



Volatile organic compounds in the atmosphere of Mexico City



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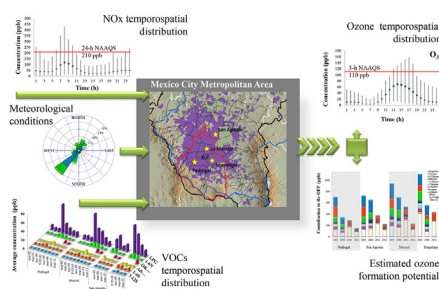
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HIGHLIGHTS

- Atmospheric concentration of 64 VOCs were measured in Mexico City during 2011–2012.
- VOC compounds related to LPG leakages exhibited the highest concentrations.
- Correlation analysis among VOCs indicates that they also come from gasoline vehicles.
- Benzene is the toxic VOC that represent the highest risk to Mexicans.
- Toluene is the VOC with the highest ozone formation potential in Mexico City.

GRAPHICAL ABSTRACT



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ABSTRACT

The Mexico City Metropolitan Area (MCMA) is one of the most polluted megacities in North America. Therefore, it is an excellent benchmark city to understand atmospheric chemistry and to implement pilot countermeasures. Air quality in the MCMA is not within acceptable levels, mainly due to high ground levels of ozone (O_3). Tropospheric O_3 is a secondary pollutant formed from the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides and sunlight. To gain a better understanding of O_3 formation in megacities, evaluate the effectiveness of already-implemented countermeasures, and identify new cost-effective alternatives to reduce tropospheric O_3 concentrations, researchers and environmental authorities require updated concentrations for a broader range of VOCs. Moreover, in an effort to protect human health and the environment, it is important to understand which VOCs exceed reference safe values or most contribute to O_3 formation, as well as to identify the most probable emission sources of those VOCs. In this work, 64 VOCs, including 36 toxic VOCs, were measured at four sites in the MCMA during 2011–2012. VOCs related to liquefied petroleum gas leakages exhibited the highest concentrations. Toxic VOCs with the highest average concentrations were acetone and ethanol. The toxic VOC benzene represented the highest risk to Mexican citizens, and toluene

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contributed the most to O₃ formation. Correlation analysis indicated that the measured VOCs come from vehicular emissions and solvent-related industrial sources.

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1. Introduction

The Mexico City Metropolitan Area (MCMA) is one of the largest cities in the world, with a population of 20.4 million inhabitants. Forty years ago, the MCMA included 8.8 million residents, a value that is expected to reach 25 million by 2025 (United Nations, 2011). This rapid growth has led to serious environmental and health problems. The MCMA is located inside an air basin at a latitude of 19.5°N and is surrounded by mountain ranges on three sides (to the west, south, and east), with a broad opening in the north and a gap in the southwest (Lei et al., 2007). The topography and meteorology of this air basin make wind circulation difficult, causing frequent thermal inversions and pollutant stagnation (De Foy et al., 2008).

In 2011, the Metropolitan Air Quality Index (IMECA) exceeded acceptable levels during 241 days (Secretaría de Medio Ambiente del Distrito Federal, 2012). High ground-level ozone (O₃) concentrations, along with elevated particulate matter (PM) concentrations, are mainly responsible for the pollution issue and make the MCMA of the most polluted cities in North America (Molina et al., 2007). Exposure to ground-level O₃ is harmful to human health and causes respiratory diseases, decreasing the capability of the lungs to perform normal functions. Tropospheric O₃, black carbon, and methane are short-lived pollutants that, after CO₂, are the most important contributors to the global warming effect, with multiple harmful impacts on human health, agriculture, and ecosystems (Institute for Governance & Sustainable Development, 2013). Tropospheric O₃ is a secondary pollutant formed from the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x) and sunlight. The rate of O₃ formation varies, depending on the amount of NO_x and VOCs in the atmosphere. Under some conditions, O₃ production increases with VOCs whereas, in others, it does not change or decreases with NO_x. To formulate effective environmental policies, the relationship between VOCs and NO_x must be studied for each location (Sillman, 1999).

VOCs are emitted as gases from various daily emission sources, such as driving cars (Thornhill et al., 2010), painting buildings (Celebi and Vardar, 2008), and cooking. Some VOCs, such as isoprene and other monoterpenes, are naturally emitted into the atmosphere (Lindfors and Laurila, 2000). Other VOCs are considered to be toxic pollutants and have short- and long-term adverse effects on human health, including irritation of the mucous membranes, eyes, and throat, as well as mutagenic, carcinogenic, and teratogenic properties (Secretaría de Medio Ambiente del Distrito Federal, 2012). The formation of O₃ is influenced by the presence of NO_x in the atmosphere. By themselves, NO_x compounds are hazardous to human health, causing respiratory illnesses. NO_x (NO + NO₂) are emitted into the atmosphere from anthropogenic and natural sources, such as fossil fuel combustion and biomass burning (Zhang et al., 2003).

Various studies in the MCMA have found that air quality problems due to NO_x are caused by industrial sources, vehicles (Secretaría de Medio Ambiente y Recursos Naturales de México, 2010), and an inefficient public transportation system (Islas et al., 2011). In recent decades, the Mexican government has focused on reducing VOC and NO_x emissions, aiming to improve air quality in this region (Molina et al., 2007, 2009). To evaluate the effectiveness of these countermeasures, several measurement campaigns were

carried out (Table 1) to determine the VOC concentrations in the MCMA over time.

Between March 1992 and March 1993, the Mexico City Air Quality Research Initiative campaign measured 25 VOCs (Streit and Guzman, 1996; Los Alamos National Laboratory, 1994). From 1992 to 2001, the MCMA campaign measured 9 VOCs during short periods of time (3–30 days) in March and November (Arriaga-Colina et al., 2004). This MCMA campaign was extended to include the measurements of 104 VOCs during February 2002 and April 2003. It also analyzed the interaction between emission patterns and meteorological parameters (Molina et al., 2007; Velasco et al., 2008). Two simultaneous campaigns were performed in March 2006: the MCMA 2006 campaign that included the analysis of 13 VOCs, and the Megacity Initiative: Local and Global Research Observations (MILAGRO) campaign that included the analysis of 50 VOCs at an urban site and 38 VOCs at a downwind site (De Foy et al., 2008; Molina et al., 2010). The MILAGRO campaign determined the sources, concentrations, and transformation processes of gases and fine particles emitted to the MCMA atmosphere by using a wide range of instruments at ground sites, on aircraft, and on satellites (Molina et al., 2010).

Since the last campaign of 2005–2006, the Mexican government has implemented several additional measures to reduce VOC emissions (Table 2). Efforts have been made to improve fuel quality, adopt cleaner technologies in automobiles, and implement programs for limiting the emission of pollutants from industries and vehicles (Molina et al., 2007, 2009). Assessment of the effectiveness of these new measures will require a new VOC measurement campaign to describe the temporospatial variations of VOCs in recent years. To assess the severity of the environmental problem, results obtained for toxic VOCs will need to be compared to reference concentrations. However, to date, VOCs have not been included in the Mexican Air Quality Standard, and a proper reference value for such comparisons has not been available. Finally, the database of VOC concentrations that is used for scientific purposes needs to be broadened and updated. A better understanding of O₃ formation in the MCMA could lead to the development of alternative approaches for reducing tropospheric O₃ concentrations and mitigating climate change due to these pollutants.

To address these needs, a new VOC measurement campaign in the MCMA was performed during 2011 and 2012. This campaign included 64 VOCs, 36 of which are toxic. This paper reports the results obtained during this campaign and estimates the O₃ formation potential (OFP) for each monitoring site. The results are compared with those of previous campaigns, with concentrations obtained for other megacities, and with reference values. Finally, probable emission sources for the measured VOCs are estimated. Conclusions reached in this work are relevant for the formulation of new, cost-effective strategies to control air pollution in megacities.

2. Materials and methods

2.1. Field campaign and sampling sites

Meteorological parameters of the MCMA are monitored by 12 automatic stations that constitute the Atmospheric Monitoring Network (REDMET). Fig. 1 shows the location of the four

Table 1
VOC measurement campaigns in the MCMA.

Campaign	Refs	VOCs	Sampling time and sites	Main results
MARI: Mexico City Air Quality Research Initiative. September 1990 February 1991 March 1992 March 1993 AGUILA project	(Ruiz et al., 1996) (Streit and Guzman, 1996) (Nickerson et al., 1992)	25 Ozone probe	Mar 3–6, 1992: Merced, Tlalnepantla, Xalostoc, Pedregal, Reforma and Cuatitlán Mar 23–31, 1993: 3 h canister; Xalostoc, Merced, Pedregal Feb 1991: Vertical measurement	<ul style="list-style-type: none"> • MCMA exhibit a NO_x limited behavior. • Merced shows high concentration of ethylene, acetylene, CO, and MTBE, which could be related to vehicle traffic. • MARI project provided a significant database for air quality modeling of the MCMA. Its emission inventory was significantly improved. • The AGUILA project provided aircraft atmospheric measurements over the MCMA • The longest record of VOC concentration in Mexico City. • Despite the growth in the vehicular fleet and population, results showed that VOC concentrations have not increased.
MCMA 1992–2001 VOCs record measurements	(Arriaga-Colina et al., 2004)	9 304 total samples	Mar and Nov: 3–30 days 3 h canister samples, Xalostoc, La Merced, Pedregal, Tlalnepantla, Iztapalapa	<ul style="list-style-type: none"> • Non-methane hydrocarbon concentrations were dominated by alkanes (60%), followed by aromatics (15%), and olefins (5%). • VOCs depend strongly on the interaction of vehicular traffic and meteorological parameters.
MCMA 2002–2003 Mexico City Metropolitan Area Feb 2002 Apr 2003	(Molina et al., 2007; Velasco et al., 2008; Velasco et al., 2007)	13, CENICA 58, Urban site. 10 min samples to 3 h canisters	CENICA: 3 Apr–May 2, 2003. Pedregal, La Merced, Xalostoc, Santa Ana, UNAM, La Reforma, Cuatitlán	<ul style="list-style-type: none"> • Evaporative fuel and industrial emission are important sources of aromatic VOCs. • LPG use continues to be an important source of low molecular weight alkanes • There are large non-biogenic sources of methanol in the MCMA basin.
MCMA 2006 MILAGRO: Megacity Initiative: Local and Global Research Observations Mar 2006	(De Foy et al., 2008; Molina et al., 2010)	50 (T0) 38 (T1) 10 min samples to 3 h Canisters	Mar 17–30, 2006: T0 urban site T1 downwind site	

meteorological stations located near downtown Mexico City: San Agustín, La Merced, Iztapalapa, and Pedregal. These meteorological stations report that the most frequent wind trajectory travels from northeast to southwest (Arriaga-Colina et al., 2004). The air quality of the MCMA has been monitored continuously since the late 1980s. Currently, the MCMA Air Quality Monitoring Network (RAMA) comprises 24 automatic stations that measure CO, NO₂, PM₁₀, PM_{2.5}, SO₂, and O₃. Fig. 2 shows the monthly average variations of these pollutants during 2005, 2006, 2011, and 2012. As previous campaigns were developed on the four aforementioned sites (Fig. 1), which represent different land uses within the MCMA (Table 3), these four sites were selected to develop the present monitoring campaign.

Currently, there is no consensus on an exact definition for VOCs. The most accepted definitions describe organic compounds as those that contain at least one C or one C–H bond, and volatile compounds as those with a boiling temperature under 250 °C at

standard pressure or a vapor pressure greater than 13.3 kPa under standard conditions (USEPA, 1999a). The number of compounds that fall within this category is quite large (10³–10⁴). The USEPA declared 189 of these compounds to be hazardous air pollutants and recommended methods for measuring 97 VOCs within this group (USEPA, 1999b). These methods are applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters and measured at the parts per billion by volume (ppbv) level. In practice, the actual number of VOCs measured is limited by the number of VOCs included within the gas used during the calibration process.

Table 4 lists the 64 VOCs that were measured in this study. These VOCs included 21 saturated alkanes of 1–12 carbons in length, 10 unsaturated light alkenes of 1–6 carbons in length, 4 aromatics, 6 BTEX, and 22 oxygenated and halogenated hydrocarbons. Thirty-six of the measured VOCs are considered to be toxic. VOCs measured

Table 2
Actions by the Mexican government aimed at controlling air pollution in the MCMA (Secretaría de Medio Ambiente del Distrito Federal, 2010).

Year	Actions
2005	<ul style="list-style-type: none"> • Metrobus construction along Insurgentes Avenue.
2006	<ul style="list-style-type: none"> • Public transport network (RTP) fleet was renewed. 100% of buses had new engine technologies. • Inauguration of arterial road “Eje vial” 3 to the east. • Regulation NOM-086 was published concerning to the physicochemical fuel conditions. • Distribution of Premium gasoline with ultra-low sulfur content. • IMECA levels were reduced for the application of the environmental contingency program.
2007	<ul style="list-style-type: none"> • Regulation NOM-041-SEMARNAT-2004 took effect in the city with tighter standard emission levels for vehicles. • Regulation NOM-045-SEMARNAT was published regarding diesel vehicle exhaust emissions. • The foreign-plated vehicles or vehicles from a state other than the State of Mexico or the Federal District were required to apply to the verification program in order to circulate inside the MCMA. • Regulation NADF-010-AMBT-2006 was published to improve gasoline vapor recovery systems.
2008	<ul style="list-style-type: none"> • Regulation NADF-011-AMB-2007 was published to establish VOCs maximum permissible emissions from point sources. • The suburban train began to operate in the route Buenavista–Cuatitlán. • The Metrobus line 2 was inaugurated. • 6 air pollution measures were implemented to reduce the pollution in the city.
2009	<ul style="list-style-type: none"> • Distribution of Magna gasoline and diesel with ultra-low sulfur content. • Inauguration of “zero” emission avenue “Eje central” and the first stage of the elevated highway (viaducto bicentenario) Torres-Lomas verdes.
2010	<ul style="list-style-type: none"> • The Metrobus line 3 began to operate in the route Etiopia–Tenayuca. • Regulation NOM-022-SSAI-2010 was published with new criteria to address the air pollution from SO₂ emissions.

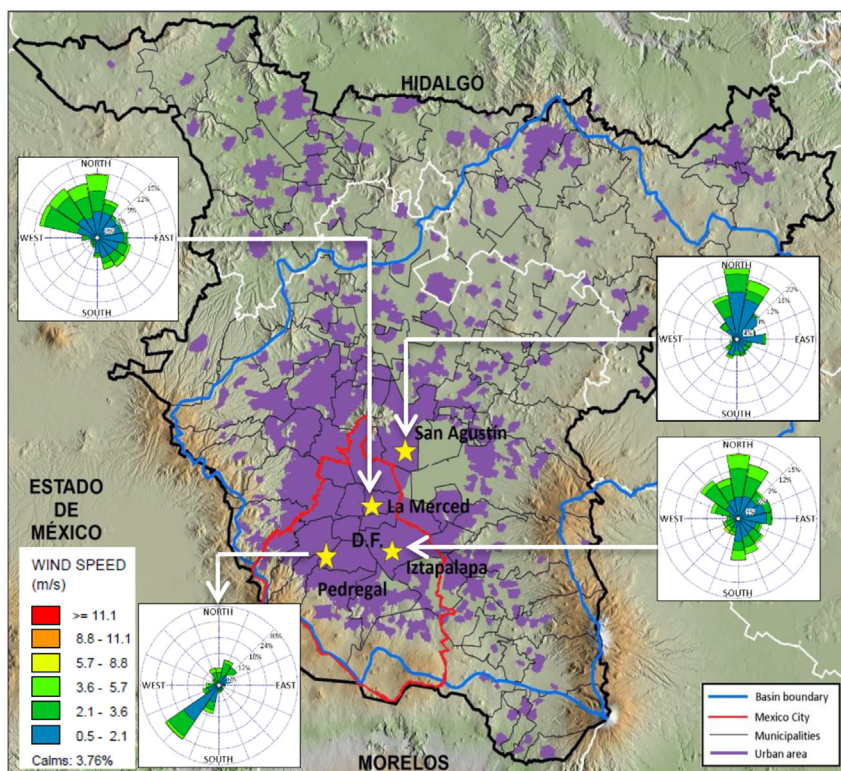


Fig. 1. Location of meteorological stations and VOC monitoring sites within the MCMA.

during the 2005–2006 and 2011–2012 campaigns are listed in the Supporting Information (SI), Tables S1–S3.

VOC measurements were carried out during the cold-dry season (Nov–Dec) and the hot-dry season (Mar–Apr; Table 2). These seasons were selected to characterize the worst scenarios in terms of O_3 concentration over the MCMA. The highest O_3 concentrations were found during the hot-dry season, when temperature reaches its highest value (Fig. 2). This observation is reasonable, considering that O_3 is a secondary pollutant formed from the reaction of NO_x and VOCs in the presence of sunlight, and that high temperatures are associated with sunny days. NO_x reached peak values during the cold-dry season (Fig. 2); therefore, this season has a high potential for O_3 formation.

Sampling periods were designed to observe VOC emissions and transformations. Samples were taken over 3 h from 07:00 to 19:00 to observe hourly variations. Additionally, 24-h samples were taken to observe daily variations. In total, 18,309 samples were obtained and analyzed during the 2011–2012 campaign.

2.2. Methods for sampling and analysis

Stainless steel 6-L electro-polished canisters were used to obtain the samples. Canisters were heated and cleaned under vacuum before use. Air was pulled down into the canister through a 1/8" diameter Teflon tube by using a vacuum pump that provides a pressure of 55 cm Hg and a critical orifice that provides a passive method for controlling air flow. A funnel was used to facilitate the airflow into the canister and to prevent accumulation of dust or rainwater within the sample. Airflows were calibrated with a soap bubble meter at 4.2 and 33 mL/min for 24- and 3-h samples, respectively. Samples were collected by using a 24-V solenoid valve with a timer programmed to open and close the airflow into the canister. Samples were analyzed in two gas chromatographic (GC)

systems: GC with flame ionization detector (GC-FID) and GC with mass spectrometry (GC-MS).

The GC-FID system consists of a canister rack with a sample controller, humidity controller, sample concentrator, and gas chromatograph (HP 6890 Series Plus) equipped with a FID. This system was used for the analysis of VOCs considered as O_3 precursors, following the USEPA protocols established within the TO-14A method (USEPA, 1999a). Measurement detection limits of this system (presented in the SI for each VOC) varied from 0.12 for *n*-hexane to 0.39 ppb for isopentane. The system was calibrated with a certified standard VOC gas mixture at ambient concentrations (Sumitomo Seika Chemicals Co.). This gas mixture contains 58 O_3 -precursor VOCs that are diluted up to 0.05–50 ppb in ultra-high-purity nitrogen (99.995%) by using a dynamic gas diluter. Calibration curves for the measurement system showed high coefficients of determination ($R^2 > 0.99$), indicating high linearity and precision, as well as slopes close to 1, indicating high accuracy.

The sample concentrator is an adsorption/desorption trap that works in two modes. In the adsorption mode, samples are transported from the canister into an adsorption trap, which is packed with three adsorbent beds of 60–80 mesh: tenax, activated alumina, and activated carbon. Once the sample has been transported into the trap, it is cooled to 5 °C by liquid nitrogen. In the desorption mode, the trap is heated with electric resistance to desorb the compounds thermally at 250 °C. Then, the sample is transported directly to a chromatographic GS-Alumina POLT column (30 m × 0.53 mm ID) for final analysis.

The GC-MS system uses a canister rack with a sample controller, concentrator system, and gas chromatograph (Agilent 6890N) coupled to a mass spectrometer (Agilent 5975B). This system was used for the analysis of toxic organic compounds (listed in the SI), following the USEPA protocols established within the TO-15 method (USEPA, 1999b). Measurement detection limits of this

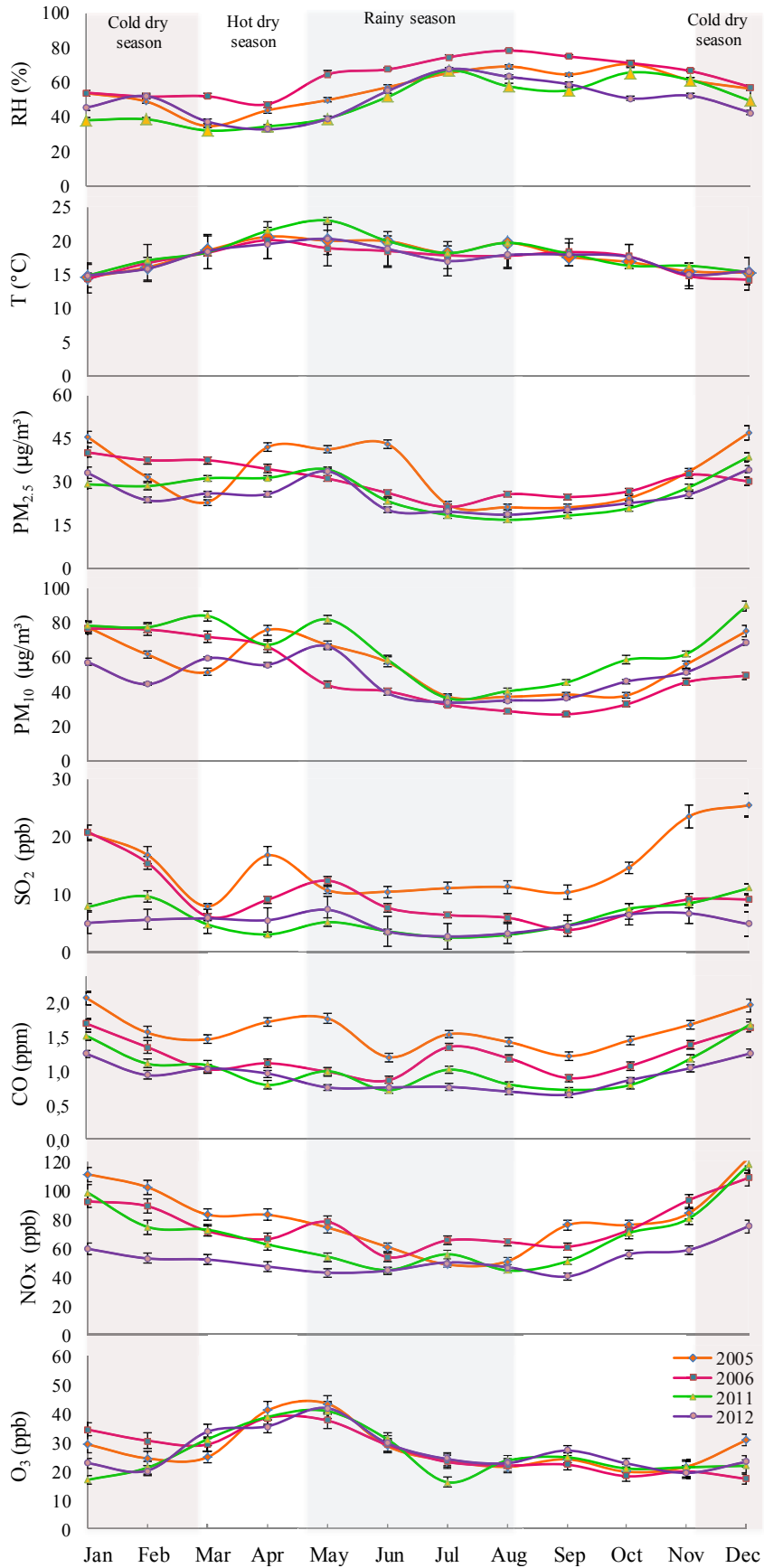


Fig. 2. Annual variations of pollutant concentration, temperature (T), and relative humidity (RH) in the MCMA during 2005, 2006, 2011, and 2012 (Secretaría de Medio Ambiente del Distrito Federal, 2013).

Table 3
Description of monitoring sites during the 2011–2012 VOC campaign in the MCMA.

Monitoring site	Location	Description
San Agustín (SAG)	Roof of the San Agustín Community Hospital 19°31'58"N, 99°1'49"W	Urban-industrial site with high NO _x and VOC emissions. Low traffic, mainly cars.
Merced (MER)	Roof of the Luis E. Ruíz Hospital 19°25'30" N, 99°7'11" W	High-traffic commercial and residential area located near to downtown. High pollution from vehicle emissions.
Pedregal (PED)	Roof of the John F. Kennedy Primary School 19°19'30"N, 99°12'15"W	Low-traffic residential area, with some vegetation nearby. Emissions from upwind.
Iztapalapa (IZT)	Roof of the National Environmental Research and Training Center building 19°21'32"N, 99°4'26"W	Residential, commercial, and medium industrial area, including small printing and painting industries. Heavy traffic consisting of old and new vehicles, as well as trucks.

system (Tables S1–S3) varied from 0.067 ppb for ethyl acetate to 0.34 ppb for hexachloro-1,3-butadiene. The system was calibrated by using a certified standard VOC gas mixture (Linde Spectra Environmental Gases) containing 63 toxic VOC compounds (including oxygenated and halogenated compounds) diluted up to 0.05–100 ppb in ultra-high-purity nitrogen (99.995%) by using a dynamic gas diluter. Calibration curves showed high coefficients of determination ($R^2 > 0.99$) and slopes close to 1.

Performance of the GC-MS system was verified with 1-bromo-3-fluoro benzene for quality control purposes and with bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d₅ as internal standards. The sample concentrator contained glass beds and tenax. Samples were transported from the canister to the concentrator and then cooled to –150 °C with liquid nitrogen. Concentrated samples were thermally desorbed at 180 °C and transported to a chromatographic column (DB 5MS, 60 m × 0.32 mm ID × 1.0 μm film thickness) for final analysis. The system was operated in the electron impact mode at 70 eV.

2.3. Methods for reporting results

Due to the large number of compounds analyzed in this study, reports and data analysis of the VOC concentrations were made by sorting VOCs into six different groups, according to their chemical functional group and carbon-chain length (Table 4). Each VOC belongs to only one group, and all compounds within a given group exhibit similar physicochemical properties. Propane, isobutane, and *n*-butane form the liquefied petroleum gas (LPG) group and, therefore, were excluded from the 1-6S group. Previous works have identified LPG as one of the most important sources of pollution in the MCMA.

Average VOC concentrations were calculated for each monitoring site. For each VOC, the 90% confidence interval was calculated by Student's *t* distribution. As with any measurement process, the determination of VOC concentrations was affected by random errors. To obtain reliable and representative values for the subsequent analysis, atypical values were identified and removed from the reference dataset. Two methods were used to identify outliers. First, data outside the confidence interval were identified by boxplots and classified as outliers. Second, outliers were detected in the functional boxplot by applying the 1.5 times the 50% central region empirical rule (Sun and Genton, 2011).

The OFP was calculated (in ppb) by multiplying the VOC concentration by the maximum incremental reactivity (MIR) index developed by Carter (Carter, 1994). This reactivity scale is based on calculations of relative O₃ impacts, expressed as the mass of the maximum additional O₃ formed per mass of VOC added to the emissions (g O₃/g VOC) for various compounds, under conditions in which the ambient O₃ concentration is most sensitive to changes in VOC emissions (Carter, 2010). Several studies have used OFP metrics to evaluate the influence of VOCs on O₃ formation and to

identify dominant VOCs and important differences in terms of the OFP (Chen and Luo, 2012; Suthawaree et al., 2012). The equation that represents this calculation is as follows:

$$OFP = \frac{1}{M_{O_3}} \sum MIR_i Y_i M_i \quad (1)$$

where Y_i is the volumetric concentration of compound *i* (in ppb), MIR_i is the MIR of compound *i* (in g O₃/g VOC_{*i*}), M_i is the molecular weight of compound *i* (in g/mol), and M_{O_3} is the molecular weight of O₃ (in g/mol).

3. Results and discussion

3.1. Hourly VOC concentrations

Propane and ethanol were the two most abundant VOCs found at all monitoring sites in 2012. Similarly to most of the VOCs measured, propane and ethanol exhibited the same pattern of a prominent peak in the early morning (05:00–09:00), followed by a constant decrement except for a slight increase around 21:00 (Fig. 3a and b). This hourly VOC concentration pattern was the same for all monitoring sites and is consistent with patterns reported in several previous works (Yang et al., 2005; White et al., 2008). The initial prominent peak during the early morning hours has been attributed to a combination of minimum boundary layer height, poor mechanical mixing due to atmospheric stability, and an increment in VOC emissions. The subsequent period of constant VOC decrement is due to continuous increments in the height of the boundary layer, the rate of mechanical mixing, and the rates of atmospheric chemical reactions that partially remove the most reactive species and form oxygenated VOCs. Finally, the slight increment in VOC concentrations observed during the early night hours has been attributed to a sharp decrement in the boundary layer height.

The hourly concentration of NO_x followed the same pattern as that of the VOCs, whereas the hourly O₃ concentration showed a prominent peak at 15 h (Fig. 3c and d). The 15-h time point does not necessarily correspond to the time when the VOC and NO_x concentrations and sunlight most favored the formation of O₃. Rather, it corresponds to the time when the interactions among meteorological conditions, atmospheric mixing height, the photochemical production rate of O₃, and O₃ depletion rate lead to the maximum volumetric O₃ accumulation.

During each season, the 24-h concentrations of the top 5 most abundant VOCs found at the Pedregal site remained essentially constant (Fig. 3e). The same behavior was observed at the other sites. Acetone, ethanol, *n*-butane, propane, and toluene were the most abundant species during the cold-dry season (Nov 2011), compared to propane, *n*-butane, ethanol, and acetone during the hot-dry season (Mar 2012). This observation is in agreement with findings from previous MCMA measurement campaigns, which

Table 4

VOCs measured during the 2011–2012 field campaign in the MCMA, grouped by emission source.

Tag	VOC group	VOC	CAS	MIR	Method		
1-6S	Saturated light alkanes, except LPG group: From 1 to 6 carbons in length. Potential source: Gasoline-vehicle emissions (Jorquera and Rappengluck, 2004; Watson et al., 2001)	Ethane	74-84-0	0.28	TO-14A		
		Cyclopentane	287-92-3	2.39	TO-14A		
		Isopentane	78-78-4	1.45	TO-14A		
		<i>n</i> -Pentane	109-66-0	1.31	TO-14A		
		Methylcyclopentane	96-37-7	2.19	TO-14A		
		Cyclohexane*	110-82-7	1.25	TO-15		
		Methylpentane	43133-95-5	1.50	TO-14A		
		<i>n</i> -Hexane*	110-54-3	1.24	TO-14A		
		2,2-Dimethylbutane	75-83-2	1.17	TO-14A		
		1-6N	Unsaturated light alkanes: From 1 to 6 carbons in length. Potential source: Petrochemical industry and vehicle emissions (Parrish et al., 2012; Schmitz et al., 2000)	Ethylene	74-85-1	9.00	TO-14A
Propylene	115-07-1			11.66	TO-14A		
1-Butene	106-98-9			9.73	TO-14A		
Cis-2-Butene	590-18-1			14.24	TO-14A		
Trans-2-Butene	624-64-6			15.16	TO-14A		
Trans-2-Pentene	646-04-8			10.56	TO-14A		
1-Pentene	109-67-1			7.21	TO-14A		
Cis-2-Pentene	627-20-3			10.38	TO-14A		
1,3 Butadiene*	106-99-0			12.61	TO-14A		
Acetylene	74-86-2			1.24	TO-14A		
LPG	Potential source: LPG leakage (Blake and Rowland, 1995; Wöhrnschimmel et al., 2010)			Propane	40811-14-1	0.49	TO-14A
				Isobutane	75-28-5	1.23	TO-14A
				<i>n</i> -butane	54597-66-9	1.15	TO-14A
7-12S	Saturated alkanes: From 7 to 12 carbons in length. Potential source: Diesel-vehicle emissions (Ogawa and Li, 2011)			Methylcyclohexane	108-87-2	1.70	TO-14A
		2,3-Dimethylpentane	565-59-3	1.34	TO-14A		
		Methylhexane	591-76-4	1.19	TO-14A		
		<i>n</i> -Heptane*	142-82-5	1.07	TO-15		
		Isooctane	540-84-1	1.26	TO-14A		
		2,3,4-Trimethylpentane	565-75-3	1.03	TO-14A		
		Methylheptane	592-27-8	1.07	TO-14A		
		<i>n</i> -Octane	111-65-9	0.90	TO-14A		
		Nonane	111-84-2	0.78	TO-14A		
		A&BTEX	Aromatics and BTEX (Benzene, toluene, and xylene). Potential source: Industry and gasoline-vehicle emissions, Oil based paint (Zheng et al., 2013; Yuan et al., 2009)	Benzene*	71-43-2	0.72	TO-15
Toluene*	108-88-3			4.00	TO-15		
Ethylbenzene*	100-41-4			3.04	TO-15		
<i>m</i> -Xylene*	108-38-3			9.75	TO-15		
<i>p</i> -Xylene*	106-42-3			5.84	TO-15		
<i>o</i> -Xylene*	95-47-6			7.64	TO-15		
Styrene*	79637-11-9			1.73	TO-15		
1-Ethyl,4-Methylbenzene*	622-96-8			7.39	TO-15		
1,3,5-Trimethylbenzene*	108-67-8			11.76	TO-15		
1,2,4-Trimethylbenzene*	95-63-6			8.87	TO-15		
Isopropylbenzene	98-82-8			2.52	TO-15		
O&HC	Oxygenated and halogenated hydrocarbons. Potential source: Exhaust and solvent emissions (Secretaría de Medio Ambiente del Distrito Federal, 2012; Guo and Murray, 2000)			Dichlorodifluoromethane*	75-71-8	–	TO-15
				Chloromethane*	74-87-3	0.04	TO-15
				Ethanol*	64-17-5	1.53	TO-15
		Trichlorofluoromethane*	75-69-4	–	TO-15		
		Acetone*	67-64-1	0.36	TO-15		
		Isopropyl alcohol*	67-63-0	0.61	TO-15		
		Chloromethylene*	2108-20-5	0.04	TO-15		
		Carbon disulfide*	75-15-0	0.25	TO-15		
		MTBE*	1634-04-4	0.73	TO-15		
		Vinyl acetate*	108-05-4	3.20	TO-15		
		Methyl Ethyl Ketone*	78-93-3	1.48	TO-15		
		Ethyl acetate*	141-78-6	1.73	TO-15		
		Trichloromethane*	67-66-3	0.02	TO-15		
		Tetrahydrofuran*	109-99-9	4.31	TO-15		
		Methyl isobutyl ketone*	108-10-1	3.14	TO-15		
		2-Hexanone*	591-78-6	3.14	TO-15		
Tetrachloroethylene*	127-18-4	0.64	TO-15				
1,3-Dichlorobenzene*	541-73-1	0.18	TO-15				
1,4-Dichlorobenzene*	106-46-7	0.18	TO-15				
1,2-Dichlorobenzene*	95-50-1	0.18	TO-15				
1,2,4-Trichlorobenzene*	120-82-1	–	TO-15				
Hexachlorobutadiene*	87-68-3	–	TO-15				

MIR: Maximum incremental reactivity value (gO_3/gVOC); CAS: Chemical Abstracts Service registry number; M: Molecular weight. *Considered as toxic. TO-14A and TO-15 represent USEPA compendium methods for determining VOCs in ambient air by collecting air in specially prepared canisters and analyzing by gas chromatography using flame ionization detector (TO-14A) and mass spectrometry (TO-15) (USEPA, 1999a; USEPA, 1999b).

have demonstrated that propane, propylene, and toluene are the VOCs that exhibit the highest concentrations (Wöhrnschimmel et al., 2010; Apel et al., 2010).

Fig. 3f shows the daily relative VOC composition for the Pedregal

site, as well as the percentages of the top 5 most abundant VOCs relative to the total VOC concentration at different hours of the day. Regardless of the hourly variations in VOC concentration, the relative VOC composition did not change drastically during the day.

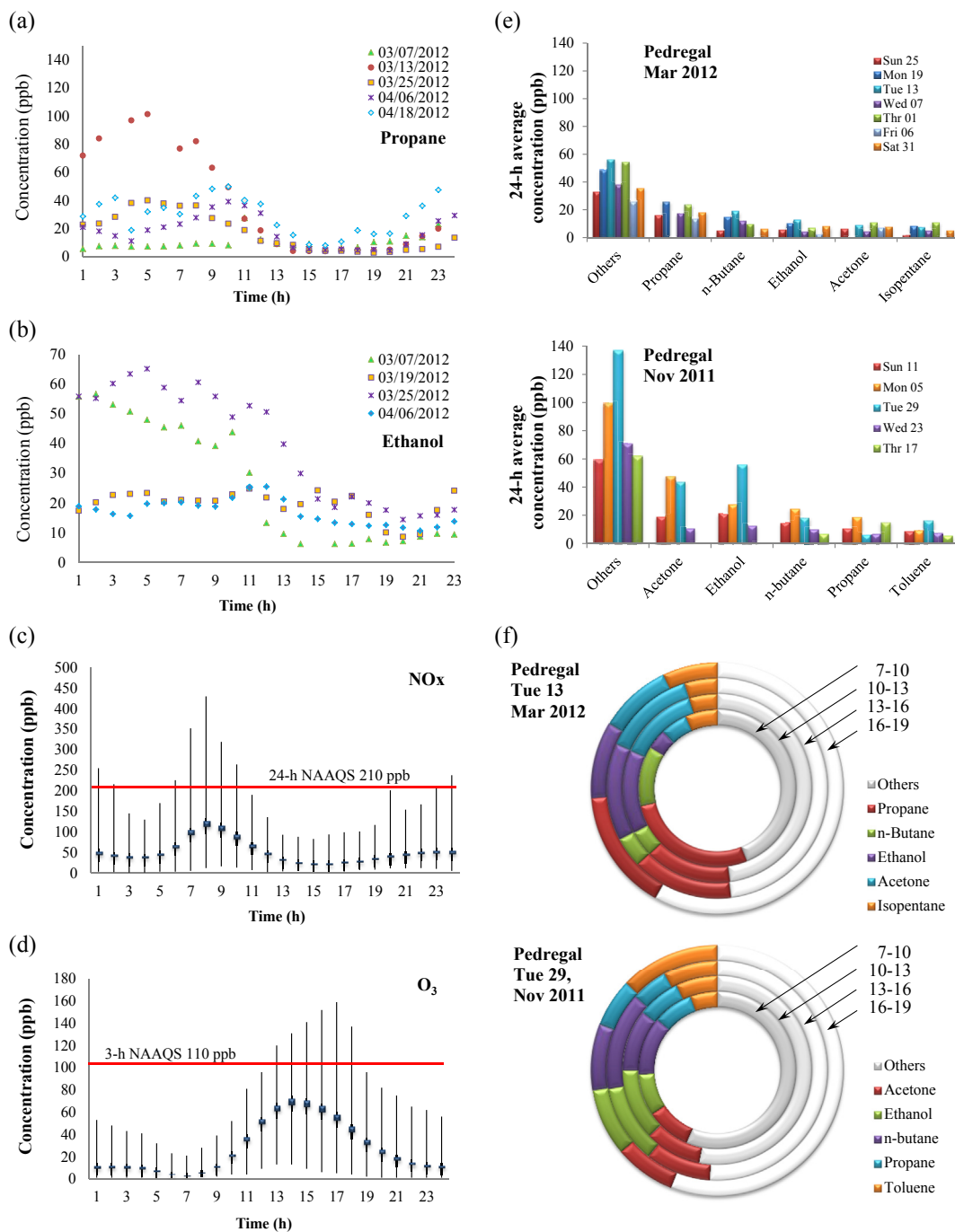


Fig. 3. Average hourly VOC concentration and composition at the Pedregal monitoring site in 2012. Hourly variations of (a) propane, (b) ethanol, (c) NO_x, and (d) O₃. (e) Most abundant VOCs during the cold-dry (Nov 2011) and hot-dry (Mar 2012) seasons. (f) VOC composition during a typical day of the cold-dry or hot-dry season.

Similar behavior was found for the other measurement days and other sites.

3.2. Hourly correlation analysis

Correlation analysis among hourly concentration time series for VOCs and CO has been used to identify potential sources of VOC emissions and to evaluate the extent of chemical reactions in the atmosphere (Von Schneidmesser et al., 2010). Therefore, these correlations were determined for each monitoring site and season (see Tables in the SI).

3.2.1. NO_x/CO

NO_x and CO are byproducts of combustion processes with an atmospheric lifetime of approximately 1.5 days and several weeks, respectively (Emmons et al., 2010; Riuttanen et al., 2013). A high correlation between these byproducts ($R^2 \sim 1$) should be expected when they come from the same source. NO_x and CO exhibited a high correlation ($R^2 > 0.97$, Fig. 4a and e). Average NO_x/CO ratios of 50.9 for the 2011 cold-dry season and 71.2 for the 2012 hot-dry season were found at all monitoring sites except Merced, which exhibited the same pattern during both seasons. Variations in the NO_x/CO ratios could be due to changes in the predominant

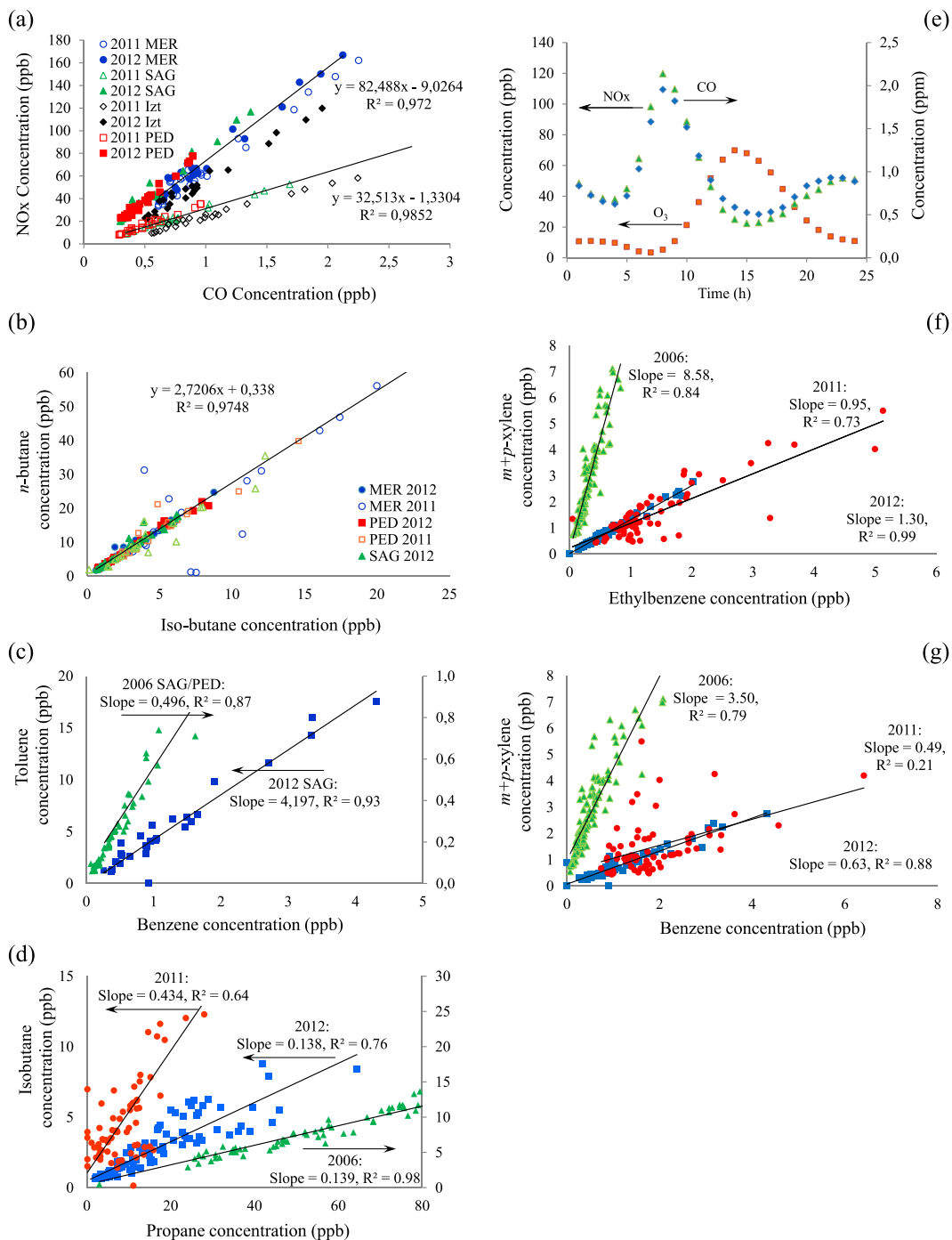


Fig. 4. Hourly correlation analysis for (a) NO_x/CO, (b) iso-*n*-butane, (c) toluene/benzene, (d) butane/propane, (f) *m + p*-xylene/ethylbenzene, and (g) *m + p*-xylene/benzene. (e) Daily trends of O₃, CO, and NO_x concentrations.

combustion source.

3.2.2. Isobutane/*n*-butane

Iso- and *n*-butane varied in a similar fashion throughout the year at all monitoring sites and were highly correlated (Fig. 4b). These species have similar atmospheric lifetimes (2.9 days and 2.8–4.7 days, respectively). The results indicate that iso- and *n*-butane might come from the same anthropogenic source, and that they are continuously emitted into the atmosphere (Arnold et al., 2007; Tsai et al., 2008). Both compounds are used in refineries to increase the gasoline octane number. In addition, *n*-butane is used

for ethylene and butadiene production, whereas isobutane is used in aerosol sprays and as a refrigerant. Gasoline evaporation could be one source of iso- and *n*-butane (Blake and Rowland, 1995; Leuchner and Rappengluck, 2010). These observations are consistent with the fact that 95% of vehicles in the MCMA fleet are fueled by gasoline (Secretaría de Medio Ambiente y Recursos Naturales de México, 2010, 2012).

3.2.3. Butane/propane

Mexican LPG is made primarily of propane (~60%) and, to a lesser extent, butane (isobutane + *n*-butane, ~40%) (Secretaría de

Energía del Gobierno Federal de México, 2008). The butane to propane ratio was constant in the MCMA (0.14 and 0.43 for the cold- and hot-dry seasons, respectively), with a high degree of correlation ($R^2 > 0.76$) at all measurement sites (Fig. 4d). The atmospheric lifetime for propane is 10 days (Atkinson, 2000). Previous results indicate these compounds might come from the same source. LPG is the most commonly used fuel for cooking and heating in dwellings in the MCMA, where there are frequent reports of LPG leakages. Moreover, butane and propane were the VOCs with the largest concentrations during the measurement campaign, at proportions similar to the LPG composition. From these observations, it can be concluded that the C1–C4 VOCs in the MCMA mainly arise from the leakage of unburned LPG fuel from domestic appliances. Previous works confirm this conclusion (Blake and Rowland, 1995).

3.2.4. Toluene/benzene

Benzene and toluene are relatively stable VOCs, with atmospheric lifetimes of 9.4 and 1.9 days, respectively (Atkinson, 2000). A high correlation between toluene and benzene was found at the Pedregal and San Agustín sites during the hot-dry seasons of 2006 and 2012, but a poor correlation was observed at all monitoring sites during the 2011 cold-dry season (Fig. 4c). Consistent with previous works developed for the MCMA, the toluene to benzene volumetric ratio (T/B) changed from 0.5 to 4.2 from 2006 to 2012. From the 2006 ambient concentration measurements, Velasco et al. (2007) reported a T/B value of 4.3 for urban sites and 7.5 for an industrial district. Rogers et al. (2006) found an average T/B value of 3. Zavala et al. (2006) reported a T/B value of 2.1 for typical Mexican vehicle fleet emissions. T/B values approaching a value of 1 are thought to indicate traffic-originating emission sources, with this ratio increasing according to the proximity of the pollution source (Gelencser et al., 1997). Values of T/B much greater than 1 indicate the presence of another source(s) of toluene. Such sources might include solvent evaporation from cleaning, painting, and printing processes, as well as from the application of adhesives, dyes, and inks (Liu et al., 2008). According to the 2010 Mexico City Toxic Emission Inventory, toluene has the highest level of released emissions in the MCMA atmosphere, mainly from vehicles, dwellings, and industrial sources (Secretaría de Medio Ambiente del Distrito Federal, 2012).

3.2.5. O₃/CO

The correlation between O₃ and CO reflects the extent of atmospheric photochemical reactions. In the MCMA, O₃ was uncorrelated with CO because these compounds exhibited very distinctive patterns of hourly concentration (Fig. 4e). The R^2 value of these two compounds was less than 0.001 for the 2012 hourly concentration at the four monitoring sites. This finding indicates that, on average, the MCMA exhibited a highly aged atmosphere.

3.2.6. Xylene/ethylbenzene

The volumetric ratio of xylene (*m*-xylene + *p*-xylene) to ethylbenzene (X/E) has been used as a preferred metric of photochemical age (Zhang et al., 2008). Vehicle exhaust and solvent use are the main sources of these two VOCs. The atmospheric lifetime is about 1.7 days for ethylbenzene, and about 14–31 h for *m* + *p*-xylene. Low X/E values are associated with active photochemical reactions (Zalel et al., 2008; Mehta et al., 2009). High correlations ($R^2 > 0.73$) were found between ethylbenzene and *m* + *p*-xylene at all monitoring sites during both seasons (Fig. 4f). The X/E ratio at all monitoring sites changed from 8.6 during the 2006 cold-dry season to 0.95 during the 2011 cold-dry season. This result indicates that the photochemical age of the MCMA atmosphere changed drastically during this time, becoming more prone to O₃ formation. The

X/E ratio changed from 0.95 during the 2011 cold-dry season to 1.3 during the 2012 hot-dry season (Fig. 4f), indicating that the MCMA atmosphere is more prone to O₃ formation during the cold-dry season.

Variations in the X/E ratio were not due to variations in the distance to emission sources because the location of the monitoring sites stayed the same throughout the campaign, and there have not been any important variations in the location of nearby emission sources. Variations in the photochemical age of the MCMA atmosphere are also unlikely to be due to variations in emissions patterns. The emissions inventory for the MAMC is elaborated on an annual basis and, therefore, does not provide information to explore seasonal variations in emission patterns. Furthermore, important difference in the consumption patterns of MCMA citizens were not observed. Most houses in the MCMA do not use heating or air conditioning systems because the ambient temperature remains within 10–25 °C during the whole year (Fig. 2). Accordingly, differences in the photochemical age of the MCMA are most likely due to variations in meteorological conditions.

3.2.7. Xylene/benzene

The distinguishing difference between benzene and xylene in terms of usage is that xylene is used in solvents, whereas benzene is not (Na et al., 2004). Compared to benzene, xylene has a higher reactivity with radicals. Both xylene and benzene have an atmospheric lifetime of 14–31 h (Mehta et al., 2009). At all monitoring sites in 2006 and 2012, *m* + *p*-xylene and benzene were found in the MCMA atmosphere with a high correlation ($R^2 > 0.8$; Fig. 4g). Volumetric ratios of *m* + *p*-xylene to benzene (X/B) in 2006 and 2012 were 4.5 and 0.67, respectively. These observations imply that, in 2012, the MCMA became much more photochemically aged than in 2006. However, in 2011, these compounds exhibited a poor correlation, which indicates possible spiking of *m* + *p*-xylene from sources additional to vehicular emissions.

3.3. Average VOC concentrations

The complete dataset with the average concentrations obtained for the 64 VOCs analyzed in this campaign is provided in the SI section. Average VOC concentrations for the most abundant species are shown in Fig. 5a. Propane was consistently the most abundant VOC in the MCMA atmosphere during the campaign. Acetone and ethanol were measured for the first time during the 2011 and 2012 campaigns and showed up as the second and third most abundant VOCs, respectively.

Atmospheric acetone could originate from terrestrial sources, such as vegetation, biomass burning, and direct anthropogenic emissions. However, the main source of acetone in urban environments is the photochemical oxidation of VOC precursors, such as propane (Hu et al., 2013; Chatfield et al., 1987). This observation is consistent with the fact that propane has been the most abundant VOC in the MCMA during the past 20 years. Atmospheric ethanol could originate from biogenic sources, with smaller influences of biomass burning, anthropogenic production, and secondary formation (Kirstine and Galbally, 2012). As reported by Yokelson et al. (2013), the most likely source of ethanol in the MCMA may be the large number of open-burning emission episodes.

The pattern of average VOC concentration was similar for all species. The trend showed an important increment between the 1992 and 2002 campaigns, after which the levels tended to decrease over the last 10 years at an average rate of –2.4 ppb/year. Propane, ethanol, and acetone showed the highest rates of decrement of –10.5, –13.8, and –8.5 ppb/year, respectively. The other VOCs showed slight decrements of less than 1 ppb/year. Propylene reached an important peak value of 26.9 ppb in 2005, but its

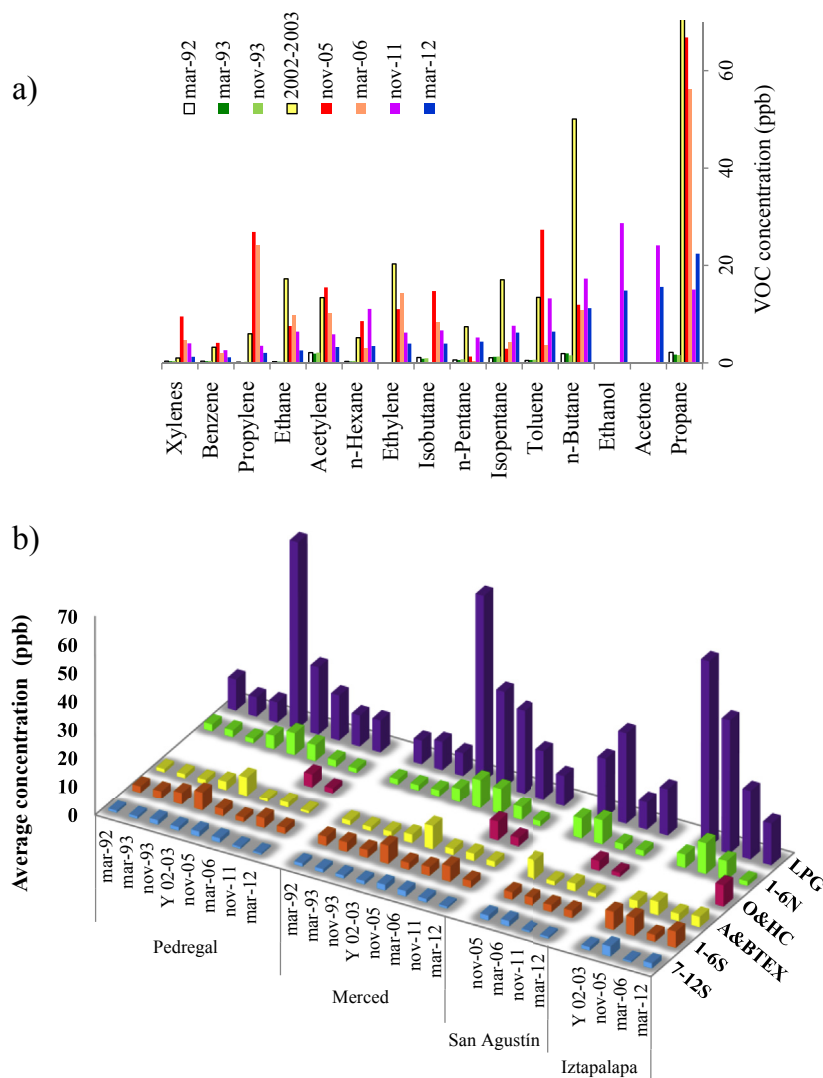


Fig. 5. Evolution of average volumetric VOC concentrations in the MCMA organized by (a) most abundant species or (b) functional group and monitoring site.

average concentration was only 2 ppb in 2012.

VOCs were classified by their chemical functional group and carbon-chain length as specified in Table 4. For the past 20 years, VOCs in the LPG group, particularly propane and *n*-butane, have exhibited the highest concentrations among VOCs (Fig. 5b). The average concentrations of the LPG VOCs showed important reductions over the past 10 years at the Merced (69%, -3.04 ppb/year), Pedregal (53%, -1.5 ppb/year), Iztapalapa (69%, -3.5 ppb/year), and San Agustín (22%, -1.9 ppb/year) sites. In 2012, the sites demonstrating the maximum concentrations of propane (28.4 ± 4.1 ppb) and *n*-butane (15.3 ± 2.3 ppb) were San Agustín and Iztapalapa, respectively.

The 1-6N group showed the second largest concentrations during the last two campaigns, with the highest concentrations being observed at the residential–industrial Iztapalapa site. Concentrations of VOCs within this group decreased 85% per year on average, at a rate of -1.1 ppm/year. Oxygenated and halogenated hydrocarbons had the third largest concentrations during the last two campaigns. In 2012, acetone and ethanol were, by far, the most abundant VOCs in this group, especially at the Iztapalapa monitoring site (average concentrations of 31.9 ± 4.6 and 30.8 ± 4.0 ppb, respectively).

The aromatics and BTEX group showed the fourth largest

concentrations during the last two campaigns, especially at the Merced site, which is a commercial area with heavy traffic. Toluene was the group member with the highest concentrations at all monitoring sites. At the Iztapalapa site in 2012, the average toluene concentration was 20.04 ± 3.82 ppb, representing an increment of 59% compared to the concentration during the 2006 cold-dry season.

The 1-6S and 7-12S groups exhibited lower VOC concentrations than the other groups. These VOCs originate from emissions from petrochemical industries and diesel-vehicle exhaust, which are not commonly found in the MCMA. Most petrochemical industries are located outside the metropolitan area, and gasoline-powered vehicles far outnumber those powered by diesel (Secretaría de Medio Ambiente y Recursos Naturales de México, 2010, 2012).

3.4. Toxic VOCs

Thirty-six toxic VOCs were measured during the present measurement campaign (SI Tables). According to the most recent Mexico City Emission Inventory sources (Secretaría de Medio Ambiente del Distrito Federal, 2012), these compounds are mainly emitted by point sources involving activities such as painting, surface coating, cleaning, and degreasing, along with

some other chemical and combustion processes. Some toxic VOCs, including several ketones (Zheng et al., 2013), can be formed as secondary VOCs. Among the four monitoring sites, Iztapalapa had the highest concentrations of toxic VOCs in 2012, especially for acetone (31.9 ± 4.6 ppb), ethanol (30.8 ± 3.9 ppb), *n*-hexane (27.1 ± 4.2 ppb), and toluene (20.0 ± 3.8 ppb) (Fig. 5). Other toxic VOCs, including 1,3-butadiene, vinyl acetate, and 2-hexanone, were not measured at this site.

To assess the MCMA air quality in terms of toxic VOCs, the 3-h and campaign peak values should be compared to reference values. Several comparisons could be made to achieve this goal. The first and most appropriate method is to compare measured values to the National Ambient Air Quality Standards (NAAQS). Similarly to the Indoor Air Quality Standards (IAQS) described below, the NAAQS have been established by organizations dedicated to protecting human health from ambient exposure to chemicals in the air. The NAAQS and IAQS have been derived from scientific studies evaluating the effects of atmospheric pollutants on human health.

The NAAQS represent safe values for outdoor ambient exposure to specific pollutants that, according to the local environmental authority, are harmful to public health and the environment. These standards differ from country to country, and are not currently available for Mexico.

The second method is to compare the campaign-measured values to NAAQS established by other environmental authorities. The Japanese and European Union (EU) environmental authorities are among the few that have established standards for benzene, with annual average values of 1 and 1.57 ppb, respectively (European Concerted Action, 1991; Ministry of the Environment Government of Japan, 1997). Fig. 6 shows that although the benzene concentration in the MCMA has been declining during the past 7 years, it still surpasses the air quality standards established by Japan (Environmental Agency of Japan, 1999) and the EU (European Concerted Action, 1991). Average values obtained from the measurement campaigns do not represent the annual average values in the MCMA, because these measurements were made during a short season. However, they do represent an upper limit of the annual average values, because they were obtained during the season of highest concentration.

As the NAAQS of Japan and the EU provide reference values only for benzene, additional reference values were needed for the other VOCs. For this purpose, the measured values were compared with

concentrations obtained in similar campaigns in other megacities, including Sao Paulo, Brazil (Martins et al., 2008), Seoul, South Korea (Na et al., 2005), Kaohsiung, Taiwan (Chang et al., 2005), Hong Kong, Japan (Lee et al., 2002), Beijing, China (Song et al., 2008), and Los Angeles, USA (Baker et al., 2008). This alternative does not provide a risk assessment of concentrations measured in the MCMA, but it does provide reference values for comparison. Other short-term VOC campaigns have focused on the measurement of toluene and benzene concentrations. Although the toluene concentration in the MCMA has been declining during the past 10 years, it is still higher than the concentrations in sister cities, including Sao Paulo, Seoul, Beijing, and Los Angeles (Martins et al., 2008; Na et al., 2005; Chang et al., 2005; Song et al., 2008; Baker et al., 2008) (Fig. 6).

The final method of assessing the human health risk of VOCs in the MCMA is to compare VOC concentrations against the IAQS. These standards represent safe values for indoor ambient exposure to chemicals in the air that, according to health authorities, almost all healthy workers can tolerate without adverse effects. The most well-known health organizations that have established IAQS are the Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH), and the World Health Organization (WHO). Recommended IAQS values are typically provided as time-weighted averages (TWAs) of the permissible exposure limit (TWA-PEL), threshold limit value (TWA-TLV), and recommended exposure limit (TWA-REL).

All of the 3-h peak VOC values measured during the 2011–2012 MCMA campaign were well below the IAQS for short-term exposure by one or two orders of magnitude (Table 5). Therefore, these VOCs do not represent a short-term risk to Mexican citizens. Among the toxic VOCs, acetone, ethanol, *n*-hexane, and toluene showed the highest 3-h peak concentrations. Of particular concern were benzene and 1,3 butadiene, which had the highest ratios of measured value to maximum recommended value (0.4% and 0.07%, respectively).

3.5. OFP

The OFP values of the 64 VOCs measured in the MCMA campaign were calculated by multiplying the measured concentration of each VOC by the corresponding MIR index. The resulting OFP values provide insight into the maximum concentration of O₃ that could eventually be formed. Among the 64 VOCs included in this study, T2&C2butane, butadiene, TM-benzene, and propylene had the highest MIR indices, whereas propylene, toluene, C2-butane, and ethylene had the highest OFPs (Fig. 7). For the 2011 and 2012 campaigns, the total average OFP values were 428.6 and 288.0 ppb, respectively, representing an average reduction of –71.1 ppb/year over the past 7 years. In 2012, the area with the highest OFP of 480 ppb was Iztapalapa. This value was three times the 1-h peak value measured at this station at 15:00 h (159 ppb) and exceeded the 1-h Mexican Air Quality Standard for O₃ (110 ppb).

In 2012, toluene became the VOC with the highest OFP at all monitoring sites, with Iztapalapa having the highest toluene OFP (116.4 ppb). According to the 2010 Mexico City Emission Inventory (Secretaría de Medio Ambiente y Recursos Naturales de México, 2012), toluene is the most emitted VOC pollutant in the city and represents 25% of all toxic VOC emissions. Toluene is mainly emitted from fuel evaporation (gasoline, use of industrial solvents and oil-based paints) and incomplete combustion in vehicle fleets. Correlation analysis among VOC concentrations and fluxes confirm this observation (Velasco et al., 2005, 2009; Karl et al., 2009). Clean air actions aiming to control tropospheric O₃ in the MCMA should

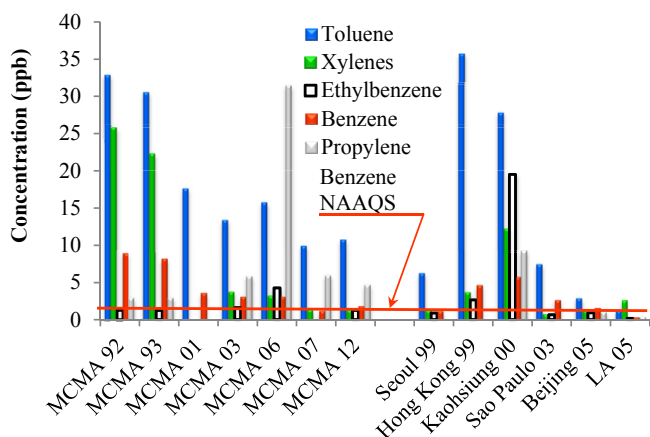


Fig. 6. Average volumetric concentrations of the most abundant toxic VOCs measured during different campaigns in the MCMA (Velasco et al., 2007; Wöhnschimmel et al., 2010; Bravo et al., 2002; Secretaría de Medio Ambiente del Distrito Federal, 2008) compared to NAAQS for benzene established by Japan and the EU (red line) and concentrations obtained by short-term measurement campaigns in similar megacities. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5

Comparison of the 3-h peak VOC values measured during the 2011–2012 MCMA campaign with IAQS established by several health authorities. Values are reported in ppm. Ca: Compound considered a potential occupational carcinogen and classified as immediately dangerous for life by the IDHL.

VOC	OSHA (Occupational Safety and Health Standards, 2012) PEL ^a	NIOSH (National Institute for Occupational Safety and Health, 2007) REL ^b	Mexico (Secretaría del Trabajo, 2002) NOM 010 STPS-1999 ^c	This study 2011/2012
Ethanol	1000	1000	1000	0.0680
Acetone	1000	250	1000	0.0510
Propane	1000	1000	—	0.0644
Toluene	200	100	50	0.0260
Benzene	1	0,1	1	0.0064
Xylenes	100	100	100	0.0116
Ethyl benzene	100	100	100	0.0051
Styrene	100	50	50	0.0059
Chloromethane	100	2000 “Ca”	50	0.0050
1,4-dichlorobenzene	75	150 “Ca”	75	0.0080
1,3-Butadiene	1	2000 “Ca”	1000	0.0059
Trichloromethane	50	500 “Ca”	10	0.0050

^a PEL: 8-h time-weighted average (TWA) of the permissible exposure limit.

^b REL: TWA of the recommended exposure limit.

^c TWA at 8 h per day and 40 h per week.

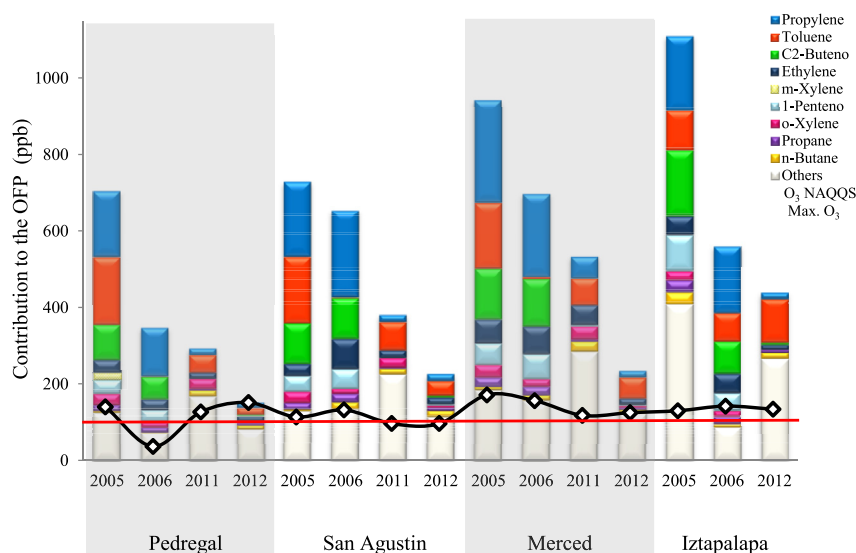


Fig. 7. OFP for each monitoring site during the 2005–2006 and 2011–2012 MCMA campaigns.

focus on controlling toluene sources. To control the emission of this pollutant, it is proposed to limit the use of oil-based paints within the MCMA and replace them with water-based paints, as was implemented by the EU (European Concerted Action, 1991). It is also proposed to limit the use of vehicles with model years before 1991, which do not have catalytic converters and still use carburetors. Currently, these vehicles represent 10% of the MCMA vehicle fleet.

Before 2011, propylene was the VOC with the highest OFP (Fig. 7). Propylene is the second most important starting product in the petrochemical industry, after ethylene. It is also produced naturally by vegetation or as a product of combustion from forest fires or motor vehicles (Goldstein et al., 1996). Propylene has not been one of the most abundant VOCs in the MCMA atmosphere. Despite its high MIR index (11.66), this compound has not received much attention in previous works for the MCMA. Its reduction in concentration in the MCMA atmosphere could be due to continuous deforestation and the reduction in total VOC emissions after 2007, when authorities established regulations for fuel quality and more restrictive limits for tail-pipe emissions of in-use vehicles (Watson et al., 2001). Finally, although propane has been the most abundant VOC in the MCMA, its MIR index is small (0.49 gO₃/gVOC) and its OFP represents less than 2% of the total OFP at each site.

4. Conclusions

High ground levels of O₃ make the MCMA one of the most polluted cities in North America. Tropospheric O₃ is a secondary pollutant formed from the oxidation of VOCs in the presence of NO_x and sunlight. During the last decade, the Mexican government has implemented several measures to reduce VOC and NO_x emissions. To assess the effectiveness of these measures, a VOC measurement campaign has been needed to describe the temporospatial variations of VOCs. To address this need, 64 VOCs, including 36 toxic VOCs, were measured at four sites in the MCMA during 2011–2012.

Iztapalapa had the highest VOC concentrations, and VOCs related to LPG leakages exhibited the highest concentrations. Propane and ethanol were the two most abundant VOCs found at all monitoring sites in 2012. Similarly to most of the VOCs measured, these two compounds exhibited the same daily pattern, with a prominent peak in the early morning (05:00–09:00) followed by a constant decrement during the rest of the day, except for a slight increase around 21:00.

Correlation analyses among iso-*n*-butane, toluene/benzene, and butane/propane indicated that these compounds arise mainly from LPG leakages and gasoline-fueled vehicles. Analyses among O₃/CO, *m* + *p*-xylene/ethylbenzene, and *m* + *p*-xylene/benzene

indicated that the MCMA atmosphere has become photochemically aged during the last 5 years, and that the MCMA is more prone to O₃ formation during the cold-dry season. Variations in these indicators of photochemical age are likely to be due to small variations in the meteorological conditions, rather than variations in emission patterns or the distance from the monitoring site to the emission source.

Measured concentrations of toxic VOCs were compared to NAAQS and concentrations obtained in similar campaigns in other megacities. Among the toxic VOCs, acetone and ethanol showed the highest average concentrations (31.9 ± 4.6 and 30.8 ± 3.9 ppb, respectively). However, the VOC of greatest concern was benzene, whose measured levels surpassed the EU NAAQS of 1 ppb. Compared to previous measurements, the OFP in the MCMA was reduced by 53%. The highest OFP was found in the Iztapalapa area, with an average value (480 ppb) that was three times the 1-h peak value and surpassed the 1-h Mexican Air Quality Standard for O₃ (110 ppb). As measures to control ground-level O₃ formation in the MCMA, we propose restrictions on the use of oil-based paints and carburetor-based vehicles.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.08.014>.

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