section analyzes the diurnal features of the measured compounds in terms of their potential emission sources. Ratios of individual NMHCs relative to CO, NO_x and the other NMHCs determined by 2-sided regression fits to the hourly data during the morning rush hour are used to evaluate the vehicular influence and contributions of other sources. According to the local emissions inventory > 98% of the CO is due to vehicular traffic (SMA-GDF, 2013) and can therefore be used as a tracer of vehicular exhaust.

5.1. The strong influence of vehicular traffic

Figures 8 and 9 show that the mixing ratios of almost all NMHCs measured here are moderately or highly correlated with CO and NO_x during the morning rush hour at both sites. With the exception of light alkanes and i-pentane at PED, all species showed correlation coefficients (r^2) equal or above 0.5. The correlations at MER were stronger than at PED in agreement with the

selection of the former as a representative site to characterize the fresh mix of NMHCs. The morning traffic in surrounding roads at MER is apparently worse than at PED. The poor correlations with i-pentane at PED were caused by 18 outlying records along the campaign. These outliers indicate the presence of i-pentane contributors other than vehicular traffic during specific periods. Removing these records an $r^2 = 0.68$ was obtained for the correlation with CO. In general, the good correlations reported for the majority of species are comparable to those reported for US cities by Baker et al. (2008) and a number of cities in developed countries by von Schneidemesser et al. (2010). These two studies concluded that the strong correlations show that the majority of VOCs in those cities are originated from on-road vehicle emissions.

The tables in both figures show $r^2 > 0.8$ between CO and NO_x, supporting the hypothesis that vehicular traffic is the main emission source of NMHCs at both sites during the rush hour period. Fujita et al. (1992) and Parrish et al. (2002) demonstrated that the ratios of ambient CO to NO_x concentrations measured during the morning rush hour provide an accurate indication of the emission ratios of these species from vehicular traffic if the measurement site is carefully selected. The observed molar ratios between CO and NO_x of 11.0 ± 0.2 and 11.8 ± 0.2 at PED and MER determined from the slopes of the the linear correlations are similar to those reported for US cities in the late-nineties (Parrish et al., 2006). Parrish et al. (2009) reported also a molar ratio of 11 for a residential site at the outskirts of Mexico City using data from 2006.

The correlations between individual NMHCs are also comparable to those reported for cities of developed nations. Using available VOC data from cities around the world, von Schneidemesser et al. (2010) divided those cities in Annex I and non-Annex I countries following the Intergovernmental Panel on Climate Change classification (United Nations, 2010), and found a significant difference in the correlation coefficients of both groups. Cities of the Annex I group (i.e., developed countries) showed much stronger correlations than cities of the non-Annex I group (i.e., developing countries). The correlations observed at MER and PED are between those of the Annex I and non-Annex I cities. Although on-road vehicle emissions are the dominant source of NMHCs in Mexico City, other emission sources are also relevant.

Figure 10 shows the relationships between ethene, n-hexane and benzene to toluene based on the 2012 measurements and samples collected in April 2003 at the same sites and during mobile vehicle chase experiments. The later were designed to characterize emissions from vehicles under actual driving conditions and included a suite of gasoline and diesel vehicles (Herndon et al.,

2005; Velasco et al., 2007). These four species were selected following the approach of Parrish et al. (2009) to investigate the relative emission patterns of representative VOCs of anthropogenic origin. Data from the whole diurnal course were included, but only data from the morning rush hour were considered to calculate the molar ratios. The figure annotation includes ratios reported for US cities in the eighties, and Tokyo and Beijing from the beginning of the current century after Parrish et al. (2009) for comparison purposes. As expected, more scattering was observed for the data covering the whole day than for the data covering only the morning rush hour, but no major variation was observed in the molar ratios. The difference in reactivity with the OH radical for these four NMHCs is apparently not significant. The ethene to toluene ratio at MER and PED was somewhat different, but at both sites it became closer to the ratio determined for mobile sources in 2003 in comparison with the samples collected at that time. The benzene and n-hexane to toluene ratios were similar at both sites, but slightly different to the ratios observed in 2003, which were closer to the vehicular traffic ratios. These results suggest that emissions from sources other than on-road vehicles have **less** importance in the case of ethene, **but not for toluene, as it is discussed below**. While the changes in the n-hexane and benzene to toluene ratios suggest that the vehicle exhaust signature changed in a period of nine years.

Going back to Figs. 4 and 5, species such as propene, 1,3-butadiene, cis-2-butene, o-xylene, m,p-xylene, benzene, ethylbenzene and 3-methylpentane show a much closer profile to CO, including its pronounced morning peak, than the other compounds. Figure 11 highlights even more this feature showing the diurnal profiles of a few selected NMHCs normalized to their maximum mixing ratio. During the first hours the pollution remainders of the previous day are trapped in the nocturnal inversion layer and form up the initial concentrations to which the emissions from the reduced traffic at night add up. Dark reactions are not strong enough to deplete them. They reach maximum mixing ratios about one or two hours after sunrise, during the peak of the rush hour (8 – 9 h). This time marks the kickoff of the O₃ concentration rise. Ozone attains minimum concentrations around sunrise (7 h) and remains low during the next two hours. The NO_x trapped in the nocturnal boundary layer plus the fresh NO emitted by traffic delay the rise of the O₃ concentration by about two hours. In the following two or three hours, the concentrations of all primary emitted NMHCs decrease rapidly by the combination of a vigorous dilution into the expanding boundary layer and an intense photochemical oxidation. Compounds with shorter lifetimes (i.e., high OH reactivity) such as 1,3-butadiene, trans-2 butene, cis-2-butene, and propene reach minimum concentrations faster, and even some drop close to zero. Through a

comprehensive study of the photochemistry in Mexico City, Shirley et al. (2006) and Volkamer et al. (2007) determined that traffic emissions of VOCs and NO_x are the main cause driving the photochemical smog formation. Their results suggest that VOCs contribute 72% to the OH reactivity, with the olefins responsible for jump-starting the morning photochemistry. After midday, during the next three hours, all primary emitted VOCs maintain minimum concentrations, **in contrast** to the OH and HO₂ radicals, O₃ and other secondary pollutants, which reach maximum concentrations. Throughout the afternoon the O₃ production decreases continuously as a result of the decreasing OH reactivity, the loss of NO_x to peroxyacetyl nitrate (PAN) and other organic nitrates, and less sunlight. This reduction in the atmospheric reactivity contributes to the evening rise of the VOC concentrations. In the late afternoon, the boundary layer collapses and the new nocturnal boundary layer starts accumulating VOCs given way to a new cycle.

5.2. The still inefficient use and distribution of liquefied petroleum gas

Propane, n-butane and i-butane are three alkanes of low molecular weight associated with the use and leakage of LPG. Their diurnal mixing ratio pattern is similar to the pattern previously described for other NMHCs, but with a larger and wider morning peak as shown in the normalized diurnal profiles for propane in Fig. 11. This larger peak is a consequence of the longer lifetime (i.e. low OH reactivity) of these species and emission origin. Although the small fleet of LPG powered vehicles (< 1% of the total fleet) composed mainly of light and heavy duty trucks and buses cannot be neglected, the high concentration of these light alkanes has been attributed to the widespread use of LPG in residential cooking and water heating since over 20 years ago (e.g., Blake & Rowland, 1995; Gamas et al., 2000; Gasca et al., 2004; Velasco et al., 2007; Bon et al., 2011). The observed reductions in the ambient concentrations of these species, already discussed, suggest that LPG leakages during handling, distribution and storage have decreased. However, the actions to improve the burning efficiency of stoves and boilers need to continue, as well as the control measures to further minimize leakages. The similitude in the LPG composition (61.4% propane, 26.4% n-butane, 12.0%, i-butane, 0.2% other species; Secretaría de Energía, 2012) with the proportion of these species in the samples collected throughout the day in both sites confirms that the LPG leaking is still a problem. The individual contributions of propane, n-butane and i-butane to their sum in the samples were on average 59.5%, 30.6% and 9.9% in MER, and 61.7%, 27.5% and 10.8% in PED.

Although olefins have their main origin in vehicular traffic, emissions from LPG combustion cannot be neglected. As shown in Table 2 propene, 1-butene, trans-2-butene and cis-2-butene among the olefins included in this study, are also produced from the combustion of propane and butane (e.g., Warnatz, 1983).

5.3. Evaporation of fossil fuels and solvents

The evaporation of fossil fuels from storage tanks and especially when filling up in gasoline service stations is also an important source of NMHCs to the atmosphere. Similarly, the evaporation of compounds associated with solvents in cleaning and degreasing products, paints, adhesives, dyes and inks can also have an important contribution to the ambient concentrations of some aromatic and oxygenated VOCs, such as toluene and methanol (e.g., Velasco et al., 2009).

Toluene recorded the highest concentrations among the aromatic species reported here at both sites in agreement with previous studies (e.g., Mugica et al., 2003; Velasco et al., 2007). Although vehicular traffic is a major contributor of toluene, the influence of other sources was evident throughout the day as shown in Fig. 11 by a much wider morning peak and less intense drop during daytime than other species. The scattering in the relationships of toluene with other three NMHCs in Fig. 10 depicts the presence of evaporation of fossil fuels and solvents. The major scattering in MER is explained by the abundant workshops and commercial establishments in surrounding blocks, including one of the busiest markets of the city. The weak correlation between toluene and CO ($r^2 = 0.49$) compared to that between benzene and CO ($r^2 > 0.80$) at both sites during the morning rush hour (see Fig. 8 and 9) suggests also an important toluene contribution from fugitive sources. A fourth evidence of the importance gain of such sources is a decreasing benzene to toluene ratio. The ratios observed in 2012 were 38% and 13% lower at MER and PED than in 2003 (Fig. 10). Gasoline vehicles equipped with catalytic converter are more efficient removing toluene than benzene from the exhaust (e.g., Schauer et al., 2002). By 2012, 91% of Mexico City vehicles counted already with emission control systems (SMA-GDF, 2013) and emitted therefore less toluene in comparison to 2003. Hence, the decrease in this ratio is not consistent with the expected increase of benzene respect to toluene from tailpipe emissions. This and the previous findings point out together that the renewal of the vehicular fleet has contributed to the reduction of both species, and stand out the toluene contribution from non-vehicular emissions, as previously reported by Rogers et al (2006).

Although all gasoline service stations in Mexico City are equipped with vapor recovery systems, Sosa et al. (2009) found that fuel evaporation in service stations is still a major contributor of toluene to the atmosphere. Similarly, despite programs to reduce the careless use of solvents, degreasers and paints to the open air, in many households, workshops and commercial establishments it is still a common practice and thereby an important emission source of toluene. The high mixing ratios of toluene at night might be related to industrial activities and asphalt application by municipal workers.

5.4. The biogenic contribution

The potential contribution of urban vegetation and forests in surrounding mountains to the total VOC burden in Mexico City had been previously assessed using modeling approaches and VOC characterization (e.g., Velasco et al., 2003; Velasco et al., 2007), but the biogenic signature in ambient concentrations was not observed until this study. The comprehensive chemical characterization conducted in previous large field campaigns (e.g., Molina et al., 2007; 2010) did not find a significant biogenic contribution in the VOC burden within the city. The afternoon mixing ratios of isoprene recorded in this study were significantly larger than those reported in 2003 by Velasco et al. (2007) and 2006 by Bon et al. (2011). Both studies concluded that the observed isoprene was associated with traffic emissions and not vegetation. This could have been a consequence of the limited duration of such studies and sampling approaches. However, changes in the photochemistry triggered by the reductions and increases of some of the NMHCs discussed above cannot be neglected.

The typical biogenic peak of isoprene in the afternoon was observed at MER and PED. Figure 11b shows the diurnal profiles of isoprene at MER by month normalized to their maximum mixing ratio. The profiles respond to the warm and sunny conditions of the subtropical location of Mexico City. Among the environmental variables controlling the biogenic emission of isoprene are temperature and light. Using as reference the model of Guenther et al. (1993), Velasco et al. (2003) found that the bulk of biogenic isoprene emission in the Valley of Mexico occurs at 13-15 h, when solar radiation peaks and ambient temperature is close to reaching its maximum. However, recent findings suggest that the synthesis of isoprene provides thermal tolerance to the leaves, thereby the temperature is the main variable that regulates the isoprene emission (e.g., Sharkey et al., 2008). The emission of isoprene as a heat tolerance mechanism in

plants helps to explain the coincidence in the peaks of ambient temperature and isoprene mixing ratios throughout the entire afternoon as shown in Fig. 11b.

In February the afternoon peak was much less pronounced than in the following months. From March to May the peak became more evident. May recorded the highest afternoon mixing ratios of isoprene at both sites. This finding is in agreement with Velasco et al. (2003) who forecasted May as the month with the highest isoprene emission as a direct consequence of the highest solar radiation experienced at the end of the dry-warm season in the Valley of Mexico. June marks the beginning of the rainy season, cooling a little bit the air and reducing the solar radiation, and thereby lowering the biogenic contribution.

The collocation of anthropogenic sources of NO_x , such as vehicular traffic, with biogenic sources of isoprene and other reactive VOCs can generate significant amounts of O_3 in urban atmospheres depending on the vegetation characteristics, climatological conditions and anthropogenic contribution. For example Chameides et al. (1988) found that in Atlanta the biogenic isoprene had a significant contribution to the O_3 formation. In contrast, more recently von Schneidemesser et al. (2011) concluded that the reduction of anthropogenic VOCs in the temperate cities of London and Paris had not resulted in a higher participation of the biogenic isoprene in the O_3 formation through its OH reactivity. For the warm and sunny climate of Mexico City, especially during the ozone-season, the biogenic contribution may gain relevance if the VOC emissions from other sources continue decreasing, as it is apparently occurring. However, its relevance still needs to be assessed by evaluating the sensitivity of O_3 production to changes in VOCs and NO_x emissions.

6. CONCLUSIONS

Results from the first set of data delivered by the NMHC monitoring network of Mexico City show the importance of such information to better assess the changes in atmospheric chemistry that have responded to continuous efforts to improve the air quality over the last 20 years. For instance, the observed reductions in mixing ratios of light alkanes associated with the consumption and distribution of LPG, as well as of aromatic compounds related to the evaporation of fossil fuels and solvents support the policies designed for their abatement. Respecting to olefins originated from on-road vehicles, the observed increase in their mixing ratio would have been even higher in the absence of the tightening of emission regulations,

driving restrictions and investments in transportation infrastructure implemented during the last decade. From 2003 to 2012 the vehicular fleet increased 36% (> 1.3 million units), but the fuel consumption only 5.6% (gasoline 6.3% and diesel 2.9%) (D. Guzmán, SEDEMA, personal communication, 2015). In context with the later, the sum of the six olefins measured in both years, and based on their average mixing ratio during the morning rush hour, increased between 10% and 16%. Demographic data suggest that for every children born (15 per 1000 inhabitants, INEGI 2012), two vehicles are registered in Mexico City, and not necessarily brand new (Gershenson, 2014). It is not surprising therefore that Mexico City ranks at the top in international surveys on traffic congestion (e.g., Gyimesi, et al., 2011). Mexico City residents spend in average 65 min commuting to work (INDRA, 2014). During the rush hour they can expect double the time stuck in traffic compared to a free flow situation (TomTom, 2015). Traffic congestion does not only matter for its impact on air pollution, it is obviously a mobility problem that threatens public health, reduces economic productivity and makes life miserable for thousands of citizens. Intelligent and innovative policies are urgently needed to solve this problem of social, economic and political nature.

The NMHC monitoring network of Mexico City will provide a unique opportunity to evaluate the effectiveness of such policies to improve mobility and therefore reduce traffic congestion and emission of toxic pollutants. The complete operation of the network including total of five monitoring sites and extending the sampling period and number of species will represent an important effort to better understand the drivers and impacts of air pollution in Mexico City and therefore contribute to a science-based design of pollution abatement strategies.

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Table 1. Geometric mean concentrations during the morning rush hour (6 – 9 h) on weekdays at the two urban sites monitored during the 2012 ozone season (Mar –May) and the MCMA-2003 field campaign. The 2003 campaign covered the last two weeks of April of that year. The numbers at the right of the $\pm$ symbol indicate one standard deviation. Species are divided by NMHC group and sorted in descending order according to their concentration in La Merced site in 2012.

Species	Ambient concentration (ppbv)			
	La Merced 2012	La Merced 2003	Pedregal 2012	Pedregal 2003
Alkanes				
Propane	89.13 $\pm$ 59.45	133.91 $\pm$ 44.64	50.89 $\pm$ 33.21	84.37 $\pm$ 28.92
n-butane	35.05 $\pm$ 22.62	56.74 $\pm$ 14.19	17.68 $\pm$ 11.32	32.31 $\pm$ 10.91
Ethane	15.04 $\pm$ 5.78	20.05 $\pm$ 10.03	8.34 $\pm$ 2.99	11.11 $\pm$ 5.29
i-pentane	13.05 $\pm$ 12.06	22.53 $\pm$ 4.51	3.34 $\pm$ 1.98	9.60 $\pm$ 3.74
i-butane	11.60 $\pm$ 7.23	20.61 $\pm$ 5.15	7.06 $\pm$ 4.34	11.88 $\pm$ 3.97
n-hexane	3.92 $\pm$ 2.27	7.20 $\pm$ 1.20	1.45 $\pm$ 0.70	2.04 $\pm$ 0.71
2,2,4-trimethylpentane	2.48 $\pm$ 1.27	---	2.22 $\pm$ 0.96	---
2,4-dimethylpentane	0.59 $\pm$ 0.36	---	0.39 $\pm$ 0.19	---
3-methylpentane	0.56 $\pm$ 0.28	4.74 $\pm$ 0.79	0.41 $\pm$ 0.20	1.81 $\pm$ 0.54
Olefins				
Ethene	19.34 $\pm$ 6.84	21.89 $\pm$ 10.95	10.38 $\pm$ 3.87	12.19 $\pm$ 7.32
Propene	11.96 $\pm$ 3.38	8.14 $\pm$ 2.71	6.47 $\pm$ 1.95	3.76 $\pm$ 1.05
1-butene	2.39 $\pm$ 1.03	---	1.22 $\pm$ 0.60	---
1,3-Butadiene	1.81 $\pm$ 0.60	0.70 $\pm$ 0.18	0.82 $\pm$ 0.32	0.29 $\pm$ 0.06
trans-2-butene	1.48 $\pm$ 0.89	1.69 $\pm$ 0.42	1.28 $\pm$ 0.64	0.59 $\pm$ 0.20
cis-2-butene	1.42 $\pm$ 0.93	1.37 $\pm$ 0.34	0.85 $\pm$ 0.44	0.64 $\pm$ 0.35
Isoprene	1.33 $\pm$ 0.77	0.24 $\pm$ 0.05	0.39 $\pm$ 0.23	0.00 $\pm$ 0.11
Aromatics				
Toluene	8.99 $\pm$ 5.18	17.88 $\pm$ 2.55	3.34 $\pm$ 1.91	5.90 $\pm$ 1.51
Benzene	1.63 $\pm$ 0.42	4.80 $\pm$ 0.80	0.80 $\pm$ 0.26	1.78 $\pm$ 0.41
m,p-xylene	1.42 $\pm$ 0.58	7.30 $\pm$ 0.91	0.42 $\pm$ 0.25	2.44 $\pm$ 0.66
o-xylene	1.09 $\pm$ 0.58	2.37 $\pm$ 0.30	0.29 $\pm$ 0.22	0.94 $\pm$ 0.24
Ethylbenzene	0.82 $\pm$ 0.45	2.07 $\pm$ 0.26	0.33 $\pm$ 0.22	0.73 $\pm$ 0.17
1,2,4-trimethylbenzene	0.78 $\pm$ 0.42	2.67 $\pm$ 0.30	0.24 $\pm$ 0.18	0.85 $\pm$ 0.22

Table 2. Emission sources of NMCHs in Mexico City (after Vega et al., 2000; Mugica et al., 2002)

Emission sources	Gasoline engines	Diesel engines	Fossil fuel storage and distribution	LPG combustion	Wood and biofuel combustion	Solvent use	Industrial processes & degreasing	Asphalt application	Food cooking	Vegetation
Alkanes										
Ethane	✓	✓		✓	✓		✓	✓	✓	
Propane	✓	✓	✓	✓	✓		✓	✓	✓	
i-butane	✓	✓	✓	✓	✓		✓	✓	✓	
n-butane	✓	✓	✓	✓	✓		✓	✓	✓	
i-pentane	✓	✓	✓	✓			✓	✓	✓	
3-methylpentane	✓	✓	✓					✓	✓	
n-hexane	✓	✓	✓	✓			✓	✓	✓	
2,4-dimethylpentane	✓	✓	✓				✓	✓		
2,2,4-trimethylpentane	✓	✓	✓	✓			✓	✓	✓	
Olefins										
Ethene	✓	✓			✓		✓	✓	✓	
Propene	✓	✓		✓	✓		✓	✓	✓	
1,3-Butadiene	✓									
1-butene		✓	✓	✓	✓			✓		
trans-2-butene	✓	✓		✓					✓	
cis-2-butene	✓	✓		✓					✓	
Isoprene	✓									✓
Aromatics										
Benzene	✓	✓	✓		✓	✓	✓	✓	✓	
Toluene	✓	✓	✓		✓	✓	✓	✓	✓	
Ethylbenzene	✓	✓	✓		✓	✓	✓	✓		
m,p-xylene	✓	✓	✓		✓	✓	✓	✓		
o-xylene	✓	✓	✓		✓	✓	✓	✓		
1,2,4-trimethylbenzene	✓	✓				✓	✓

Fig. 1. Design of the VOC monitoring network of Mexico City. The black lines at 45° intersecting at the emissions centroid delimit the upwind and downwind sectors at the northeast and southwest of the urban sprawl. The stations were selected following the methodology described in the text covering areas with different characteristics in terms of ozone and VOC patterns. The urban sprawl covers municipalities from the State of Mexico and Federal District. The blue and red spots indicate the selected air quality monitoring station for VOC monitoring. The 2012 campaign included only the stations MER and PED. The wind roses indicate the main wind direction during the ozone season.

Fig. 2. Geographical location of the two monitoring stations included in the 2012 campaign. The map in the center shows their location within the city and the VOC emissions distribution according to the emissions inventory of 2008.

Fig. 3. Monthly data coverage for each monitored species at both sites.

Fig. 4. Diurnal variations of selected NMHCs and other trace gases measured during the first six months of 2012 at La Merced site. The black lines with white circles indicate the geometric average diurnal patterns on weekdays during the ozone season (Mar – May). Public holidays have been excluded. Profiles on Saturdays and Sundays correspond also to the ozone season and are indicated by the continuous blue and red lines with circles. The grey shaded areas represent ± 1 standard deviation from the average profiles on weekdays during the ozone season and give an indication of the day-to-day variability at every hour of the day. The dashed lines indicate the monthly geometric averages.

929

930 Fig. 5. Diurnal variations of selected NMHCs and other trace gases measured during the first six
 931 months of 2012 at Pedregal site. The black lines with white circles indicate the geometric average
 932 diurnal patterns on weekdays during the ozone season (Mar – May). Public holidays have been
 933 excluded. Profiles on Saturdays and Sundays correspond also to the ozone season and are
 934 indicated by the continuous blue and red lines with circles. The grey shaded areas represent ± 1
 935 standard deviation from the average profiles on weekdays during the ozone season and give an
 936 indication of the day-to-day variability at every hour of the day. The dashed lines indicate the
 937 monthly geometric averages.

Fig. 6. Average diurnal patterns of the energy fluxes measured in the residential neighbourhood of Escandón (a - d) and meteorological parameters measured at La Merced (e – h) and Pedregal (i – l) sites during the first six months of 2012. The black lines with white circles indicate the average diurnal patterns during the ozone season (Mar – May). The grey shaded areas represent ± 1 standard deviation from the average profiles and give an indication of the day-to-day variability at every hour of the day. The dashed lines indicate the monthly averages. The sensible (Q_H) and latent (Q_E) heats were measured by eddy covariance. The incoming and outgoing shortwave components of the net radiation (Q^*) were directly measured. The longwave components were estimated using the approach described in Velasco et al. (2011) using cloudiness data from the city airport. The storage heat (ΔQ_s) includes the anthropogenic heat and was calculated as the residual of Q^* and the other two energy components.

Fig. 7. Reactivity with the OH radical by NMHC group during the morning rush hour (6 – 9 h) on weekdays at the two urban sites monitored during the 2012 ozone season and the MCMA-2003 field campaign. Colored bars indicate averages and black bars $\pm$ one standard deviation. The reactivity is calculated as the product of the individual NMHC concentrations (molecule cm^{-3}) with their corresponding OH reaction rate coefficients at 298 K and 1 atm ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \times 10^{-12}$, Atkinson, 1994, 1997).

PEDREGAL (PED)		CO	NOx	ethane	propane	i-butane	n-butane	i-pentane	3-methylpentane	hexane	2,4-dime- thylpentane	2,2,4-tri-methyl- pentane	ethene	propene	1-3-butadiene	1-butene	t-2-butene	c-2-butene	isoprene	benzene	toluene	ethylbenzene	m,p-xylene	o-xylene	1,2,4-trimethyl- benzene
CO		1.00																							
NOx		0.83	1.00																						
Ethane		0.63	0.59	1.00																					
Propane		0.35	0.40	0.56	1.00																				
i-butane		0.40	0.47	0.61	0.95	1.00																			
n-butane		0.37	0.43	0.60	0.94	0.99	1.00																		
i-pentane		0.10	0.15	0.15	0.08	0.17	0.20	1.00																	
3-methylpentane		0.65	0.66	0.64	0.53	0.61	0.61	0.45	1.00																
Hexane		0.61	0.62	0.74	0.55	0.61	0.61	0.32	0.88	1.00															
2,4-dimethylpentane		0.65	0.72	0.68	0.42	0.51	0.50	0.38	0.82	0.80	1.00														
2,2,4-trimethylpentane		0.81	0.77	0.63	0.48	0.51	0.49	0.17	0.77	0.75	0.79	1.00													
Ethane		0.79	0.77	0.57	0.34	0.42	0.40	0.14	0.64	0.69	0.74	0.77	1.00												
Propene		0.67	0.67	0.69	0.83	0.84	0.81	0.13	0.72	0.76	0.70	0.78	0.65	1.00											
1-3-butadiene		0.67	0.71	0.79	0.73	0.80	0.78	0.27	0.79	0.83	0.81	0.80	0.73	0.92	1.00										
1-butene		0.60	0.62	0.64	0.82	0.85	0.82	0.23	0.74	0.77	0.73	0.73	0.58	0.92	0.94	1.00									
t-2-butene		0.50	0.55	0.57	0.75	0.81	0.80	0.46	0.76	0.74	0.73	0.66	0.48	0.82	0.88	0.92	1.00								
c-2-butene		0.49	0.54	0.57	0.72	0.79	0.79	0.51	0.78	0.73	0.72	0.65	0.48	0.78	0.86	0.88	0.97	1.00							
Isoprene		0.39	0.47	0.45	0.31	0.43	0.44	0.75	0.71	0.61	0.72	0.52	0.43	0.46	0.65	0.58	0.77	0.78	1.00						
Benzene		0.84	0.75	0.71	0.51	0.56	0.54	0.20	0.74	0.81	0.80	0.79	0.76	0.79	0.81	0.75	0.66	0.64	0.53	1.00					
Toluene		0.49	0.53	0.62	0.66	0.68	0.67	0.13	0.68	0.75	0.56	0.63	0.53	0.76	0.72	0.72	0.64	0.62	0.39	0.65	1.00				
ethylbenzene		0.72	0.75	0.66	0.63	0.68	0.65	0.16	0.72	0.77	0.77	0.77	0.70	0.81	0.85	0.80	0.71	0.69	0.52	0.85	0.77	1.00			
m,p-xylene		0.67	0.71	0.67	0.68	0.71	0.69	0.17	0.74	0.78	0.76	0.77	0.67	0.85	0.86	0.82	0.73	0.71	0.53	0.81	0.82	0.95	1.00		
o-xylene		0.64	0.69	0.66	0.69	0.71	0.69	0.16	0.72	0.78	0.74	0.74	0.62	0.82	0.85	0.80	0.73	0.71	0.52	0.78	0.80	0.94	0.96	1.00	
1,2,4-trimethylbenzene		0.72	0.76	0.70	0.58	0.64	0.61	0.17	0.75	0.75	0.78	0.77	0.67	0.76	0.83	0.76	0.69	0.69	0.55	0.79	0.70	0.89	0.87	0.85	

959

960 **Fig. 8.** Correlations (r^2) between mixing ratios of NMHCs, CO and NO_x measured along the morning rush hour (6 – 9 h) at Pedregal.
961 Correlations were taken from the liner-least-squares fits. Cells marked in yellow and blue indicate correlations > 0.8 and between 0.7 and
962 0.8, respectively.

LA MERCED (MER)		CO	NO _x	ethane	propane	i-butane	n-butane	i-pentane	3-methylpentane	hexane	2,4-dime- thylpentane	2,2,4-tri-methyl- pentane	ethylene	propene	1-3-butadiene	1-butene	t-2-butene	c-2-butene	isoprene	benzene	toluene	ethylbenzene	m,p-xylene	o-xylene	1,2,4-trimethyl- benzene
CO		1.00																							
NO _x		0.91	1.00																						
Ethane		0.58	0.60	1.00																					
Propane		0.68	0.63	0.60	1.00																				
i-butane		0.71	0.65	0.58	0.94	1.00	0.98																		
n-butane		0.69	0.62	0.54	0.91	0.98	1.00	1.00																	
i-pentane		0.40	0.33	0.28	0.39	0.53	0.59	1.00																	
3-methylpentane		0.66	0.63	0.52	0.66	0.65	0.65	0.57	1.00																
Hexane		0.62	0.66	0.54	0.60	0.61	0.61	0.49	0.61	1.00															
2,4-dimethylpentane		0.72	0.62	0.43	0.63	0.67	0.69	0.51	0.72	0.51	1.00														
2,2,4-trimethylpentane		0.75	0.72	0.58	0.70	0.64	0.62	0.38	0.80	0.59	0.64	1.00													
Ethane		0.86	0.83	0.64	0.58	0.58	0.55	0.33	0.64	0.60	0.60	0.72	1.00												
Propene		0.90	0.86	0.66	0.86	0.85	0.82	0.43	0.73	0.67	0.72	0.82	0.83	1.00											
1-3-butadiene		0.89	0.83	0.57	0.67	0.74	0.73	0.49	0.65	0.59	0.73	0.68	0.81	0.89	1.00										
1-butene		0.83	0.77	0.61	0.80	0.85	0.85	0.55	0.71	0.65	0.73	0.73	0.75	0.92	0.90	1.00									
t-2-butene		0.64	0.56	0.40	0.58	0.70	0.75	0.85	0.65	0.48	0.69	0.60	0.56	0.69	0.75	0.80	1.00								
c-2-butene		0.64	0.57	0.46	0.64	0.74	0.81	0.84	0.67	0.57	0.71	0.62	0.56	0.71	0.74	0.81	0.96	1.00							
Isoprene		0.68	0.58	0.38	0.55	0.67	0.71	0.79	0.67	0.43	0.74	0.52	0.58	0.89	0.88	0.84	0.88	0.86	1.00						
Benzene		0.88	0.82	0.60	0.70	0.71	0.70	0.41	0.75	0.64	0.74	0.82	0.84	0.89	0.88	0.84	0.88	0.65	0.68	1.00					
Toluene		0.49	0.46	0.39	0.60	0.60	0.60	0.30	0.62	0.51	0.42	0.51	0.40	0.56	0.47	0.54	0.45	0.50	0.38	0.49	1.00				
Ethylbenzene		0.83	0.79	0.59	0.78	0.79	0.78	0.41	0.72	0.66	0.67	0.75	0.72	0.86	0.83	0.83	0.63	0.65	0.66	0.88	0.66	1.00			
m,p-xylene		0.77	0.75	0.58	0.76	0.77	0.75	0.39	0.72	0.66	0.63	0.74	0.69	0.85	0.78	0.81	0.59	0.62	0.60	0.86	0.65	0.96	1.00		
o-xylene		0.75	0.71	0.53	0.72	0.77	0.75	0.39	0.65	0.61	0.58	0.64	0.63	0.79	0.76	0.76	0.56	0.59	0.60	0.82	0.62	0.93	0.95	1.00	
1,2,4-trimethylbenzene		0.85	0.79	0.57	0.77	0.78	0.76	0.43	0.72	0.53	0.67	0.77	0.73	0.89	0.82	0.82	0.63	0.65	0.68	0.87	0.57	0.90	0.87	0.87	1.00

Fig. 9. Correlations (r^2) between mixing ratios of NMHCs, CO and NO_x measured along the morning rush hour (6 – 9 h) at La Merced. Correlations were taken from the liner-least-squares fits. Cells marked in yellow and blue indicate correlations > 0.8 and between 0.7 and 0.8, respectively.

Fig. 10. Relationships between mixing ratios of ethene (C_2H_4), n-hexane (C_6H_{14}) and benzene (C_6H_6) with toluene (C_7H_8) measured at the Pedregal and La Merced sites in 2012 during 6 months and the MCMA-2003 field campaign during 12 days of April 2003. The 2003 study included the collection of samples during mobile vehicle chase experiments; their relationships are included for comparison to the vehicle exhaust signature. Open and filled markers indicate individual 1-hour data collected in 2012 throughout the diurnal course and the morning rush hour (6 – 9 h), respectively. The solid and dashed lines indicate the best average molar ratios for the morning rush-hour samples of 2012 and all samples available from 2003. The length of the lines indicates the range of observed concentrations for each data set. The average ratios correspond to the slopes of the linear-least-square fits to the measurements, with the y -intercept of the line forced through zero. The slopes reported by Parrish et al. (2009) for 71 US cities in the eighties, and Tokyo and Beijing during the first lustrum of this century are included in the figure annotation for comparison with data from other cities.

Fig. 11. Normalized diurnal profiles of selected NMHCs and criteria pollutants (a), and isoprene, and ambient temperature (b) measured at La Merced site during the ozone season and from Feb-Jun 2012, respectively. The mean hourly mixing ratios obtained from the geometric means were normalized to the maximum diurnal mean of every individual compound or parameter. In both panels the yellow shaded area corresponds to the incoming shortwave radiation ($K\downarrow$) measured at the Escandón site during the same period of time as a component of Q^* shown in Fig. 6a. $K\downarrow$ represents to the actinic flux available for daytime photochemistry.