Volatile organic compounds in the atmosphere of Mexico City

Jessica P. Garzón ^a, José I. Huertas ^{*,a}, Miguel Magaña ^b, María E. Huertas ^f, Beatriz Cárdenas ^c,
Takuro Watanabe ^d, Tsuneaki Maeda ^d, Wakamatsu Shinji ^e, Salvador Blanco ^b

^a *Tecnológico de Monterrey, Toluca, México*

^b *National Institute of Ecology and Climate Change, México City, México*

^c *Independent consultant*

^d *National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan*

^e *Ehime University, Matsuyama, Ehime, Japan*

^f *Universidad Tecnológica de Bolívar, Cartagena, Colombia*

*Corresponding author email: jhuertas@itesm.mx; phone: +52 (722) 2799990 ext. 2113; fax: +52 (722) 274-1178.

Table of contents (TOC) art

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 contributed the most to O_3 formation. Correlation analysis indicated that the measured VOCs come from vehicular emissions and solvent-related industrial sources.

Keywords: Volatile organic compound, Toxic volatile organic compound, Ozone, Ozone formation potential

49 **CAPSULE ABSTRACT**

50 VOC measurements revealed that compounds related to liquefied petroleum gas leakages are the
51 most abundant, the toxic VOC benzene represents the highest risk to citizens, and toluene is the
52 greatest VOC contributor to O₃ formation in Mexico City.

53

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 [1]. 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 [2]. The topography and meteorology of this air basin make wind circulation difficult, causing frequent thermal inversions and pollutant stagnation [3].

In 2011, the Metropolitan Air Quality Index (IMECA) exceeded acceptable levels during 241 days [4]. High ground-level ozone (O_3) concentrations, along with elevated particulate matter (PM) concentrations, are mainly responsible for the pollution issue and make the MCMA one of the most polluted cities in North America [5]. Exposure to ground-level O_3 is harmful to human health and causes respiratory diseases, decreasing the capability of the lungs to perform normal functions. Tropospheric O_3 , black carbon, and methane are short-lived pollutants that, after CO_2 , are the most important contributors to the global warming effect, with multiple harmful impacts on human health, agriculture, and ecosystems [6]. Tropospheric O_3 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 O_3 formation varies, depending on the amount of NO_x and VOCs in the atmosphere. Under some conditions, O_3 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 [7].

VOCs are emitted as gases from various daily emission sources, such as driving cars [8], painting buildings [9], and cooking. Some VOCs, such as isoprene and other monoterpenes, are naturally emitted into the atmosphere [10]. 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 [11]. 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 [12].

Various studies in the MCMA have found that air quality problems due to NO_x are caused by industrial sources, vehicles [13], and an inefficient public transportation system [14]. In recent decades, the Mexican government has focused on reducing VOC and NO_x emissions, aiming to improve air quality in this region [5, 15]. 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 [16, 17]. From 1992 to 2001, the MCMA campaign measured 9 VOCs during short periods of time (3–30 days) in March and November [18]. 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 [5, 19]. 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 [3, 20]. 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 [20].

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	[21] [16] [22]	25 Ozone probe	Mar 3-6, 1992: Merced, Tlalnepantla, Xalostoc, Pedregal, Reforma and Cuatitlán Mar 23-31, 1993: 3h 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
MCMA 1992-2001 VOCs record measurements	[18]	9 304 total samples	Mar and Nov: 3 to 30 days 3h canister samples, Xalostoc, La Merced, Pedregal, Tlalnepantla, Iztapalapa	<ul style="list-style-type: none"> • 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 2002-2003 Mexico City Metropolitan Area Feb 2002 Apr 2003	[5, 19, 23]	13, CENICA 58, Urban site. 10 min samples to 3h canisters	CENICA: 3 Apr - May 2, 2003. Pedregal, La Merced, Xalostoc, Santa Ana, UNAM, La Reforma, Cuatitlan	<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 2006 MILAGRO:				
Megacity		50 (T0)		
Initiative: Local	[3,	38 (T1)	Mar 17-30, 2006:	•Evaporative fuel and industrial emission are important sources of aromatic VOCs.
and Global	20]	10 min	T0 urban site	•LPG use continues to be an important source of low molecular weight alkanes
Research		samples to	T1 downwind site	•There are large non-biogenic sources of methanol in the MCMA basin.
Observations		3h		
Mar 2006		Canisters		

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 [5, 15]. 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.

Table 2

Actions by the Mexican government aimed at controlling air pollution in the MCMA [24].

Year	Actions
2005 2006	<ul style="list-style-type: none"> • Metrobus construction along Insurgentes Avenue. • 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-Cuatitlan. • 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 Etipia-Tenayuca. • Regulation NOM-022-SSAI-2010 was published with new criteria to address the air pollution from SO₂ emissions.

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 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 [18]. 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.

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

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.

154

155 **Fig. 2.** Annual variations of pollutant concentration, temperature (T), and relative humidity (RH)

156 in the MCMA during 2005, 2006, 2011, and 2012 [25].

157

Table 4.

158

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

Tag	VOC group	VOC	CAS	Formula	MIR	M	Method
I-6S	<i>Saturated light alkanes, except LPG group: From 1 to 6 carbons in length. Potential source: Gasoline-vehicle emissions [28, 29]</i>	Ethane	74-84-0	C ₂ H ₆	0,28	30,1	TO-14A
		Cyclopentane	287-92-3	C ₅ H ₁₀	2,39	70,1	TO-14A
		Isopentane	78-78-4	C ₅ H ₁₂	1,45	72,2	TO-14A
		<i>n</i> -Pentane	109-66-0	C ₅ H ₁₂	1,31	72,2	TO-14A
		Methylcyclopentane	96-37-7	C ₆ H ₁₂	2,19	84,2	TO-14A
		Cyclohexane*	110-82-7	C ₆ H ₁₂	1,25	84,2	TO-15
		Methylpentane	43133-95-5	C ₆ H ₁₄	1,50	86,2	TO-14A
		<i>n</i> -Hexane*	110-54-3	C ₆ H ₁₄	1,24	86,2	TO-14A
		2,2-Dimethylbutane	75-83-2	C ₆ H ₁₄	1,17	86,2	TO-14A
		Ethylene	74-85-1	C ₂ H ₄	9,00	28,1	TO-14A
I-6V	<i>Unsaturated light alkanes: From 1 to 6 carbons in length. Potential source: Petrochemical industry and vehicle emissions [32, 33]</i>	Propylene	115-07-1	C ₃ H ₆	11,66	42,1	TO-14A
		1-Butene	106-98-9	C ₄ H ₈	9,73	56,1	TO-14A
		Cis-2-Butene	590-18-1	C ₄ H ₈	14,24	56,1	TO-14A
		Trans-2-Butene	624-64-6	C ₄ H ₈	15,16	56,1	TO-14A
		Trans-2-Pentene	646-04-8	C ₅ H ₁₀	10,56	70,1	TO-14A
		1-Pentene	109-67-1	C ₅ H ₁₀	7,21	70,1	TO-14A
		Cis-2-Pentene	627-20-3	C ₅ H ₁₀	10,38	70,1	TO-14A
		1,3 Butadiene*	106-99-0	C ₄ H ₆	12,61	54,1	TO-14A
		Acetylene	74-86-2	C ₂ H ₂	1,24	26,0	TO-14A
		Propane	40811-14-1	C ₃ H ₈	0,49	44,0	TO-14A
LPG	<i>Potential source: LPG leakage [30, 31]</i>	Isobutane	75-28-5	C ₄ H ₁₀	1,23	58,1	TO-14A
		<i>n</i> -butane	54597-66-9	C ₄ H ₁₀	1,15	58,1	TO-14A
7-12S	<i>Saturated alkanes: From 7 to 12 carbons in length. Potential source: Diesel-vehicle emissions [34]</i>	Methylcyclohexane	108-87-2	C ₇ H ₁₄	1,70	98,2	TO-14A
		2,3-Dimethylpentane	565-59-3	C ₇ H ₁₆	1,34	100,2	TO-14A
		Methylhexane	591-76-4	C ₇ H ₁₆	1,19	100,2	TO-14A
		<i>n</i> -Heptane*	142-82-5	C ₇ H ₁₆	1,07	100,2	TO-15
		Isooctane	540-84-1	C ₈ H ₁₈	1,26	114,2	TO-14A
		2,3,4-Trimethylpentane	565-75-3	C ₈ H ₁₈	1,03	114,2	TO-14A
		Methylheptane	592-27-8	C ₈ H ₁₈	1,07	114,2	TO-14A
		<i>n</i> -Octane	111-65-9	C ₈ H ₁₈	0,90	114,2	TO-14A
		Nonane	111-84-2	C ₉ H ₂₀	0,78	128,3	TO-14A

Tag	VOC group	VOC	CAS	Formula	MIR	M	Method
A&BTEX	<i>Aromatics and BTEX (Benzene, toluene, and xylene). Potential source: Industry and gasoline-vehicle emissions, Oil based paint [35, 36]</i>	Benzene*	71-43-2	C ₆ H ₆	0,72	78,1	TO-15
		Toluene*	108-88-3	C ₇ H ₈	4,00	92,1	TO-15
		Ethylbenzene*	100-41-4	C ₈ H ₁₀	3,04	106,2	TO-15
		<i>m</i> -Xylene*	108-38-3	C ₈ H ₁₀	9,75	106,2	TO-15
		<i>p</i> -Xylene*	106-42-3	C ₈ H ₁₀	5,84	106,2	TO-15
		<i>o</i> -Xylene*	95-47-6	C ₈ H ₁₀	7,64	106,2	TO-15
		Styrene*	79637-11-9	C ₈ H ₈	1,73	104,2	TO-15
		1-Ethyl,4-Methylbenzene*	622-96-8	C ₉ H ₁₂	7,39	120,2	TO-15
		1,3,5-Trimethylbenzene*	108-67-8	C ₉ H ₁₂	11,76	120,2	TO-15
		1,2,4-Trimethylbenzene*	95-63-6	C ₉ H ₁₂	8,87	120,2	TO-15
O&HC	<i>Oxygenated and halogenated hydrocarbons. Potential source: Exhaust and solvent emissions [11, 37]</i>	Isopropylbenzene	98-82-8	C ₉ H ₁₂	2,52	120,2	TO-15
		Dichlorodifluoromethane*	75-71-8	Cl ₂ CF ₂	-	120,9	TO-15
		Chloromethane*	74-87-3	CH ₃ Cl	0,04	50,5	TO-15
		Ethanol*	64-17-5	C ₂ H ₆ O	1,53	46,1	TO-15
		Trichlorofluoromethane*	75-69-4	CCl ₃ F	-	137,4	TO-15
		Acetone*	67-64-1	C ₃ H ₆ O	0,36	58,0	TO-15
		Isopropyl alcohol*	67-63-0	C ₃ H ₈ O	0,61	60,1	TO-15
		Chloromethylene*	2108-20-5	CHCl	0,04	48,5	TO-15
		Carbon disulfide*	75-15-0	CS ₂	0,25	76,1	TO-15
		MTBE*	1634-04-4	C ₅ H ₁₂ O	0,73	88,2	TO-15
		Vinyl acetate*	108-05-4	C ₄ H ₆ O ₂	3,20	86,0	TO-15
		Methyl Ethyl Ketone*	78-93-3	C ₄ H ₈ O	1,48	72,1	TO-15
		Ethyl acetate*	141-78-6	C ₄ H ₈ O ₂	1,73	104,2	TO-15
		Trichloromethane*	67-66-3	CHCl ₃	0,02	119,4	TO-15
		Tetrahydrofuran*	109-99-9	C ₄ H ₈ O	4,31	72,1	TO-15
		Methyl isobutyl ketone*	108-10-1	C ₆ H ₁₂ O	3,14	100,2	TO-15
		2-Hexanone*	591-78-6	C ₆ H ₁₂ O	3,14	100,2	TO-15
		Tetrachloroethylene*	127-18-4	Cl ₂ C=CCl ₂	0,64	165,8	TO-15
		1,3-Dichlorobenzene*	541-73-1	1,3-Cl ₂ C ₆ H ₄	0,18	147,0	TO-15
		1,4-Dichlorobenzene*	106-46-7	1,4-Cl ₂ C ₆ H ₄	0,18	147,0	TO-15
		1,2-Dichlorobenzene*	95-50-1	1,2-Cl ₂ C ₆ H ₄	0,18	147,0	TO-15
		1,2,4-Trichlorobenzene*	120-82-1	1,2,4-Cl ₃ C ₆ H ₃	-	181,5	TO-15
		Hexachlorobutadiene*	87-68-3	C ₄ Cl ₆	-	260,8	TO-15

159

160

161

MIR: Maximum incremental reactivity value (gO₃/g/VOC); 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) [26, 27].

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 [26]. The number of compounds that fall within this category is quite large (10^3 – 10^4). The USEPA declared 189 of these compounds to be hazardous air pollutants and recommended methods for measuring 97 VOCs within this group [27]. 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 to 12 carbons in length, 10 unsaturated light alkenes of 1 to 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 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 O₃ concentration over the MCMA. The highest O₃ concentrations were found during the hot-dry season, when temperature reaches its highest value (Fig. 2). This observation is reasonable, considering that O₃ 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 O₃ formation.

Sampling periods were designed to observe VOC emissions and transformations.

Samples were taken over 3 hours from 07:00 to 19:00 to observe hourly variations. Additionally, 24-hour 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 cmHg 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-hour 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 O₃ precursors, following the USEPA protocols established within the TO-14A method [26]. 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 O₃-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 [27]. Measurement detection limits of this system (Appendix A) 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-difluorobezene, 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 [38].

The OFP was calculated (in ppb) by multiplying the VOC concentration by the maximum incremental reactivity (MIR) index developed by Carter [39]. 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 [40]. 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 [41, 42]. 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 [43, 44]. 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 O_3 concentration showed a prominent peak at 15 hours (Fig. 3c and d). The 15-hour time point does not necessarily correspond to the time when the VOC and NO_x concentrations and sunlight most favored the formation of O_3 . Rather, it corresponds to the time when the interactions among meteorological conditions, atmospheric mixing height, the photochemical production rate of O_3 , and O_3 depletion rate lead to the maximum volumetric O_3 accumulation.

During each season, the 24-hour 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 have demonstrated that propane, propylene, and toluene are the VOCs that exhibit the highest concentrations [31, 45].

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

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.

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 [46]. 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 [47, 48]. 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 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 [49, 50]. 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 [30, 51]. These observations are consistent with the fact that 95% of vehicles in the MCMA fleet are fueled by gasoline [13, 52].

3.2.3. Butane/propane. Mexican LPG is made primarily of propane (~60%) and, to a lesser extent, butane (isobutane + *n*-butane, ~40%) [53]. 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 [54]. 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 [30].

3.2.4. Toluene/benzene. Benzene and toluene are relatively stable VOCs, with atmospheric lifetimes of 9.4 and 1.9 days, respectively [54]. A high correlation between toluene and benzene was found at the Pedregal and San Agustin 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 [23]. Rogers et al. (2006) found an average T/B value of 3 [55]. Zavala et al. (2006) reported a T/B value of 2.1 for typical Mexican vehicle fleet emissions [57]. 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 [56]. 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 [58]. 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 [11].

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.

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 [59]. 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 to 31 hours for *m*+*p*-xylene. Low X/E values are associated with active photochemical reactions [60, 61]. 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 [62]. Compared to benzene, xylene has a higher reactivity with radicals. Both xylene and benzene have an atmospheric lifetime of 14 to 31 hours [61]. 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 [63, 64]. 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 [65]. 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 [66].

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 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 Agustin (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 Agustin 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 [13, 52].

a)

b)

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

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 [11], 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 [35], 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-hour 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 [67, 68]. 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 [77] and the EU [67]. 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.

Fig. 6. Average volumetric concentrations of the most abundant toxic VOCs measured during different campaigns in the MCMA [23][31][69, 70] compared to NAAQS for benzene established by Japan and the EU (red line) and concentrations obtained by short-term measurement campaigns in similar megacities.

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 [71], Seoul, South Korea [72], Kaohsiung, Taiwan [73], Hong Kong, Japan [74], Beijing, China [75], and Los Angeles, USA [76]. 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 [71-73, 75, 76] (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-hour 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-hour 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).

Table 5

Comparison of the 3-hour peak VOC values measured during the 2011–2012 MCMA campaign with IAQS established by several health authorities.

VOC	OSHA [78] PEL*	NIOSH [79] REL**	Mexico [80] NOM 010 STPS- 1999***	This study 2011/12
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

Values are reported in ppm. Ca: Compound considered a potential occupational carcinogen and classified as immediately dangerous for life by the IDHL. * PEL: 8-hour time-weighted average (TWA) of the permissible exposure limit; ** REL: TWA of the recommended exposure limit; *** TWA at 8 hours per day and 40 hours per week.

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-hour peak value measured at this station at 15:00 h (159 ppb) and exceeded the 1-hour 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 [11], 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 [81-83]. Clean air actions aiming to control tropospheric O₃ in the MCMA should 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 [67]. 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.

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

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 [84]. 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 [29]. 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-hour peak value and surpassed the 1-hour 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

This work was conducted as part of the “Joint Research Project on Formation Mechanism of Ozone, VOCs, and PM_{2.5} and Proposal of Countermeasure Scenarios” undertaken by the Science and Technology Research Partnership for Sustainable Development (SATREPS) funded by the Japan Science and Technology Agency (JST) and the Japan International Cooperation Agency (JICA). The authors acknowledge the contributions of the National Institute of Ecology (INECC), the Secretariat of the Environment of Mexico City (SMA-GDF), and SEMARNAT for supporting the field campaign and for providing data from the Air Quality Monitoring Network. We thank Eng. Susana Gonzalez from INECC for processing the data acquired during the field campaign.

References

1. *World Urbanizations Prospects: The 2011 revision*; United Nations: New York, 2011;
http://esa.un.org/unup/pdf/WUP2011_Highlights.pdf.
2. Lei, W.; De Foy, B.; Zavala, M.; Volkamer, R.; Molina, L. T. Characterizing ozone production in the Mexico City Metropolitan Area: a case study using a chemical transport model. *Atmospheric Chemistry and Physics* **2007**, 7, 1347-1366.
3. De Foy, B.; Fast, J. D.; Paech, S. J.; Phillips, D.; Walters, J. T.; Coulter, R. L.; Martin, T. J.; Pekour, M. S.; Shaw, W. J.; Kastendeuch, P. P.; Marley, N. A.; Retama, A.; Molina, L. T. Basin-scale wind transport during the MILAGRO field campaign and comparison to climatology using cluster analysis. *Atmospheric Chemistry and Physics* **2008**, 8, (5), 1209-1224.
4. *Calidad del aire en la Ciudad de México: 25 años de monitoreo atmosférico 1986-2011*; Informe 2011; Secretaria del Medio Ambiente del Distrito Federal: Ciudad de México, DF, 2012; http://www.sedema.df.gob.mx/flippingbook/informe_anual_calidad_aire_2011.
5. Molina, L. T.; Kolb, C. E.; de Foy, B.; Lamb, B. K.; Brune, W. H.; Jimenez, J. L.; Ramos-Villegas, R.; Sarmiento, J.; Paramo-Figueroa, V. H.; Cardenas, B.; Gutierrez-Avedoy, V.; Molina, M. J. Air quality in North America's most populous city - overview of the MCMA-2003 campaign. *Atmospheric Chemistry and Physics* **2007**, 7, (10), 2447-2473.
6. *Primer on short-lived climate pollutant*; Institute for Governance & Sustainable Development: Washington, DC, 2013; <http://www.igsd.org/documents/PrimeronShort-LivedClimatePollutants23april2013EV.pdf>
7. Sillman, S. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment* **1999**, 33, (12), 1821-1845.

- 632 8. Thornhill, D. A.; Williams, A. E.; Onasch, T. B.; Wood, E.; Herndon, S. C.; Kolb, C. E.;
633 Knighton, W. B.; Zavala, M.; Molina, L. T.; Marr, L. C. Application of positive matrix
634 factorization to on-road measurements for source apportionment of diesel- and gasoline-
635 powered vehicle emissions in Mexico City. *Atmospheric Chemistry and Physics* **2010**, *10*,
636 (8), 3629-3644.
- 637 9. Celebi, U. B.; Vardar, N. Investigation of VOC emissions from indoor and outdoor painting
638 processes in shipyards. *Atmospheric Environment* **2008**, *42*, (22), 5685-5695.
- 639 10. Lindfors, V.; Laurila, T. Biogenic volatile organic compound (VOC) emissions from forests
640 in Finland. *Boreal Environment Research* **2000**, *5*, (2), 95-113.
- 641 11. *Inventario de Emisiones de la Zona Metropolitana del Valle de México: Contaminantes*
642 *Tóxicos*; Secretaría de Medio Ambiente del Distrito Federal: Ciudad de México, DF, 2012;
643 <http://www.sedema.df.gob.mx/flippingbook/inventario-emisiones-zmvm-toxicos2010/>.
- 644 12. Zhang, R. Y.; Tie, X. X.; Bond, D. W. Impacts of anthropogenic and natural NO_x sources
645 over the US on tropospheric chemistry. *Proceedings of the National Academy of Sciences of*
646 *the United States of America* **2003**, *100*, (4), 1505-1509.
- 647 13. *Inventario de Emisiones de la Zona Metropolitana del Valle de México: Contaminantes*
648 *criterio*; Secretaria de Medio Ambiente y Recursos Naturales de México: Ciudad de
649 México, DF, 2010; [http://www.sedema.df.gob.mx/flippingbook/inventario-emisiones-](http://www.sedema.df.gob.mx/flippingbook/inventario-emisiones-zmvm-criterio2010/)
650 [zmvm-criterio2010/](http://www.sedema.df.gob.mx/flippingbook/inventario-emisiones-zmvm-criterio2010/).
- 651 14. Islas, V. H., S.; Arroyo, J.; Lelis, M.; Ruvalcaba, J. Implementing sustainable urban travel
652 policies in Mexico. *Proceedings of the International Transport Forum*, **2011**, *14*, 1-45.
- 653 15. Molina, L. T.; de Foy, B.; Vásquez-Martínez, O.; Páramo, V. H. Air quality, weather and
654 climate in Mexico City. *WMO Bulletin: Weather-Climate-Water* **2009**, *58*, (1), 48-53.

- 655 16. Streit, G. E.; Guzman, F. Mexico City air quality: Progress of an international collaborative
656 project to define air quality management options. *Atmospheric Environment* **1996**, *30*, (5),
657 723-733.
- 658 17. *MARI: Mexico City Air Quality Initiative*; Los Alamos National Laboratory and the Mexican
659 Petroleum Institute Report # LA-12699: Los Alamos, New Mexico, 1994;
660 <http://www.osti.gov/scitech/servlets/purl/10161823>.
- 661 18. Arriaga-Colina, J. L.; West, J. J.; Sosa, G.; Escalona, S. S.; Ordunez, R. M.; Cervantes, A.
662 D. M. Measurements of VOCs in Mexico City (1992-2001) and evaluation of VOCs and CO
663 in the emissions inventory. *Atmospheric Environment* **2004**, *38*, (16), 2523-2533.
- 664 19. Velasco, E.; Marquez, C.; Bueno, E.; Bernabe, R. M.; Sanchez, A.; Fentanes, O.;
665 Wohrnschimmel, H.; Cardenas, B.; Kamilla, A.; Wakamatsu, S.; Molina, L. T. Vertical
666 distribution of ozone and VOCs in the low boundary layer of Mexico City. *Atmospheric*
667 *Chemistry and Physics* **2008**, *8*, (12), 3061-3079.
- 668 20. Molina, L. T.; Madronich, S.; Gaffney, J. S.; Apel, E.; de Foy, B.; Fast, J.; Ferrare, R.;
669 Herndon, S.; Jimenez, J. L.; Lamb, B.; Osornio-Vargas, A. R.; Russell, P.; Schauer, J. J.;
670 Stevens, P. S.; Volkamer, R.; Zavala, M. An overview of the MILAGRO 2006 Campaign:
671 Mexico City emissions and their transport and transformation. *Atmospheric Chemistry and*
672 *Physics* **2010**, *10*, (18), 8697-8760.
- 673 21. Ruiz, M. E. A., Jose L.; Garcia, Isidoro. Determinación de compuestos orgánicos volátiles
674 en la atmósfera de la Ciudad de México mediante el uso de sistemas ópticos y métodos
675 convencionales. *Atmósfera-Universidad Nacional Autónoma de México (UNAM)* **1996**, *9*,
676 (2), 119-135.

- 677 22. Nickerson, E. C.; Sosa, G.; Hochstein, H.; McCaslin, P.; Luke, W.; Schanot, A. Project
678 AGUILA - Insitu measurements of Mexico City air pollution by a research aircraft.
679 *Atmospheric Environment Part B-Urban Atmosphere* **1992**, 26, (4), 445-451.
- 680 23. Velasco, E.; Lamb, B.; Westberg, H.; Allwine, E.; Sosa, G.; Arriaga-Colina, J. L.; Jobson,
681 B. T.; Alexander, M. L.; Prazeller, P.; Knighton, W. B.; Rogers, T. M.; Grutter, M.;
682 Herndon, S. C.; Kolb, C. E.; Zavala, M.; de Foy, B.; Volkamer, R.; Molina, L. T.; Molina,
683 M. J. Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic
684 compounds in the Valley of Mexico during the MCMA 2002 & 2003 field campaigns.
685 *Atmospheric Chemistry and Physics* **2007**, 7, 329-353.
- 686 24. *Calidad del aire en la Ciudad de México: Informe 2010*; Secretaria de Medio Ambiente del
687 Distrito Federal: Ciudad de México, DF, 2010;
688 http://www.sedema.df.gob.mx/flippingbook/informe_anual_calidad_aire_2010.
- 689 25. *Base de datos del sistema de monitoreo atmosférico de la Ciudad de México (SIMAT)*.
690 Secretaría de Medio Ambiente del Distrito Federal: Ciudad de México, DF, 2013;
691 <http://www.aire.df.gob.mx/default.php?opc=%27aKBhnmI=%27&opcion=Zg==>.
- 692 26. USEPA. *Compendium Method TO-14A. Determination of volatile organic compounds*
693 *(VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas*
694 *chromatography*. 1999. EPA/625/R-96/010b.
- 695 27. USEPA. *Compendium Method TO-15. Determination Of Volatile Organic Compounds*
696 *(VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas*
697 *Chromatography/Mass Spectrometry (GC/MS)*. 1999. EPA/625/R-96/010b.
- 698 28. Jorquera, H.; Rappengluck, B. Receptor modeling of ambient VOC at Santiago, Chile.
699 *Atmospheric Environment* **2004**, 38, (25), 4243-4263.

29. Watson, J. G.; Chow, J. C.; Fujita, E. M. Review of volatile organic compound source apportionment by chemical mass balance. *Atmospheric Environment* **2001**, *35*, (9), 1567-1584.
30. Blake, D. R.; Rowland, F. S. Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality. *Science* **1995**, *269*, (5226), 953-956.
31. Wöhrnschimmel, H.; Magaña, M.; Stahel, W. A.; Blanco, S.; Acuña, S.; Pérez, J. M.; González, S.; Gutiérrez, V.; Wakamatsu, S.; Cárdenas, B. Measurements and receptor modeling of volatile organic compounds in Southeastern Mexico City, 2000-2007. *Atmospheric Chemistry and Physics* **2010**, *10*, (18), 9027-9037.
32. Parrish, D. D.; Ryerson, T. B.; Mellqvist, J.; Johansson, J.; Fried, A.; Richter, D.; Walega, J. G.; Washenfelter, R. A.; de Gouw, J. A.; Peischl, J.; Aikin, K. C.; McKeen, S. A.; Frost, G. J.; Fehsenfeld, F. C.; Herndon, S. C. Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region. *Atmospheric Chemistry and Physics* **2012**, *12*, (7), 3273-3288.
33. Schmitz, T.; Hassel, D.; Weber, F. J. Determination of VOC-components in the exhaust of gasoline and diesel passenger cars. *Atmospheric Environment* **2000**, *34*, (27), 4639-4647.
34. Ogawa, H.; Li, T. Volatile organic compounds in exhaust gas from diesel engines under various operating conditions. *International Journal of Engine Research* **2011**, *12*, (1), 30-40.
35. Zheng, J.; Garzón, J. P.; Huertas, M. E.; Zhang, R.; Levy, M.; Ma, Y.; Huertas, J. I.; Jardón, R. T.; Ruíz, L. G.; Tan, H.; Molina, L. T. Volatile organic compounds in Tijuana during the Cal-Mex 2010 campaign: Measurements and source apportionment. *Atmospheric Environment* **2013**, *70*, (0), 521-531.

36. Yuan, Z. B.; Lau, A. K. H.; Shao, M.; Louie, P. K. K.; Liu, S. C.; Zhu, T. Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing. *Journal of Geophysical Research-Atmospheres* **2009**, *114*.
37. Guo, H.; Murray, F. Characterization of total volatile organic compound emissions from paints. *Clean Products and Processes* **2000**, *2*, (1), 28-36.
38. Sun, Y.; Genton, M. G. Functional Boxplots. *J. Comput. Graph. Stat.* **2011**, *20*, (2), 316-334.
39. Carter, W. P. L. Development of Ozone Reactivity scales for volatile organic compounds. *Journal of Air & Waste Management Association* **1994**, *44*:881-899.
40. Carter, W. P. L. Updated Maximum Incremental Reactivity scale and hydrocarbon bin reactivities for regulatory applications. *California Air Resources Board*, **2010**; *1*:1-23.
41. Chen, J. J.; Luo, D. M. Ozone formation potentials of organic compounds from different emission sources in the South Coast Air Basin of California. *Atmospheric Environment* **2012**, *55*, 448-455.
42. Suthawaree, J.; Tajima, Y.; Khunchornyakong, A.; Kato, S.; Sharp, A.; Kajii, Y. Identification of volatile organic compounds in suburban Bangkok, Thailand and their potential for ozone formation. *Atmos. Res.* **2012**, *104*, 245-254.
43. Yang, K. L.; Ting, C. C.; Wang, J. L.; Wingenter, O. W.; Chan, C. C. Diurnal and seasonal cycles of ozone precursors observed from continuous measurement at an urban site in Taiwan. *Atmospheric Environment* **2005**, *39*, (18), 3221-3230.
44. White, M. L.; Russo, R. S.; Zhou, Y.; Mao, H.; Varner, R. K.; Ambrose, J.; Veres, P.; Wingenter, O. W.; Haase, K.; Stutz, J.; Talbot, R.; Sive, B. C. Volatile organic compounds in northern New England marine and continental environments during the ICARTT 2004 campaign. *Journal of Geophysical Research-Atmospheres* **2008**, *113*, (D8).

45. Apel, E. C.; Emmons, L. K.; Karl, T.; Flocke, F.; Hills, A. J.; Madronich, S.; Lee-Taylor, J.; Fried, A.; Weibring, P.; Walega, J.; Richter, D.; Tie, X.; Mauldin, L.; Campos, T.; Weinheimer, A.; Knapp, D.; Sive, B.; Kleinman, L.; Springston, S.; Zaveri, R.; Ortega, J.; Voss, P.; Blake, D.; Baker, A.; Warneke, C.; Welsh-Bon, D.; de Gouw, J.; Zheng, J.; Zhang, R.; Rudolph, J.; Junkermann, W.; Riemer, D. D. Chemical evolution of volatile organic compounds in the outflow of the Mexico City Metropolitan area. *Atmospheric Chemistry and Physics* **2010**, *10*, (5), 2353-2375.
46. von Schneidemesser, E.; Monks, P. S.; Plass-Duelmer, C. Global comparison of VOC and CO observations in urban areas. *Atmospheric Environment* **2010**, *44*, (39), 5053-5064.
47. Emmons, L. K.; Apel, E. C.; Lamarque, J. F.; Hess, P. G.; Avery, M.; Blake, D.; Brune, W.; Campos, T.; Crawford, J.; DeCarlo, P. F.; Hall, S.; Heikes, B.; Holloway, J.; Jimenez, J. L.; Knapp, D. J.; Kok, G.; Mena-Carrasco, M.; Olson, J.; O'Sullivan, D.; Sachse, G.; Walega, J.; Weibring, P.; Weinheimer, A.; Wiedinmyer, C. Impact of Mexico City emissions on regional air quality from MOZART-4 simulations. *Atmospheric Chemistry and Physics* **2010**, *10*, (13), 6195-6212.
48. Riuttanen, L.; Hulkkonen, M.; Dal Maso, M.; Junninen, H.; Kulmala, M. Trajectory analysis of atmospheric transport of fine particles, SO₂, NO_x and O₃ to the SMEAR II station in Finland in 1996-2008. *Atmospheric Chemistry and Physics* **2013**, *13*, (4), 2153-2164.
49. Arnold, S. R.; Methven, J.; Evans, M. J.; Chipperfield, M. P.; Lewis, A. C.; Hopkins, J. R.; McQuaid, J. B.; Watson, N.; Purvis, R. M.; Lee, J. D.; Atlas, E. L.; Blake, D. R.; Rappenglueck, B. Statistical inference of OH concentrations and air mass dilution rates from successive observations of nonmethane hydrocarbons in single air masses. *Journal of Geophysical Research-Atmospheres* **2007**, *112*, (D10).

- 768 50. Tsai, D.-H.; Wang, M.-L.; Wang, C.-H.; Chan, C.-C. A study of ground-level ozone
769 pollution, ozone precursors and subtropical meteorological conditions in central Taiwan.
770 *Journal of Environmental Monitoring* **2008**, *10*, (1), 109-118.
- 771 51. Leuchner, M.; Rappengluck, B. VOC source-receptor relationships in Houston during
772 TexAQS-II. *Atmospheric Environment* **2010**, *44*, (33), 4056-4067.
- 773 52. *Inventario de Emisiones de la Zona Metropolitana del Valle de México: Contaminantes*
774 *tóxicos*; Secretaria de Medio Ambiente y Recursos Naturales de México: Ciudad de México,
775 DF, 2012;
776 http://www.sma.df.gob.mx/sma/links/download/biblioteca/inventarios_emisiones2010/ieTO
777 [X10_.pdf](http://www.sma.df.gob.mx/sma/links/download/biblioteca/inventarios_emisiones2010/ieTO).
- 778 53. *Liquefied Petroleum Gas Market Outlook 2008-2017*; Secretaría de Energía del Gobierno
779 Federal de México: Ciudad de México, DF, 2008;
780 http://www.sener.gob.mx/res/PE_y_DT/pub/LPG%20Outlook%202008-2017.pdf.
- 781 54. Atkinson, R. Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment* **2000**, *34*,
782 2063-2101.
- 783 55. Rogers, T. M.; Grimsrud, E. R.; Herndon, S. C.; Jayne, J. T.; Kolb, C. E.; Allwine, E.;
784 Westberg, H.; Lamb, B. K.; Zavala, M.; Molina, L. T.; Molina, M. J.; Knighton, W. B. On-
785 road measurements of volatile organic compounds in the Mexico City metropolitan area
786 using proton transfer reaction mass spectrometry. *International Journal of Mass*
787 *Spectrometry* **2006**, *252*, (1), 26-37.
- 788 56. Gelencser, A.; Siszler, K.; Hlavay, J. Toluene-benzene concentration ratio as a tool for
789 characterizing the distance from vehicular emission sources. *Environmental Science &*
790 *Technology* **1997**, *31*, (10), 2869-2872.

57. Zavala, M.; Herndon, S. C.; Slott, R. S.; Dunlea, E. J.; Marr, L. C.; Shorter, J. H.; Zahniser, M.; Knighton, W. B.; Rogers, T. M.; Kolb, C. E.; Molina, L. T.; Molina, M. J. Characterization of on-road vehicle emissions in the Mexico City Metropolitan Area using a mobile laboratory in chase and fleet average measurement modes during the MCMA-2003 field campaign. *Atmospheric Chemistry and Physics* **2006**, *6*, 5129-5142.
58. Liu, P.-W. G.; Yao, Y.-C.; Tsai, J.-H.; Hsu, Y.-C.; Chang, L.-P.; Chang, K.-H. Source impacts by volatile organic compounds in an industrial city of southern Taiwan. *Sci. Total Environ.* **2008**, *398*, (1-3), 154-163.
59. Zhang, J.; Wang, T.; Chameides, W. L.; Cardelino, C.; Blake, D. R.; Streets, D. G. Source characteristics of volatile organic compounds during high ozone episodes in Hong Kong, Southern China. *Atmospheric Chemistry and Physics* **2008**, *8*, (16), 4983-4996.
60. Zalel, A.; Yuval; Broday, D. M. Revealing source signatures in ambient BTEX concentrations. *Environmental Pollution* **2008**, *156*, (2), 553-562.
61. Mehta, D.; Nguyen, A.; Montenegro, A.; Li, Z. A Kinetic Study of the Reaction of OH with Xylenes Using the Relative Rate/Discharge Flow/Mass Spectrometry Technique. *Journal of Physical Chemistry* **2009**, *113*, (46), 12942-12951.
62. Na, K.; Kim, Y. P.; Moon, I.; Moon, K. C. Chemical composition of major VOC emission sources in the Seoul atmosphere. *Chemosphere* **2004**, *55*, (4), 585-594.
63. Hu, L.; Millet, D. B.; Kim, S. Y.; Wells, K. C.; Griffis, T. J.; Fischer, E. V.; Helmig, D.; Hueber, J.; Curtis, A. J. North American acetone sources determined from tall tower measurements and inverse modeling. *Atmospheric Chemistry and Physics* **2013**, *13*, (6), 3379-3392.

- 813 64. Chatfield, R. B.; Gardner, E. P.; Calvert, J. G. Sources and sinks of acetone in the
814 troposphere - behavior of reactive hydrocarbons and a stable product. *Journal of*
815 *Geophysical Research-Atmospheres* **1987**, 92, (D4), 4208-4216.
- 816 65. Kirstine, W. V.; Galbally, I. E., The global atmospheric budget of ethanol revisited.
817 *Atmospheric Chemistry and Physics* **2012**, 12, (1), 545-555.
- 818 66. Yokelson, R. J.; Burling, I. R.; Gilman J. B.; Warneke, C.; Stockwell, C. E.; De Gouw, J.;
819 Akagi, S. K.; Urbanski, S. P.; Veres, P.; Roberts, J. M.; Kuster, W. C.; Reardon, J.; Griffith,
820 D. W. T.; Johnson, T. J. Hosseini, S.; Miller, J. W.; Cocker, D. R.; Jung, H. and Weise, D.
821 R. Coupling field and laboratory measurements to estimate the emission factors of identified
822 and unidentified trace gases for prescribed fires. *Atmospheric Chemistry and Physics*. **2013**,
823 13, 89–116, doi:10.5194/acp-13-89-2013.
- 824 67. *Effects of indoor air pollution on human health*; Report No. 10; European Concerted Action:
825 Luxembourg, 1991; http://buildingecology.com/publications/ECA_Report10.pdf.
- 826 68. *Environmental Quality Standards in Japan: Air Quality*; Ministry of the Environment
827 Government of Japan: Tokyo, Japan, 1997; <http://www.env.go.jp/en/air/aq/aq.html>.
- 828 69. Bravo, H.; Sosa, R.; Sanchez, P.; Bueno, E.; Gonzalez, L. Concentrations of benzene and
829 toluene in the atmosphere of the Southwestern area at the Mexico City Metropolitan Zone.
830 *Atmospheric Environment* **2002**, 36, (23), 3843-3849.
- 831 70. *Informe Técnico de Monitoreo y Evaluación de las Concentraciones de Compuestos*
832 *Orgánicos Volátiles en la Zona Metropolitana de la Ciudad de México*; Secretaría de Medio
833 Ambiente del Distrito Federal e Instituto Nacional de Ecología y Cambio Climático: Ciudad
834 de México, DF, 2008;
835 http://www.sma.df.gob.mx/sma/links/download/archivos/informe_tecnico_covs.pdf.

836 71. Martins, L. D.; Andrade, M. D.; Ynoue, R. Y.; de Albuquerque, E. L.; Tomaz, E.;
837 Vasconcellos, P. D. Ambiental volatile organic compounds in the megacity of Sao Paulo.
838 *Quim. Nova* **2008**, *31*, (8), 2009-2013.

839 72. Na, K.; Moon, K. C.; Kim, Y. P. Source contribution to aromatic VOC concentration and
840 ozone formation potential in the atmosphere of Seoul. *Atmospheric Environment*, **2005**, *39*,
841 (30), 5517-5524.

842 73. Chang, C. C.; Sree, U.; Lin, Y. S.; Lo, J. G. An examination of 7:00-9:00 PM ambient air
843 volatile organics in different seasons of Kaohsiung city, southern Taiwan. *Atmospheric*
844 *Environment* **2005**, *39*, (5), 867-884.

845 74. Lee, S. C.; Chiu, M. Y.; Ho, K. F.; Zou, S. C.; Wang, X. Volatile organic compounds
846 (VOCs) in urban atmosphere of Hong Kong. *Chemosphere* **2002**, *48*, (3), 375-382.

847 75. Song, Y.; Dai, W.; Shao, M.; Liu, Y.; Lu, S.; Kuster, W.; Goldan, P. Comparison of receptor
848 models for source apportionment of volatile organic compounds in Beijing, China.
849 *Environmental Pollution* **2008**, *156*, (1), 174-183.

850 76. Baker, A. K.; Beyersdorf, A. J.; Doezema, L. A.; Katzenstein, A.; Meinardi, S.; Simpson, I.
851 J.; Blake, D. R.; Rowland, F. S. Measurements of nonmethane hydrocarbons in 28 United
852 States cities. *Atmospheric Environment* **2008**, *42*, (1), 170-182.

853 77. *Administration of Air Pollution Control*; Environmental Agency of Japan: Tokyo, Japan,
854 1999.

855 78. Occupational Safety and Health Standards. Toxic and Hazardous Substances: Identification,
856 Classification, and Regulation of Carcinogens. Public law OSHA – 29 CFR, 2012;
857 [https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id](https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=11378)
858 [=11378](https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=11378).

- 859 79. National Institute for Occupational Safety and Health: NIOSH Pocket guide to Chemical
860 Hazards. Public law Publication No. 2005-149, 2007;
861 <http://www.cdc.gov/niosh/idlh/intridl4.html>.
- 862 80. Secretaría del Trabajo y Previsión Social de México. Norma Oficial Mexicana NOM-010-
863 STPS-1999, 2002; [http://www.stps.gob.mx/bp/secciones/dgsst/normatividad/normas/Nom-](http://www.stps.gob.mx/bp/secciones/dgsst/normatividad/normas/Nom-010.pdf)
864 010.pdf.
- 865 81. Velasco, E.; Lamb, B.; Pressley, S.; Allwine, E.; Westberg, H.; Jobson, B. T.; Alexander, M.;
866 Prazeller, P.; Molina, L.; Molina, M. Flux measurements of volatile organic compounds
867 from an urban landscape. *Geophysical Research Letters* **2005**, 32, (20).
- 868 82. Velasco, E.; Pressley, S.; Grivicke, R.; Allwine, E.; Coons, T.; Foster, W.; Jobson, B. T.;
869 Westberg, H.; Ramos, R.; Hernandez, F.; Molina, L. T.; Lamb, B. Eddy covariance flux
870 measurements of pollutant gases in urban Mexico City. *Atmospheric Chemistry and Physics*
871 **2009**, 9, (19), 7325-7342.
- 872 83. Karl, T.; Apel, E.; Hodzic, A.; Riemer, D. D.; Blake, D. R.; Wiedinmyer, C. Emissions of
873 volatile organic compounds inferred from airborne flux measurements over a megacity.
874 *Atmospheric Chemistry and Physics* **2009**, 9, (1), 271-285.
- 875 84. Goldstein, A. H.; Fan, S. M.; Goulden, M. L.; Munger, J. W.; Wofsy, S. C. Emissions of
876 ethene, propene, and 1-butene by a midlatitude forest. *Journal of Geophysical Research-*
877 *Atmospheres* **1996**, 101, (D4), 9149-9157.