

Volatile Organic Compounds and Carbonyls Pollution in Mexico City and an Urban Industrialized Area of Central Mexico

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ABSTRACT

A total of 130 volatile organic compounds (VOCs) and 14 carbonyls were measured at the Jasso (JAS) and Tepeji (TEP) sites during the warm-dry season of 2006 in Tula, Hidalgo, Mexico, a highly industrialized area with more than 120 industries. These data were compared with those obtained in Mexico City during 2006 and 2012 at an urban center (Merced, MER) site and a southwest residential (Pedregal, PED) site. Average VOC concentrations in Tula were dominated by alkanes (40.8–42.2% of the total VOCs), followed by alkenes (10.3–11.9%), oxygenated compounds (10.0–11.5%), aromatics (7.3–12.5%), halogenated species (7.0–9.3%), and acetylene (1.6–2.4%), denoting a highly reactive atmosphere. High concentrations of propane and nButane are associated with leakage, handling, and distribution of liquified petroleum gas (LPG). The highest concentrations were found for formaldehyde at $87.2 \mu\text{g m}^{-3}$, followed by acetaldehyde ($52.1 \mu\text{g m}^{-3}$) and acetone ($49.7 \mu\text{g m}^{-3}$), accounting for 96% of the total carbonyls in Tula. VOC emission sources associated with industrial processes (such as oil refineries, power plants, plastic manufacturing, asphalt production, and solvent usage), vehicular exhaust, evaporated gasoline, LPG, food cooking, and biogenic emissions were identified using the Positive Matrix Factorization (PMF) solution to the chemical mass balance (CMB) model. A health risk assessment for toxic species such as benzene, toluene, ethyl benzene and xylenes (BTEX), found a decreasing trend from 2006 to 2012. Lifetime cancer risks (LCR) from benzene ranged from 1.5×10^{-5} to 6.1×10^{-5} in 2006 and from 8.8×10^{-6} to 2.2×10^{-5} in 2012 for the urban MER site. This database establishes baselines for evaluating the effectiveness of emission reduction strategies.

Keywords: Industrial pollution, VOCs, Risk assessment, Sources of VOCs, BTEX

1 INTRODUCTION

Volatile organic compounds (VOCs) are of concern due to their adverse effects on human respiratory symptoms, sensory irritation, toxic reactions, and cancer (Boeglin *et al.*, 2006; Jaimes-Palomera *et al.*, 2016; Kotzias, 2021). VOCs also engender the formation of secondary organic aerosols (SOAs) and photochemical ozone (O_3) (Dumanoglu *et al.*, 2014; Jaimes-Palomera *et al.*, 2016). Major anthropogenic VOC emitters include petrochemical processes, petroleum refineries, and industries using fossil fuels (Lin *et al.*, 2004; Dumanoglu *et al.*, 2014; Ramírez *et al.*, 2020;

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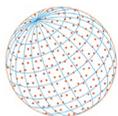
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Silva et al., 2022). Vehicular exhaust and evaporative emissions are also major emitters of VOCs in urban areas (*Vega et al., 2000, 2011*).

The industrial corridor of Tula, Hidalgo, central Mexico, has been identified as one of the most polluted areas in the country. Potential major emitters include the Miguel Hidalgo oil refinery and the Francisco Perez Rios thermoelectric power plant that are powered by fuel oils. The remaining ~120 industries include five cement plants using recycled alternative fuels and industrial wastes that may contain dioxins and furans, acid gases, volatile chlorinated organic compounds, and polycyclic aromatic hydrocarbons (PAHs). Emission estimates in the Tula industrial corridor includes 35,739 tons year⁻¹ of particulate matter (PM), 115,162 tons year⁻¹ of sulfur dioxide (SO₂), 21,997 tons year⁻¹ of nitrogen oxides (NO_x), 284,252 tons year⁻¹ of carbon monoxide (CO), and 70,641 tons year⁻¹ of VOC (*IEEH, 2016*).

The urban area of Mexico City is located ~60 km south of the Tula industrial corridor with a land area of 1,494.6 km² at 2,240 m above mean sea level, bordered by mountains to the south, east, and west and open at the north, where the industrial area is located. Under prevailing northerly winds, emissions from this region can affect air quality in the Mexico City (*Sosa et al., 2013, 2020*). Mexico City was once one of the most polluted megacities, but aggressive emission reduction measures have succeeded in reducing air pollution levels (*Sosa et al., 2020*).

This study evaluates concentrations of 130 VOCs and 14 carbonyls in Tula during the warm-dry season of 2006. These levels are compared with 2006 and 2012 VOCs measured in Mexico City. Sources are inferred by applying the Positive Matrix Factorization (PMF)-Chemical Mass Balance (CMB) receptor model. Toxic and carcinogenic species are used to evaluate health risks. As VOCs are not routinely acquired in Mexico's compliance monitoring network, this historical data set provides a baseline to assist policy makers in establishing control strategies and assessing the effectiveness of emission control measures in the recent past.

2 EXPERIMENTAL METHOD

2.1 Site Locations and Measurements

VOCs and carbonyls were measured at the Jasso (JAS) (99.31°W, 20.02°N) site, located 5 km SW of the Francisco Perez Rio power plant and the Miguel Hidalgo oil refinery; and the Tepeji (TEP) (99.29°W, 19.86°N) site, located 24 km downwind of major sources, close to a highway and a limestone quarry that supplied the cement plants as shown in *Fig. 1*. These sites were selected to capture fresh emissions from major sources and to determine downwind concentrations (*Sosa et al., 2013; Vega et al., 2021*).

The two Mexico City sites represent different types of land use: 1) Merced (MER) (99.07°W, 19.25°N), located downtown with a mix of commercial and residential areas, surrounded by major paved roads with heavily travelled light- and heavy-duty vehicles, and 2) Pedregal (PED) (99.12°W, 19.19°N), located southwest in a residential area adjacent to lightly travelled paved roads and downwind of the city center (*Velasco et al., 2007*). An asphalt production plant located 5 km east of PED site is the only recorded industrial source in the area (*Vega et al., 2000*). The highest VOC concentrations have been reported at the MER site, whereas the Mexican air quality standard for one hour O₃ (110 ppb) is frequently exceeded at the PED site (*Jaimes-Palomera et al., 2016*).

2.2 Sampling and Analytical Methods

From 29 March to 21 April 2006, a total of 220 VOC samples from the two Tula sites were acquired daily within two 12-hour periods (i.e., daytime, 07:00–19:00 and nighttime, 19:00–next day 07:00 local time [LT]) with passivated stainless steel canisters using automated sample changers (VOCCS and AVOCS, Andersen Instruments, Waltham, MA, USA). VOCs (C₂–C₁₁) for 130 compounds were quantified using cryogenic preconcentration/high-resolution gas chromatography (GC) following the TO-14A protocol (*U.S. EPA, 1999*) as described previously (*Vega et al., 2000; Arriaga-Colina et al., 2004*). Daily, 12-hour (07:00 to 19:00 LT) carbonyl samples were acquired with dinitrophenylhydrazine (DNPH)-Silica cartridges (Water Sep-Pak, Milford, MA, USA). The 14 carbonyls were analyzed by high performance liquid chromatography (HPLC) equipped with an ultraviolet photodiode array detector following the TO-11A protocol (*Arriaga-Colina et al., 2004*).

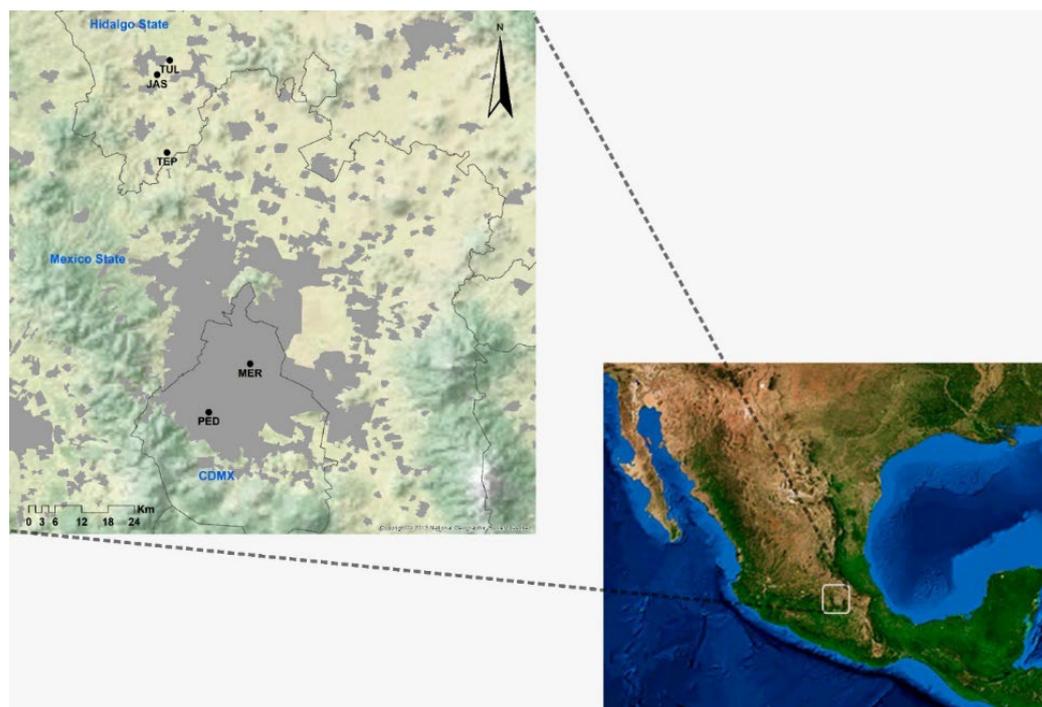
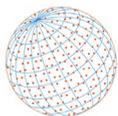


Fig. 1. Locations of Jasso (JAS) and Tepeji (TEP) monitoring sites in Hidalgo, and Merced (MER) and Pedregal (PED) sites in Mexico City, Mexico.

Additional 24-hour VOC canister samples (midnight–24:00 LT) were collected every sixth day at the MER and PED sites from 24 March to 23 May, 2006 and from 28 March to 24 April, 2012. Details of the sampling campaigns and chemical analyses are provided in [Reyes *et al.* \(2008\)](#) and [Jaimes-Palomera *et al.* \(2016\)](#).

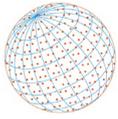
Different sampling periods were chosen to coincide with the field campaign duration in Tula. A longer sampling period (March to May, 2006) was selected for the 24-hour VOCs due to the infrequent sampling schedule (i.e., every sixth day) to accommodate the statistical stability for follow up data analysis and modeling. In addition, VOC measurements from the northeast industrial Xalistic (XAL) and southeast services (CES) sites from 2003, 2006, and 2012 were obtained for comparison.

Meteorological conditions conducive to pollution buildups during the warm-dry season in Tula have been examined by [Fast *et al.* \(2007\)](#) and [Sosa *et al.* \(2013\)](#). A shallow stable layer with light south-southwesterly winds often forms early in the morning, limiting pollutant dispersion. After midday, a well-developed mixing layer with prevailing northerly winds favor pollutant mixing and transport. Similar situations occurred during the warm-dry season of 2006 and 2012 for Mexico City ([Gobierno de la Ciudad de México, 2022](#)).

2.3 Source Identification

PMF version 5.0 software ([Paatero, 1997](#); [Norris *et al.*, 2014](#)) was applied to identify possible VOC sources. Observables submitted to the PMF-CMB solution included C3–C11 alkanes, C4–C6 alkenes, C6–C9 aromatics, acetylene, three oxygenated compounds, and five carbonyls (i.e., formaldehyde, acetaldehyde, acetone, propionaldehyde, and crotonaldehyde). A minimum of 75% valid data was required for a species to be included as a fitting species.

Uncertainties were calculated following the methodology proposed by [Amato *et al.* \(2009\)](#). Species were classified using the signal-to-noise (S/N) ratio defined by [Paatero *et al.* \(2003\)](#). Species with $S/N < 2$ were generally defined as weak variables. Since S/N is sensitive to sporadic values much higher than the level of noise, the percentage of data above detection limit was used ([Ramírez *et al.*, 2018](#)). To obtain the best solution that met goodness-of-fit parameters (e.g., observed vs. estimated values, correlation coefficients and residual analysis), 5 to 7 factors were used in addition to the G-space plot to assess rotational ambiguity and possible relationships



among the factor contributions. The Fpeak rotation tool was used to provide stability to the solution. The proximity of Q_{robust} and Q_{theory} values was used as the criterion for choosing the best fit to the input data (Reff *et al.*, 2007). Q_{theory} was calculated following the procedure suggested by Norris *et al.* (2014). The basic equation that refers to the solution of the mass balance is:

$$X_{ij} = \sum_{k=1}^p g_{ik} x f_{kj} + e_{ij} \quad (1)$$

where X_{ij} is the concentration of species j measured on sample i ; p is the number of factors contributing to the samples; f_{kj} is the concentration of species j in factor profile k ; g_{ik} is the relative contribution of profile k to sample i ; and e_{ij} is error of the PMF model for the j species measured on sample i . The values of g_{ik} and f_{kj} are adjusted until a minimum value of Q for a given p is found. Q is defined as:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2 \quad (2)$$

where σ_{ij} is the uncertainty of the j th species concentration in sample i ; n is the number of samples; and m is the number of species.

2.4 Health Risk Estimates

BTEX (benzene, toluene, ethylene, and xylene) is a VOC group of high interest due to carcinogenic and non-carcinogenic effects on human health (Hu *et al.*, 2018; Abbasi *et al.*, 2020). Health risks were estimated based on the assumption that inhalation is the major exposure pathway. Since benzene is a Group 1 carcinogen and ethylbenzene is a Group 2B carcinogen (IARC, 2000, 2018), cancer risks were estimated for these two compounds, while non-carcinogenic risks included all BTEX compounds. Carcinogenic and non-carcinogenic risks were estimated by calculating the Lifetime Cancer Risk (LCR) and Hazard Quotient (HQ), respectively, following the guidance of the U.S. EPA (2009, 2011) as described by the following equations (Dehghani *et al.*, 2018; Mohammadi *et al.*, 2020; Ghaffari *et al.*, 2021):

$$CE = ((C \times ET \times EF \times ED)/AT) \quad (3)$$

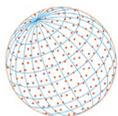
$$LCR = CE \times IUR \quad (4)$$

$$HQ = CE/(RfC \times 1000) \quad (5)$$

$$HI = \sum_{i=1}^n HQ_i \quad (6)$$

where CE is the cumulative exposure ($\mu\text{g m}^{-3}$); C is the measured pollutant concentration ($\mu\text{g m}^{-3}$); ET is the exposure time (24 hours day^{-1}); EF is the exposure frequency (365 hours day^{-1}); ED is the exposure duration set at 6 and 24 years for children and adults, respectively (Wang *et al.*, 2018; Vega *et al.*, 2021); and AT is the average lifetime (hours = 75 years \times 365 days $\text{year}^{-1} \times$ 24 hours day^{-1}), where 75 years is the life expectancy in Mexico (Gobierno de México, 2019). The IUR is the inhalation unit risk ($\mu\text{g m}^{-3}$) $^{-1}$ and RfC is the inhalation reference concentration (mg m^{-3}). In addition, a hazard index (HI) was used to sum the HQs of all the BTEX compounds (Eq. (6)), where HQ_i is the HQ calculated for each i th compound.

Based on the Office of Environmental Health Hazard Assessment (OEHHA) (<https://oehha.ca.gov/>), the IUR for benzene is 2.9×10^{-5} ($\mu\text{g m}^{-3}$) $^{-1}$ and for ethylbenzene is 2.5×10^{-6} ($\mu\text{g m}^{-3}$) $^{-1}$. The RfD values of benzene, toluene, ethylbenzene, and xylenes are 0.03 mg m^{-3} , 5.0 mg m^{-3} , 1.0 mg m^{-3} , and 0.1 mg m^{-3} , respectively, which are obtained from the Integrated Risk Information System (IRIS, www.epa.gov/iris).



3 RESULTS AND DISCUSSION

3.1 Concentrations in Tula Industrial Corridor

3.1.1 Volatile organic compounds (VOCs)

Average 24-hour VOCs (07:00 to next day 07:00 LT) at JAS consisted of 2.4% acetylene, 40.8% alkanes, 10.3% alkenes, 9.3% halogenated compounds, 12.5% aromatics, 11.5% oxygenated compounds, and 13.3% non-identified. TEP averages consisted of 1.6% acetylene, 42.2% alkanes, 11.9% alkenes, 7.0% halogenated compounds, 7.3% aromatics, 10.0% oxygenated compounds, and 20.2% non-identified. These compositions are similar to those reported at Salamanca in Central Mexico (Vega *et al.*, 2011). Velasco *et al.* (2007) found that VOCs in Mexico City consisted of 60% alkanes, 5% alkenes, 15% aromatics, 2% oxygenated compounds, and 18% of non-identified species. Higher percent composition of alkenes (10.3–11.9%) and oxygenated compounds (10–11.5%) at the JAS and TEP sites contrasted with the 5% and 2% averages, respectively, in Mexico City, consistent with higher reactivity potentials in the Tula atmosphere. Aromatics constituted 7–15% of VOCs in both the Tula region and Mexico City, indicating potential contributions from industrial emissions such as solvents, painting, graphic arts, and dry cleaning.

Higher VOC concentrations were observed at TEP than at JAS for both daytime and nighttime samples, with average and maximum 24-hour concentrations of 313.6 ppbC and 586.0 ppbC at TEP, and 259.5 and 395.0 ppbC at JAS, respectively. Among the different groups of VOCs, alkanes showed the highest 12-hour concentrations. As shown in Fig. 2, average nighttime alkanes concentrations were 160.5 ppb at TEP and 102.3 ppbC at JAS. Propane and nButane are higher during nighttime than daytime, whereas propane and toluene exhibit less day/night differences. Oxygenated compounds show the opposite trend with higher concentrations found during day time. These findings are consistent with past studies, attributing to VOC conversion and high mixing heights during daytime which leads to lower VOC levels (An *et al.*, 2014; Gu *et al.*, 2020).

At TEP, average acetylene and alkanes were 200% and 26% higher during nighttime than daytime, respectively. Maximum concentrations accounted for 65% of the nighttime samples for acetylene and 12% for alkanes. In contrast, aromatics concentration maxima were found in 18% of the daytime samples as compared to 5% during nighttime. Maximum nighttime halogenated and oxygenated compounds contributed to 12.5% and 18.7% of the total VOCs at TEP, respectively, twofold higher than those during daytime. These levels are higher than the maximum halogenated and oxygenated compounds during nighttime at JAS which accounted for 6.8% and 11.9%, of total VOCs, respectively.

Average total VOC concentrations of 259.5 ppbC at JAS and 313.6 ppbC at TEP were lower than the 1.1 and 6.7 ppmC reported for the PED (southwest residential) and XAL (northeast industrial) sites, respectively, in Mexico City (Arriaga-Colina *et al.*, 2004). Diurnal variations of VOCs in Tula were associated with the accumulation of local emissions due to a shallow boundary layer along with SOA formation (de Gouw *et al.*, 2009). During the warm-dry season with enhanced photochemical reactions, alkanes and aromatics react with hydroxyl radicals (OH[•]) in the gas-phase while alkenes react with O₃, nitrate radical, and OH[•] to form SOA.

Table 1 summarizes average and maximum concentrations of 22 VOCs in Tula. Average propane concentration (52.4 ppbC) were highest at TEP, followed by 111-trichloroethane (26.8 ppbC), used as an industrial solvent and for consumer products. The highest VOC at JAS was 111-trichloroethane (33.7 ppbC). Markers associated with handling and distribution of liquefied petroleum gas (LPG) at JAS include propane (13.5 ppbC), nButane (12.9 ppbC), iPentane (8.6 ppbC), and iButane (5.3 ppbC), constituting 16% of the total VOCs. Toluene (6.8 ppbC) was the highest aromatic, followed by xylenes (5.7 ppbC), and benzene (2.1 ppbC).

Among the alkenes and alkynes, acetylene (5.5 ppbC) was the most abundant species, followed by ethylene (1.7 ppbC) at JAS. At TEP, nButane (26.6 ppbC) and iButane (11.4 ppbC) contributed 20% of the total VOCs, with ~30% lower toluene (4.8 ppbC), 35% lower xylene (3.7 ppbC), ~30% lower benzene (1.5 ppbC) and acetylene (4.6 ppbC) than concentrations at JAS. Isoprene from natural sources was low at 2.5 ppbC. At TEP, LPG constituents (e.g., propane and butane) were important contributors to low molecular weight alkenes, accounting for 25–40% of the sum of 22 VOCs and 12–29% of the total VOCs. A high correlation ($r = 0.93$) between propane and nButane was found at TEP, consistent with contributions from LPG handling, distribution, and leakage.

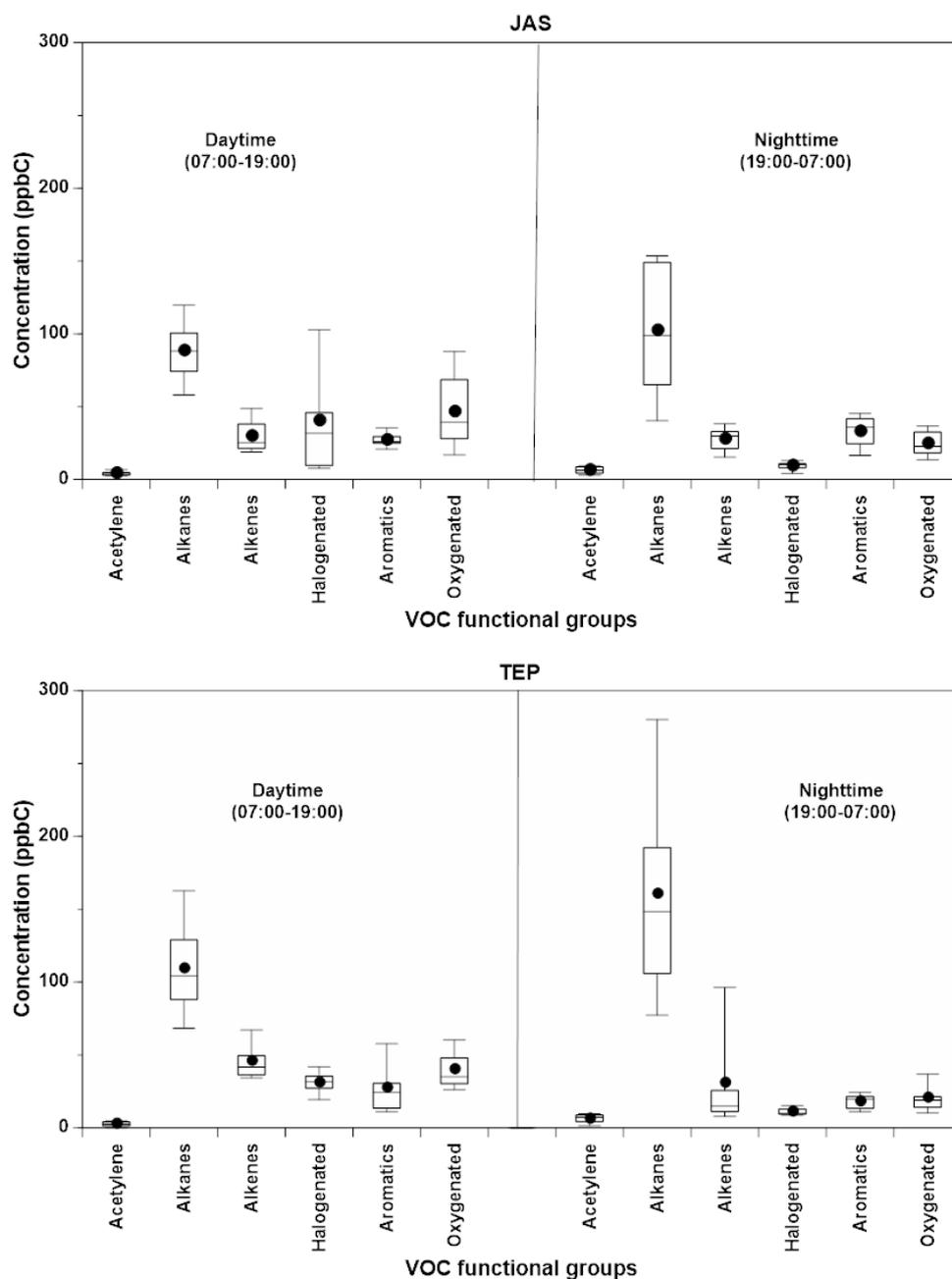
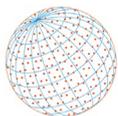
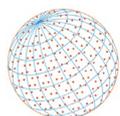


Fig. 2. Basic statistics for 12-hour average (07:00 to 19:00 and 9:00 to 07:00 LT) VOCs at the JAS and TEP sites. Dots represent average VOCs concentrations; horizontal lines inside the box represent the median; bottom and top of the boxes represent the 25% and 75% limits, respectively; and the bottom and the top whiskers represent the 5% and 95% limits, respectively.

This is consistent with data reported for Mexico City (Vega *et al.*, 2000). A high correlation ($r = 0.93$) was also found between *i*Butane and *n*Butane at JAS, compounds used in refineries to increase the gasoline octane ratings. These high correlations are consistent with gasoline evaporative emissions.

Previous studies indicate that emissions from light-duty gasoline and heavy-duty diesel vehicles are dominated by ethylene, acetylene, propene, *n*/*i*-Pentane, 2,2-dimethylbutane, 2-methylpentane, benzene, toluene, and xylenes (Blake and Rowland, 1995; Vega *et al.*, 2000). Supplemental Fig. S1 shows vehicular VOC emissions measured in 2000 (Vega *et al.*, 2000) versus 2018 (Mugica-Alvarez *et al.*, 2020), suggesting relatively consistent source compositions over this period. The dominant compounds were C5 alkanes such as *i*Pentane, methylpentanes, trimethylpentanes, *n*Butane, toluene and hexane, with low > C10 compounds.

**Table 1.** Average 24-hour (07:00-next day 07:00 local time) and maximum concentration (ppbC) for 22 volatile organic compounds at Jasso (JAS) and Tepeji (TEP) sites during 29 March to 21 April, 2006.

Compounds	JAS			TEP		
	24-hour average	Standard Deviation	24-hour maximum	24-hour average	Standard Deviation	24-hour maximum
Ethane	4.4	± 1.3	6.6	4.4	± 1.5	6.4
Propane	13.5	± 3.4	20.2	52.3	± 38.1	151.9
iButane	5.3	± 1.2	6.9	11.4	± 6.3	27.2
nButane	12.9	± 3.7	18.4	26.6	± 17.9	77.7
iPentane	8.6	± 4.2	16.2	4.1	± 1.8	8.1
nPentane	4.0	± 2.9	7.6	1.8	± 1.1	3.7
2-Methylpentane	2.7	± 1.8	4.8	2.1	± 1.0	4.0
3-Methylpentane	3.0	± 0.9	4.2	14.4	± 5.9	25.3
nHexane	2.3	± 1.7	4.6	1.1	± 0.8	2.6
Ethylene	1.7	± 0.8	3.0	9.9	± 1.2	94.3
c2Butene	2.7	± 2.2	6.8	17.8	± 4.5	25.0
Isoprene	2.5	± 0.9	3.9	2.1	± 0.9	3.8
Propylene	6.0	± 2.8	10.3	16.4	± 38.0	130.5
Styrene	1.6	± 0.4	2.5	1.5	± 0.4	2.4
Acetylene	5.5	± 1.1	6.8	4.6	± 1.9	6.7
Benzene	2.1	± 0.7	3.4	1.5	± 0.5	2.3
Toluene	6.8	± 1.3	9.1	4.8	± 2.7	11.0
Xylenes	5.7	± 0.4	7.3	3.7	± 0.3	5.3
Methanol/ethanol/acetone	4.2	± 1.3	5.4	2.7	± 0.8	3.8
111-trichloethane	33.7	± 14.9	58.9	26.8	± 7.6	35.7
Sum 22 VOCs	125.7	± 0.4		227.5	± 4.1	
Total VOCs	259.5	± 65	395.0	313.6	± 103	586.0

3.1.2 Distribution of BTEX

Fig. 3 compares BTEX concentrations in Tula with those reported in Mexico City during 2003. Average total BTEX concentrations at JAS (16.1 ppbC) and TEP (11.3 ppbC) were one to two orders of magnitude lower than those found in Mexico City. Compared to the Tula region, average BTEX compounds in Mexico City were ~25-fold higher at the northern Mexico City industrial area (XAL, 342.3 ppbC), ~15-fold higher at downtown (MER, 202.1 ppbC) and southeast services (CES, 198.7 ppbC), and ~6-fold higher at the southwest residential (PED, 82.8 ppbC) sites. Elevated BTEX in the urban area of Mexico City may be due to the abundant use of solvents, degreasing and fueling stations (Vega *et al.*, 2000; Jaimes-Palomera *et al.*, 2016).

BTEX sources include fueling stations, vehicular maintenance facilities, factories and refineries, and road traffic (Edgerton *et al.*, 1989). Correlations between *m*-xylene and *o*-xylene were higher at JAS ($r = 0.93$) than TEP ($r = 0.72$). A high correlation was also found between ethylbenzene and *o*-xylene ($r = 0.96$) at JAS, with moderate correlation between toluene and ethylbenzene ($r = 0.71$) as well as toluene and styrene ($r = 0.75$). Higher correlations were found between benzene and sum of xylenes (*m*-, *p*- and *o*-isomers) at JAS ($r = 0.62$) than at TEP (0.50). In Mexico City, high correlations were also observed between ethylbenzene and xylenes ($r > 0.95$) and between benzene and ethylbenzene (0.98) at all sites. The high correlation between ethylbenzene and xylenes suggests the impact from gas station and mobile sources.

Vega *et al.* (2011) reported a tenfold higher benzene concentration (19.5 ppbC) and threefold higher toluene and xylene concentrations at Salamanca, another region influenced by refinery emissions. Toluene is produced during petroleum refining operations and may also be emitted by industry, paints, paint thinners, adhesive, and solvents used in degreasing and coating.

Toluene has been the most abundant aromatic species in Mexico City with maximum concentrations ranging 102–172 ppbC in the central area and 58–71 ppbC in the southern areas. From 2002 to 2013, average toluene concentrations decreased by ~50%, being 99.7, 57.9 and 52.6 ppbC in 2003, 2006 and 2012, respectively at MER and 41.8, 41.7 and 22.8 ppbC at PED.

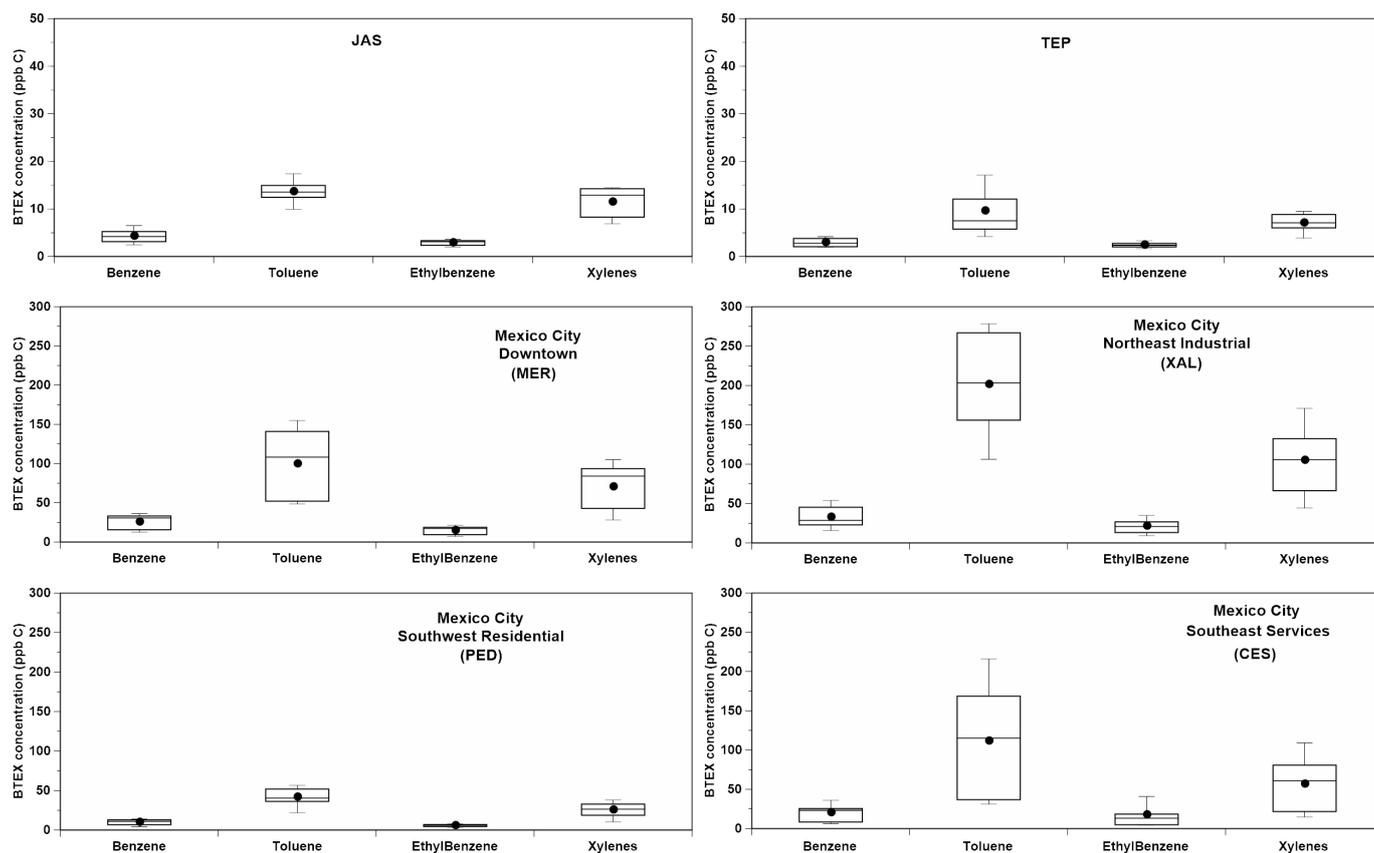
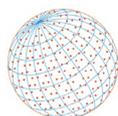
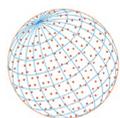


Fig. 3. Average 24-hour concentrations for benzene, toluene, ethylbenzene and xylene in the Tula region and Mexico City during 2003. Dots represent the average mass concentration; horizontal lines inside box represent the median; bottom and top of the boxes represent the 25% and 75% limits, respectively; and the bottom and the top whiskers represent the 5% and 95% limits respectively.

Consistent reductions were found for benzene with a 52% decrease at MER and 32% at PED from 2003 to 2006 and 72% reduction at MER and 55% at PED from 2003 to 2012. These reductions are attributed to catalytic converters required on newer vehicles (Jaimes-Palomera *et al.*, 2016).

Toluene/benzene ratios (T/B) have been used as indicators of photochemical reactivity and aging (Dehghani *et al.*, 2018). Higher T/B ratios (> 8) have been associated with coal and biofuel combustion (Duan and Li, 2017). Ratios of 2–8 signify vehicular emissions whereas lower T/B ratios suggest evaporation of solvents from dry cleaning and degreasing, paints, and other area source emissions such as fueling stations (Vega *et al.*, 2000, 2007). Average 24-hour T/B ratios were 3.6 for JAS and 3.3 at TEP. Lower T/B ratios at TEP may partially be due to toluene attenuation by photochemical reactions. These T/B ratios are lower than the average 5.1 for Mexico City in 2003, ranging from 3.9 (MER, downtown, heavy traffic) to 6.5 (XAL, northeast industrial site) (Vega *et al.*, 2000). High correlations ($r > 0.8$) between toluene and benzene and between ethylbenzene and xylenes were found at both sites in 2006, but there was no correlation between toluene and benzene. Average T/B ratios at MER increased from 4.5 in 2006 to 7.1 in 2012, consistent with changes in both tailpipe and evaporative emissions. Tailpipe emissions were regulated by the catalytic converters while evaporative emissions were less controlled (Hata *et al.*, 2020). The T/B ratios at PED (4.1–5) are similar to those calculated (4.6–5) by Hata *et al.* (2020) using the data with summer grade gasoline.

The mp-xylene/ethylbenzene ratios (X/E), ranging from 2.8 to 4.6, have been used to characterize vehicular emissions (Edgerton *et al.*, 1989). Similar X/E ratios of 2.3 and 2.9 and high correlation ($r > 0.9$) were found at TEP and JAS, respectively, consistent with vehicular emissions. In Mexico City, the X/E ratios, ranged from 3.0 to 3.6 with an average of 3.3 and high correlation (> 0.96).



3.1.3 Carbonyls

Formaldehyde (20–26.5 $\mu\text{g m}^{-3}$) was the most abundant carbonyl, followed by acetone (17.9–18.0 $\mu\text{g m}^{-3}$) and acetaldehyde (13.2–14.2 $\mu\text{g m}^{-3}$). The maximum formaldehyde concentration was 87.2 $\mu\text{g m}^{-3}$, followed by acetaldehyde (52.1 $\mu\text{g m}^{-3}$) and acetone (49.7 $\mu\text{g m}^{-3}$). These three compounds accounted for 94–96% of the total carbonyls (Σ Carbonyls, sum of 14 carbonyl compounds), higher than the 43–79% found in Mexico City. Total carbonyls were similar between JAS (61 $\mu\text{g m}^{-3}$) and TEP (54.7 $\mu\text{g m}^{-3}$); with maximum concentrations of 198.6 $\mu\text{g m}^{-3}$ and 176.3 $\mu\text{g m}^{-3}$, respectively, on 29 March 2006. Average 12-hour carbonyls (Table S1 of supplementary material) shows that Σ Carbonyls in the Tula region were similar to those measured in Mexico City in 2003 at the downtown MER and southwest residential PED sites (61.0 and 46.7 $\mu\text{g m}^{-3}$), but they were over twofold higher (140 and 105 $\mu\text{g m}^{-3}$) at the northeast industrial (XAL) and southeast services (CES) sites.

Few carbonyl measurements have been made in Mexico for comparison. Levels in Mexico are lower than 174 $\mu\text{g m}^{-3}$ total carbonyl (with \sim 82 $\mu\text{g m}^{-3}$ acetone) found in India (Sarkar *et al.*, 2017). However, total carbonyls in Tula were much higher than the \sim 20 $\mu\text{g m}^{-3}$ reported at urban sites in China (Liu *et al.*, 2021b) and of 8.1 $\mu\text{g m}^{-3}$ in San Jose, Costa Rica (Murillo *et al.*, 2012).

In Tula, carbonyls are produced from incomplete combustion of fossil fuels along with photochemical reaction products that lead to the formation of free radicals (e.g., peroxyacetyl nitrates) and O_3 (Grosjean *et al.*, 2002). The predominant contributor to carbonyls in Mexico City is vehicular emissions with formaldehyde being the most abundant compound in diesel exhaust emissions (Grosjean *et al.*, 2001). Acetone concentrations (29.9 and 26.3 $\mu\text{g m}^{-3}$ from northeast industrial XAL and southeast services CES sites) were 60% higher than those measured in Tula, partially due to the use of acetone as a solvent.

Elevated carbonyls and VOCs in northern Mexico City reflect impacts from the Tula industrial corridor under prevailing northerly winds (\sim 4.0 m s^{-1}). Average acetaldehyde concentrations of 13.2–14.2 $\mu\text{g m}^{-3}$ in Tula were higher than those reported in Brazil (10.4 $\mu\text{g m}^{-3}$) where ethanol is used as a fuel and a gasoline additive (Grosjean *et al.*, 2002).

Formaldehyde/acetaldehyde ratios (FA/AA) provide information about atmospheric dynamics and the reactivity of organic compounds, potential emission sources, contribution differences among vehicular emissions, ethanol fuels, and biogenic sources (Delikhooon *et al.*, 2018). FA/AA has also been associated with the primary or secondary origin of the photochemical production of aldehydes (Nogueira *et al.*, 2017). The FA/AA ratios were 1.7 in Tula, 2.3–2.7 in Mexico City, and 1.04 in Brazil (Grosjean *et al.*, 2002). Ethanol in the fuel may react with hydroxyl radicals, resulting in lower FA/AA ratios in Brazil. Higher FA/AA ratios in Mexico City, especially at XAL (FA/AA = 2.5) and CES (FA/AA = 2.7) sites, may reflect the influence of both natural and anthropogenic VOCs that lead to formaldehyde formation. Good correlations ($0.8 < r < 0.9$) among carbonyls were found in Tula, higher than those found in Mexico City (mostly with $r < 0.7$), suggesting origination from common sources.

Ratios of average acetaldehyde/propionaldehyde (AA/PA) indicate anthropogenic origins of carbonyls, as propionaldehyde is associated with hydrocarbon precursors (Bakeas *et al.*, 2003). While acetaldehyde (7.3–10.9 $\mu\text{g m}^{-3}$) levels in Mexico City were 23–45% lower than those found in Tula (13.2–14.2 $\mu\text{g m}^{-3}$), propionaldehyde (7.7–11.0 $\mu\text{g m}^{-3}$) in Mexico City was five- to sevenfold higher than those of Tula. Average AA/PA ratios of 7.5 and 9.3 were found at JAS and TEP, respectively, 90–92% higher than those found in Mexico City, but similar to 7.4 reported for Nairobi, Kenya (Bakeas *et al.*, 2003).

3.2 Concentrations in Mexico City

VOC concentrations at the MER and PED sites consisted of alkanes, alkenes, aromatics, and acetylene. The distribution of VOCs during 2006 was dominated by alkanes (56.1 and 54.3% in MER and PED, respectively), followed by alkenes (27.3% at MER and 26.7% at PED) with aromatics of 16.6% in MER and 19.0% in PED. Velasco *et al.* (2007) also found the abundant alkanes at different rural, suburban, and urban sites in Mexico City metropolitan area (MCMA), varying from 43–61%. Alkane abundances during 2012 increased by 15–19%, ranging from 71.5% (MER) to 73.7% (PED) of VOCs, whilst alkenes were reduced by 12–14%, ranging from 13.5% (MER) to 14.3% (PED). The aromatic group (BTEX and 1,2,4-trimethylbenzene) varied by 2–7% with 15.0% at MER and 12.0% at PED in 2012, as shown in Fig. 4.

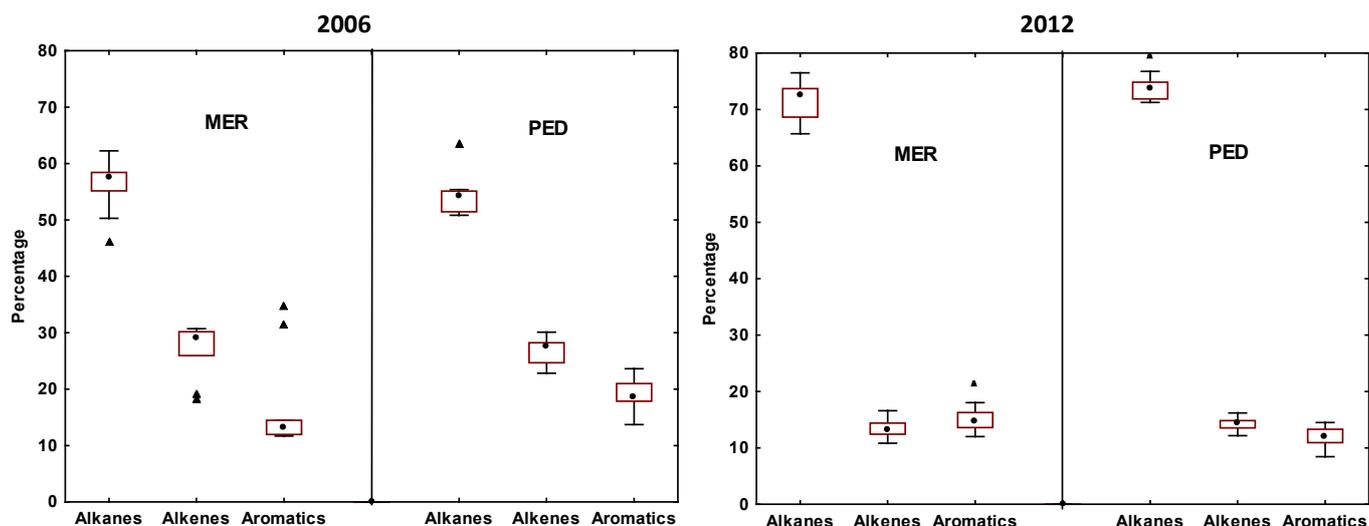
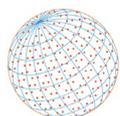


Fig. 4. Percentage of VOCs groups for MER and PED during 2006 and 2012. Dots represent the median concentration; bottom and top of the boxes represent the 25 and 75% limits, respectively; the bottom and the top whiskers represent the 5 and 95% limit, respectively; and diamonds are extreme values (± 1.5 S.D.)

In 2006, the most abundant compound was propane (152.5 ppbC and 103.0 ppbC at MER and PED), followed by propylene (71.8 ppbC and 45.6 ppbC, respectively). Chemical species related to LPG leaks (e.g., propane, iButane, and nButane) were the major source, with high correlations ($r > 0.98$), highlighting the importance of LPG leaks to the VOC burden (Blake and Rowland, 1995; Vega *et al.*, 2000; Gasca *et al.*, 2004; Jaimes-Palomera *et al.*, 2016). LPG leaks may occur during storage, transportation, distribution, and consumption processes of this gas, which is the main fuel used for heating and cooking in domestic and commercial appliances (Gamás *et al.*, 2000).

Among the alkene species, propylene and ethylene showed the maximum concentrations, whereas aromatics were dominated by toluene, as it shown in Table 2. Propane (169.9 ppbC at MER and 98.4 ppbC at PED) was the most abundant VOC in 2012, followed by nButane (91.0 ppbC at MER and 45.5 ppbC at PED), and toluene (54.5 ppbC at MER and 23.0 ppbC at PED). Air pollution in Mexico City has been improving, because of strengthened regulatory and control policies, such as switching from fuel oil to natural gas to reduce emissions at major sources (e.g., power plants and refineries); implementing catalytic converters for internal combustion engines; enacting vehicle inspection and maintenance programs; producing cleaner fuels; improving public transport with cleaner technologies (e.g., electric buses); and installing vapor recovery systems at fuel service stations (Vega *et al.*, 2000; Jaimes-Palomera *et al.*, 2016; Sosa *et al.*, 2020).

Changes in implementation and combustion products can also be associated with health risks. Jaimes-Palomera *et al.* (2016) found an increase of isoprene in Mexico City, attributing this VOC to both traffic (gasoline engines) and biogenic emissions (as synthesis of isoprene provides thermal tolerance to the leaves). Temperature is one of the main variables that affects isoprene emission, consistent with the occurrence of peak ambient temperature and isoprene mixing ratios. Other studies (Velasco, 2003) found that the bulk of biogenic isoprene emissions in the Valley of Mexico occurred at 13:00–15:00 local time, when solar radiation peaked and ambient temperatures reached their maxima. For i-pentane, increases may be due to changes in gasoline composition in addition to vehicular and LPG emissions.

3.3 Source Identification

After sensitivity tests that evaluated Q-values, Fpeak rotations, and physical consistency with source profile measurements, PMF-CMB factors were assigned to represent real-world source types. Daytime (07:00–19:00 LT) data consisting of 58 VOCs and 5 carbonyls (i.e., formaldehyde, acetaldehyde, acetone, propionaldehyde and crotonaldehyde) were included in the PMF analysis to determine the added value of including carbonyl measurements; nighttime carbonyl was not acquired. Different factors were derived for each sampling site. Several factors suggest a mixture

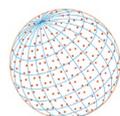
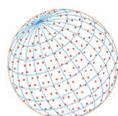


Table 2. Average 24-hour (00:00–24:00 LT) ambient concentrations of VOCs (ppbC) at the MER and PED sites during 24 March to 23 May, 2006 and 28 March to 24 April, 2012.

Compounds	Merced 2006		Pedregal 2006		Merced 2012		Pedregal 2012	
	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Alkanes	Ethane	25.07 ± 8.00	8.54 ± 1.78	18.39 ± 5.19	12.30 ± 2.18			
	Propane	152.48 ± 49.85	103.03 ± 30.58	169.98 ± 76.87	98.43 ± 24.79			
	iButane	33.20 ± 10.53	20.47 ± 5.78	29.29 ± 12.47	17.78 ± 4.10			
	nButane	62.74 ± 24.25	9.01 ± 2.70	91.05 ± 39.39	45.48 ± 11.16			
	iPentane	22.89 ± 7.48	10.85 ± 2.25	53.10 ± 23.06	14.21 ± 4.28			
	nPentane	1.57 ± 0.56	0.62 ± 0.22	±	±			
	2,2-dimethylbutane	0.95 ± 0.30	0.75 ± 0.39	±	±			
	Cyclopentane	1.25 ± 0.54	0.84 ± 0.36	±	±			
	2,3-dimethylbutane	6.45 ± 3.78	4.47 ± 2.37	2.52 ± 0.90	2.13 ± 0.58			
	Hexane	12.92 ± 11.51	9.01 ± 5.48	18.63 ± 7.87	7.84 ± 2.23			
	Methylcyclopentane	1.53 ± 1.25	0.88 ± 0.24	±	±			
	2,4-dimethylpentane	1.47 ± 0.48	0.83 ± 0.29	3.14 ± 1.15	2.08 ± 0.57			
	Cyclohexane	1.80 ± 0.47	1.05 ± 0.49	±	±			
	2-methylhexane	1.90 ± 0.72	0.61 ± 0.21	±	±			
	2,3-dimethylpentane	4.97 ± 1.66	3.23 ± 1.44	±	±			
	3-methylhexane	2.05 ± 0.55	1.20 ± 0.44	±	±			
	Heptane	2.99 ± 1.09	1.87 ± 0.71	±	±			
	2,2,4-trimethylpentane	8.74 ± 3.38	4.31 ± 1.17	14.67 ± 5.40	14.65 ± 4.17			
	Methylcyclohexane	5.83 ± 4.47	2.51 ± 0.77	±	±			
	2,3,4-trimethylpentane	5.93 ± 7.19	2.29 ± 0.79	±	±			
	2-methylheptane	3.10 ± 6.52	0.83 ± 0.19	±	±			
	Octane	5.15 ± 9.56	1.34 ± 0.48	±	±			
	Nonane	5.49 ± 8.84	1.85 ± 0.81	±	±			
Decane	7.87 ± 9.23	3.87 ± 3.06	±	±				
Alkenes	Ethylene	51.35 ± 23.74	16.73 ± 7.29	25.38 ± 8.22	17.08 ± 4.53			
	Propylene	71.82 ± 23.89	45.59 ± 12.69	26.38 ± 6.99	13.30 ± 2.27			
	t-2-butene	2.07 ± 1.10	1.16 ± 0.55	4.13 ± 1.69	3.01 ± 0.81			
	1-butene	1.44 ± 0.58	0.50 ± 0.16	6.47 ± 2.19	3.38 ± 0.89			
	c2butene	29.90 ± 9.54	17.02 ± 4.97	4.00 ± 1.63	1.98 ± 0.53			
	1-pentene	33.23 ± 17.48	17.70 ± 7.93	±	±			
	Isoprene	0.47 ± 0.15	0.45 ± 0.09	5.72 ± 1.99	2.13 ± 0.57			
	t-2-pentene	2.43 ± 1.01	0.88 ± 0.21	±	±			
	c-2-pentene	2.44 ± 0.91	1.30 ± 0.46	±	±			
	1-hexene	4.86 ± 1.58	3.35 ± 1.39	±	±			
Alkyne	Acetylene	23.78 ± 6.31	14.42 ± 4.06	±	±			
Aromatics	Benzene	11.90 ± 3.58	6.62 ± 2.03	7.39 ± 1.88	4.45 ± 0.90			
	Toluene	54.46 ± 21.02	37.88 ± 6.93	54.47 ± 19.43	23.04 ± 7.12			
	Ethylbenzene	13.96 ± 16.54	6.38 ± 1.70	5.34 ± 2.04	2.66 ± 0.97			
	m-xylene	10.15 ± 12.12	4.23 ± 1.24	8.86 ± 2.83	2.99 ± 1.00			
	p-xylene	20.49 ± 15.77	9.22 ± 2.22	±	±			
	Styrene	8.70 ± 7.23	3.72 ± 1.27	±	±			
	o-xylene	8.90 ± 7.77	5.96 ± 3.48	6.35 ± 2.44	2.21 ± 0.84			
	ipropylbenzene	14.16 ± 28.55	5.47 ± 4.36	±	±			
	n-propylbenzene	2.94 ± 5.87	1.31 ± 1.29	±	±			
	m-ethyltoluene	5.27 ± 8.09	2.31 ± 1.35	±	±			
	1,3,5-trimethylbenzene	18.93 ± 31.51	6.36 ± 4.22	±	±			
	o-ethyltoluene	8.28 ± 10.54	3.60 ± 2.44	±	±			
	1,2,4-trimethylbenzene	2.31 ± 3.32	2.12 ± 1.89	4.95	2.43	1.80	0.64	
1,2,3-trimethylbenzene	4.50 ± 3.55	4.56 ± 4.70	±	±				

**Table 3.** Positive Matrix Factorization (PMF) for VOCs and carbonyls (left columns), and VOCs without carbonyls (right columns) at the Jasso and Tepeji sites during 29 March to 21 April, 2006 (07:00–19:00 LT).

Site	VOCs and carbonyls				VOCs without carbonyls			
	Jasso (JAS)		Tepeji (TEP)		Jasso (JAS)		Tepeji (TEP)	
	Source Mnemonic	% contribution	Source Mnemonic	% contribution	Source Mnemonic	% contribution	Source Mnemonic	% contribution
Factor 1	LDV EX	13.3	IND SOLV	14.4	LDV EX	12.6	IND SOLV	11.9
Factor 2	OIL REF	15.4	HDV EX	12.2	OIL REF	13.9	HDV EX	18.4
Factor 3	PLAST MAN	14.2	LDV EV/BIO	14.8	PLAST MAN	19.9	LDV EV/BIO	15.0
Factor 4	POWER PLANT/ IND SOLV	13.4	LPG D/IND COAT	14.2	IND SOLV	9.3	LPG D	9.5
Factor 5	LPG/FOOD C	18.1	LDV EX	13.3	LPG/FOOD C	14.7	LDV EX	20.6
Factor 6	HDV EX	19.1	PLAST MAN	16.1	HDV EX	17.3	PLAST MAN	12.2
Factor 7	LDV EV/BIO	6.5	LPG/FOOD C	15.0	LDV EV/BIO	12.3	LPG/FOOD C	12.3

Table 4. Positive Matrix Factorization (PMF) for VOCs in Mexico City at the Merced (MER) and Pedregal (PED) sites during March to May, 2006 and March to April, 2012 (00:00–24:00 LT).

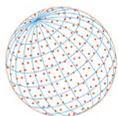
Site	2006				2012			
	Merced (MER)		Pedregal (PED)		Merced (MER)		Pedregal (PED)	
	Source Mnemonic	% contribution	Source Mnemonic	% contribution	Source Mnemonic	% contribution	Source Mnemonic	% contribution
Factor 1	IND SOLV	13.8	LDV EX	18.9	LPG/ LDV EV	17.4	IND SOLV	14.8
Factor 2	LDV EV	12.9	IND SOLV/COAT	14.9	LDV EX	29.7	LDV EX	15.6
Factor 3	LDV EX	24.3	LDV EV	14.0	HDV EX	11.0	LPG/HDV EX	15.5
Factor 4	HDV EX/ PLAST MAN	11.6	LPG/FOOD C	21.4	IND SOLV	17.7	FOOD C	29.3
Factor 5	FOOD C	18.5	IND ASPH	19.7	FOOD C	24.2	LDV EV/ BIO	24.8
Factor 6	LPG	18.9	HDV EX	11.1				

of sources caused by correlations among the variables that are not separated by PMF. Tables 3 and 4 summarize the PMF-resolved factors, the corresponding sources, and the estimated contributions to VOC mass in the Tula region and Mexico City, respectively. The chemical species representing each factor are displayed in Tables S2–S5 of supplementary material.

3.3.1 Jasso (JAS)

Factor 1, light-duty vehicle engine exhaust (LDV-EX), contributed 13.3% of the total VOCs, with higher abundances of formaldehyde, iPentane, acetone, and acetaldehyde, followed by < C4 alkenes and alkanes, and acetylene. These species are largely emitted by gasoline engines (Vega *et al.*, 2000; Watson *et al.*, 2001; Liu *et al.*, 2008; Li *et al.*, 2015). Dutta *et al.* (2009) and Gao *et al.* (2021) attributed the presence of carbonyl compounds to incomplete combustion of gasoline. In addition, acetone, formaldehyde and acetaldehyde exhibited high correlation with nitrogen monoxide ($r > 0.8$), a marker for fresh vehicular emissions.

Factor 2, oil refining (OIL-REF), contributed 15.4% of the total VOCs. Ethanol was the major compound, followed by < C6 alkanes, toluene and carbonyls. Sources of ethanol are diverse, including natural activities, biomass burning, and several chemical industrial processes. Past studies (Millet *et al.*, 2012; Li *et al.*, 2015; Zhou *et al.*, 2021) found that C6–C8 alkanes, styrene, and ethanol were the dominant species in oil refinery emissions. However, emissions from an oil refinery are complex and depend on the products, hence compounds such as propylene, ethylene, butane, ethane, toluene, and benzene have been reported (Lin *et al.*, 2004; Liu *et al.*, 2008; Ragothaman and Anderson, 2017; Rajabi *et al.*, 2020; Gao *et al.*, 2021; Liu *et al.*, 2021a). Since the main products of the Miguel Hidalgo oil refinery are gasoline- and diesel-fuels, it is probable that light alkanes and alkenes, aromatics, and oxygenated compounds are the dominant species.



Factor 3, plastics manufacturing (PLAST MAN), contributed 14.2% of total VOCs with high abundances of formaldehyde, acetaldehyde, acetone, ethanol, nButane, and styrene which has been associated with industrial emissions (Watson *et al.*, 2001). The carbonyl compounds showed correlation with styrene ($r > 0.79$) (Di Tomasso *et al.*, 2014).

Factor 4, a mixture of power plant and industrial solvents (POWER-PLANT/IND-SOLV), contributed 13.4% of total VOCs, with markers such as ethanol, formaldehyde and C4 alkenes, followed by benzene, nButane, acetone, toluene, acetaldehyde, and C4–C6 alkanes. Zhang *et al.* (2021) found emissions from thermal power plants were the major sources of formaldehyde, whilst Pudasainee *et al.* (2010) detected benzene and carbon tetrachloride as major compounds. Ethanol, acetone, and aromatics have been related to solvent usage and industrial coating (Vega *et al.*, 2007; Guo *et al.*, 2013; Chen *et al.*, 2019; Yang *et al.*, 2019; Huang *et al.*, 2021).

Factor 5, domestic heating and cooking (LPG/FOOD C), contributed 18.1% of total VOCs, associated with emissions from handling and distribution of LPG. Besides the key LPG species (i.e., propane, butane and isobutane). This factor exhibited high abundances of acetone, pentane and acetylene, which have been measured in commercial food cooking and charcoal grills (Mugica *et al.*, 2001). The LPG leaks that occur during distribution and domestic consumption are the principal sources of propane, butane and isobutane in the atmosphere (Gamas *et al.*, 2000). Table S2 shows that formaldehyde and acetaldehyde also are important compounds in this factor. In addition, carbonyl species showed moderate correlations ($r > 0.76$) with butane and propane. Recent research on commercial and domestic food cooking emissions revealed the presence of carbonyls and other organics, while the presence of ethanol is attributed to combustion during cooking, particularly from restaurants using charcoal (Cheng *et al.*, 2015; He *et al.*, 2020; Lin *et al.*, 2021).

Factor 6, heavy-duty vehicles (HDV EX), contributed 19.1% of total VOCs. This factor contained markers for diesel-powered vehicle exhaust such as octane, nonane and decane mixed with < C6 alkanes and ethane (Watson *et al.*, 2001; Liu *et al.*, 2008).

Factor 7, a mixture of light-duty vehicle engine exhaust, evaporative gasoline, and biogenic sources, (LDV EV/BIO), contributed 6.5% of total VOCs. This factor showed abundant 1,2,4-trimethylbenzene, < C6 alkanes, C4 alkenes (trans-2-butene, 1-pentene, 1butene, ibutylene), toluene, and formaldehyde, markers of evaporated gasoline (Vega *et al.*, 2007; Liu *et al.*, 2008; Dai *et al.*, 2013; Wang *et al.*, 2020b). Isoprene, which ranked second in this factor, is a compound characterized by biogenic sources.

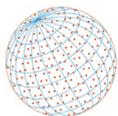
3.3.2 Tepeji (TEP)

Based on analysis of variance (ANOVA), statistical differences between JAS and TEP were found for VOC markers such as benzene (1.90 ppbC and 1.39 ppbC morning average for JAS and TEP, respectively), m/p-xylenes (3.84 ppbC and 2.88 ppbC), propane (11.03 ppbC and 27.42 ppbC), and ethanol (38.36 ppbC and 3.98 ppbC). In contrast, carbonyls showed no statistical difference between the two sites.

Factor 1, industrial solvents (IND SOLV), contributed 14.4% of the total VOCs with markers such as < C5 alkanes, formaldehyde, acetone, and acetaldehyde (Vega *et al.*, 2007; Guo *et al.*, 2013; Yang *et al.*, 2019). Factor 2, (HDV EX), contributed 12.2% of the total VOC with markers such as carbonyls, nonane, octane, toluene, acetylene and lighter compounds (Vega *et al.*, 2007; Liu *et al.*, 2008; Gao *et al.*, 2021). Factor 3, (LDV EV/BIO), contributed 14.8% of the VOCs, with markers such as < C5 alkanes and alkenes, and carbonyls. These markers are commonly found in evaporated or liquid gasoline (Vega *et al.*, 2007; Dai *et al.*, 2013; Wang *et al.*, 2020b). Isoprene is of biogenic origin, so it is evident that this PMF factor represents a mixed source.

Factor 4, a mixture of LPG distribution and industrial coatings (LPG/IND COAT), contributed 14.2% of total VOCs, with abundant propene, a highly reactive compound that is emitted by several industrial processes such as petroleum refining, iron/steel industry, solvent usage, pesticide use, and paving (Watson *et al.*, 2001; Deng *et al.*, 2018; Liu *et al.*, 2021a). Other abundant VOCs included propane, nButane, formaldehyde, c-2-butene, acetone, and toluene. LPG-related species showed proportions close to commercial LPG composition (Gamas *et al.*, 2000), consistent with a distribution center near TEP. As toluene was also abundant, suggesting emissions from painting/coating operations (Vega *et al.*, 2007; Li *et al.*, 2015; Liu *et al.*, 2021a) also present in this source.

Factor 5, LDV EX, contributed 13.3% of total VOCs, with markers such as light alkanes (< C7),



ethylene, carbonyls, and toluene (Liu *et al.*, 2008; Chen *et al.*, 2016). The low toluene/benzene ratio (0.64) and good correlation with CO ($r > 0.79$) supports this association. Factor 6, plastic manufacture (PLAST MAN), contributed 16.1% of total VOC with abundant oxygenated species followed by light alkanes and alkenes, styrene, and mp-xylenes. Moreover, carbonyl compounds showed strong association with styrene ($r > 0.79$), consistent with emissions from plastic manufacturing (Di Tomasso *et al.*, 2014). Factor 7, a mixture of LPG/FOOD C, contributed 15% of total VOCs, showed the highest abundances for key LPG-related species (i.e., propane, nButane, and iButane) combined with carbonyls, alkanes < C5, alkenes (propylene, c2butene) and toluene, resembling the species detected in food cooking emissions (LPG/FOOD C) (Mugica *et al.*, 2001; Cheng *et al.*, 2015; He *et al.*, 2020; Lin *et al.*, 2021).

The Tula region experienced elevated formaldehyde, acetaldehyde, and acetone levels. PMF was applied to a data set that excluded carbonyls (Table 3, right columns) to compare model performance and source identification. Although a seven-factor solution was found for VOCs, the PMF factors were not as uniquely identifiable as those derived with carbonyls included (see Table S3 for description of PMF factors obtained using only VOCs). For example, Factor 2, OIL REF, at JAS site showed VOC markers for oil refinery emissions, but this association was not as convincing as it was when carbonyls were included, particularly for the presence of acetone (Huang *et al.*, 2021). The calculated refinery contribution decreased from 15.4% to 13.9% (percentages with and without carbonyl species, respectively).

Without carbonyls, Factor 4 was identified as industrial solvent usage (IND SOLV), without thermal power plant emissions (POWER PLANT/IND SOLV) due to the lack of formaldehyde (Zhang *et al.*, 2021). At the TEP site, Factor 7 was assigned to the LPG/FOOD C source. However, without acetone this factor only represents LPG. Vehicular sources showed no significant changes that could compromise their identification as a mixture of LDV EV/BIO, since markers such as 1,2,4-trimethylbenzene and < C5 alkanes (for evaporated gasoline) and isoprene (for biogenic) showed high percentages in both analyses.

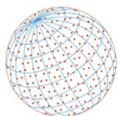
Overall, omitting carbonyls from the PMF input data reduced the contributions from industrial sources, and increased contributions from vehicular sources. Without carbonyl, LPG/FOOD C contribution is reduced from 18% to 15% at JAS and from 29% (sum of 15% LPG/FOOD C and 14%, LPG D/IND COAT in Table 3) to 12% at TEP.

3.3.3 Mexico City 2006

Table 4 summarizes the six PMF factors derived for MER and PED. For the MER site, Factor 1, IND SOLV, contributed 13.8% of total VOCs with markers such as C4- and C3-benzenes, followed by toluene and hexane, and small proportions of light alkanes, alkenes and xylenes (Vega *et al.*, 2000; Li *et al.*, 2015; Liu *et al.*, 2021a; Zhang *et al.*, 2021). Factor 2, LDV EV, contributed 12.9% of total VOCs with markers such as < C5 alkanes, alkenes and aromatic compounds (Watson *et al.*, 2001; Vega *et al.*, 2007; Dai *et al.*, 2013; Wang *et al.*, 2020b). Factor 3, LDV EX, contributed 24.3% of total VOCs, characterized by light alkanes, aromatics, ethylene, ethane, and acetylene.

Factor 4, a mixture of HDV EX/PLAST MAN, contributed 11.6% of total VOCs, denoted by high abundances of C8–C10 alkanes and ethane (Watson *et al.*, 2001; Vega *et al.*, 2007; Liu *et al.*, 2008; Gao *et al.*, 2021) for heavy-duty diesel emissions along with elevated aromatic species (C3-benzene and styrene) associated with plastics manufacturing (Di Tomasso *et al.*, 2014). Factor 5, FOOD C, contributed 18.5% of total VOCs characterized by high concentrations of propane and butanes combined with alkenes and aromatic compounds, markers of food cooking (Mugica *et al.*, 2001; He *et al.*, 2020). Factor 6, LPG, contributed 18.9% of total VOCs with abundances of propane and butanes, close to the commercial LPG composition used in Mexico City (Gamas *et al.*, 2000). In addition, ethylene, < C5 alkanes, alkenes and toluene suggest that this factor represents leakages during transport and handling of LPG.

At PED, Factor 1, LDV EV, contributed 18.9% of total VOCs. This factor was characterized by higher abundances of 1-pentene, aromatics, propane, ethylene, acetylene, 1,2,4-trimethylbenzene and a mixture of C2–C4 benzenes, suggesting vehicular exhaust emissions (Watson *et al.*, 2001; Vega *et al.*, 2007; Liu *et al.*, 2008; Li *et al.*, 2015). The average T/B ratio of 1.3 supports the association with vehicular source (Barletta *et al.*, 2008). Factor 2, IND SOLV/COAT, contributed 14.9% of total VOCs (Wang *et al.*, 2020b), with markers such as propane, propylene, toluene and



hexane, followed by < C5 alkanes and C3 benzenes, consistent with solvent use in painting and coating. Factor 3, LDV EX, contributed 14% of total VOCs, was associated with evaporative or liquid gasoline, characterized by aromatics (C2 and C3 benzenes), < C5 alkanes, alkenes, and propane (Vega *et al.*, 2007; Dai *et al.*, 2013; Wang *et al.*, 2020b).

Factor 4, a mixture of LPG/FOOD C, contributed 21.4% of total VOCs, with markers such as propane, butanes in similar proportions of LPG (Gamas *et al.*, 2000), along with propylene, toluene, hexane and acetylene in food cooking (Mugica *et al.*, 2001; He *et al.*, 2020). Factor 5, industrial asphalt pavement production (IND ASPH), contributed 19.7% of total VOCs. This factor was characterized by propane, propylene, ethylene, toluene and styrene, characteristics of as reported by Wang *et al.* (2020a). PED site is located 5 km to the east of an asphalt plant, the only industrial source within the area. Factor 6, HDV EX, contributed 11.1% of total VOCs. This factor was associated with diesel-powered vehicles emissions, exhibiting major proportions of propane, toluene, propylene, acetylene, and decane.

3.3.4 Mexico City 2012

Five factors were identified by PMF in Table 4 for the 2012 VOCs. For the MER site, Factor 1, a mixture of LPG/LDV EV, contributed 17.4% of total VOCs. This factor was characterized by propane, butane, toluene, hexane isopentane, 1,2,4-trimethylbenzene, and propylene. Factor 2, LDV EX, contributed 20.7% of total VOCs. This factor was marked by ethylene and acetylene, consistent with gasoline vehicular emissions. Factor 3, HDV EX, contributed 11% of total VOCs. This factor showed similar markers as Factor 2, but with a different proportion of propylene associated with heavy-duty vehicular emissions. According to Watson *et al.* (2001) and Li *et al.* (2015), one of the key differences between gasoline and diesel combustion emissions is the proportion of propylene, being lower in gasoline.

Factor 4, IND SOLV, contributed 17.7% of total VOCs representing industrial solvent emissions that were characterized by aromatics (C2, C3-benzenes, xylenes, and toluene), isobutane, and propane. Factor 5, FOOD C, contributed 24.2% of total VOCs. This factor exhibited markers for food cooking emissions such as propane, toluene, ethylene, nButane and propylene (Mugica *et al.*, 2001; He *et al.*, 2020).

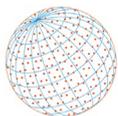
At PED, Factor 1, IND SOLV, contributed 14.8% of total VOCs. This factor showed markers of industrial solvent usage such as aromatics and light alkanes (Wang *et al.*, 2020b). Factor 2, LDV EX, contributed 15.6% of total VOCs, representing light-duty vehicular emissions with high abundances of pentanes, ethane and ethylene. Factor 3, a mixture of LPG/HDV EX, contributed 15.5% of total VOCs. This factor was marked by propane, nButane, isobutane (LPG) as well as propylene, ethane, and ethylene (Li *et al.*, 2015).

Factors 4 and 5 were characterized by the presence of propane and nButane but with higher abundances of nButane, suggesting combustion processes. Factor 4, FOOD C, contributed 29.3% of total VOCs, the presence of toluene, ethylene, ethane, propylene and hexane points to characterize emissions from food cooking (Mugica *et al.*, 2001; He *et al.*, 2020). Factor 5, LDV EX/BIO, contributed 24.8% of total VOCs, with elevated abundances of isopentane, toluene, isobutane, and butanes (markers of evaporative/liquid gasoline) and isoprene (marker for biogenic source).

The largest difference since 2006 is that contributions from the asphalt plant were not identified in 2012, signifying the effectiveness of implementing pollution control measure. PMF analysis shows that cooking emissions accounted for 19–29% of total VOCs, orders of magnitude higher than those shown in the emission inventory with ~1% charcoal cooking. The 2006 Emission Inventory attributed ~11% to LPG leakage, lower than the 15–19% estimated by PMF (SEMARNAT, 2008; SEDEMA, 2013). Research is needed to further resolve the discrepancies.

3.4 Health Risk Assessment

A risk assessment was conducted with 24-hour average BTEX concentrations due to their adverse effects (Davidson *et al.*, 2021). The U.S. EPA (2011) recommends an acceptable safety limit for LCR below 1.0×10^{-6} and a threshold risk limit beyond 1.0×10^{-4} as an unacceptable LCR. For non-carcinogenic risks, a HQ > 1 indicates potentially non-carcinogenic effects of concern, whereas HQ < 1 represents that no health effects are expected to occur following exposure to pollutant (Abbasi *et al.*, 2020; Kumari *et al.*, 2021).



The highest BTEX values of cumulative exposure (CE) for both children and adults were found at MER during 2006 with values between 0.52–2.49 and 2.09–9.97 $\mu\text{g m}^{-3}$, respectively (Table S6). Considering all sampling sites, the LCR for benzene was estimated to be in the range of 1.8×10^{-6} to 1.5×10^{-5} for children, and of 7.3×10^{-6} to 6.1×10^{-5} for adults. This suggests that benzene at MER during 2006 exceeded the minimum acceptable risk level (1.0×10^{-6}) but not posing an unacceptable cancer risk. Meanwhile, the LCR at MER during 2006 slightly exceeded the acceptable safety limit for children for ethylbenzene. It ranged from 1.3×10^{-7} to 1.7×10^{-6} for children, and from 5.3×10^{-7} to 6.8×10^{-6} for adults. Only the TEP site had an LCR below the minimum acceptable risk level for adults during 2006 (5.3×10^{-7}).

LCR values for benzene were similar to those reported in Agra, India (Kumari *et al.*, 2021) and Shiraz, a populous city in Iran (Abbasi *et al.*, 2020), but higher than Shiraz, Iran (Dehghani *et al.*, 2018) and an urban area in Delhi, India (Garg and Gupta, 2019). Sampling sites with traffic influence such as Delhi, India (Mehta *et al.*, 2020) and Beijing, China (Zhang *et al.*, 2012; Li *et al.*, 2014) reported the highest cancer risk by benzene. LCR values for ethylbenzene were similar to Agra, India (Kumari *et al.*, 2021), but much lower than those observed in roadsides Delhi, India (Mehta *et al.*, 2020).

Table S6 shows large reductions in exposure concentrations and cancer risks for benzene and ethylbenzene at both MER and PED sites from 2006 to 2012. Both HQ and HI of all BTEX were below unity, suggesting no serious chronic non-cancer health effect for the population exposure (Abbasi *et al.*, 2020).

Results of the risk analysis show the benefits of pollution control measures to reduce VOC emissions in Mexico. These control measures include reducing evaporative emissions from petrol stations; replacing the use of solvents with water in paints and in asphalt application; switching from fuel oil to natural gas in major sources; and improving of public transport with cleaner technologies (Vega *et al.*, 2000; Jaimes-Palomera *et al.*, 2016; Sosa *et al.*, 2020). However, to further reduce the health risk from BTEX exposure, it is necessary to continue working on improving the handling of LPG transportation and distribution; implementing control of fugitive and solvent emissions; and reducing benzene emissions to minimize harmful health effects. The risk analysis presented here serve as guidance for the environmental public health administration to assess future air quality and health effects.

4 CONCLUSIONS

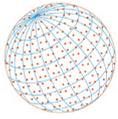
This study focused on VOC compositions and concentrations including carbonyls, in Tula, Hidalgo, during the warm-dry season of 2006. A comparison was made between the Tula industrial corridor with those measured in Mexico City. The PMF solution to the CMB receptor model was employed to determine the sources of VOCs. Although a seven factors solution was found for VOCs without carbonyls, the PMF factors were not uniquely identifiable, signifying the importance of concurrent measurements of VOCs and carbonyls for source apportionment. Changes in source contributions after implementation of control measures were found, as were inconsistencies with emission inventory estimates.

This study provides a baseline to evaluate past and future air quality in one of the most polluted industrial corridors in Mexico. This information is useful for determining the effectiveness of air pollution control measures implemented in the region and the reduced risks resulting from human exposures. The data obtained also provides a complement emissions inventory estimates that are used for prognostic air quality modeling.

The research documents historical measurements of air pollution in industrial areas, particularly in developing countries such as Mexico, where air quality monitoring focuses on urban areas more than regional emission impacts. A routine monitoring network for VOCs including carbonyls needs to be established to better understand the photooxidation process and to reduce O_3 concentrations.

DISCLAIMER

Reference to any companies or specific commercial products does not constitute an endorsement by the authors.



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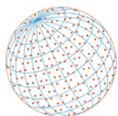
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SUPPLEMENTARY MATERIAL

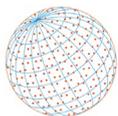
Supplementary material for this article can be found in the online version at <https://doi.org/10.4209/aaqr.210386>

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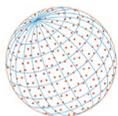
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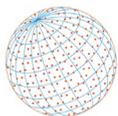
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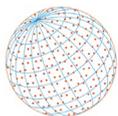
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