

# Diurnal and seasonal variation of BTEX in the air of Monterrey, Mexico: preliminary study of sources and photochemical ozone pollution

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**Abstract** Atmospheric levels of benzene, toluene, ethylbenzene, and xylenes (BTEX) were measured in an urban site located in Nuevo Leon, Mexico, during summer and autumn 2013. A total of 60 samples were collected using carbon-packed cartridges at 0900, 1200, and 1500 h and then analyzed using gas chromatography with flame ionization detector. Meteorological parameters and criteria air pollutants were measured and correlated with BTEX by a principal component analysis (PCA). The relative abundance of BTEX followed the order: benzene > toluene > ethylbenzene > *p*-xylene with mean concentrations of 55.24  $\mu\text{g m}^{-3}$ , 22.24  $\mu\text{g m}^{-3}$ , 6.94  $\mu\text{g m}^{-3}$ , and 4.17  $\mu\text{g m}^{-3}$ , respectively, during summer. Mean concentrations during autumn were 21.079  $\mu\text{g m}^{-3}$  for benzene, 3.648  $\mu\text{g m}^{-3}$  for toluene, 2.521  $\mu\text{g m}^{-3}$  for ethylbenzene, and 2.115  $\mu\text{g m}^{-3}$  for *p*-xylene. All measured BTEX showed clear diurnal and seasonal patterns. The highest mean levels for benzene were obtained during the midday. Toluene,

ethylbenzene, and *p*-xylene showed the highest levels during afternoon period. BTEX levels were higher when wind blew from NE and ESE during summer and from ESE during autumn. The municipalities of Apodaca and Guadalupe are located in these directions where important industries, high traffic volume, many oil and gas service stations, and the biggest airport in this region are found. These sources could contribute to the BTEX concentrations measured during the sampling period.

**Keywords** BTEX · Ozone · Air pollution · Nuevo Leon · COVs

## Introduction

Volatile organic compounds (VOCs) play a critical role in atmospheric photochemical reactions and multiphase processes (Calvert et al. 2002; Wang et al. 2010a, b). VOCs can undergo reactions initiated by hydroxyl radicals (OH) to form peroxy radicals ( $\text{RO}_2$ ), which react rapidly with nitric oxide (NO) to form nitrogen dioxide ( $\text{NO}_2$ ), an essential step in the formation of ground level ozone ( $\text{O}_3$ ) (Calvert et al. 2002). This pollutant is the main oxidant in the troposphere and is related to adverse effects on human health, vegetation, and materials (Cerón Bretón et al. 2010a, b). VOCs are organic compounds with boiling points between 50 and 150 °C. Within this group, there is a subgroup commonly called BTEX which includes benzene, toluene, ethylbenzene, and xylenes. Anthropogenic activities are responsible for most of the VOC emissions in and around heavily populated urban areas (Li et al. 2007; Wang et al. 2009; Apel et al. 2010). In cities like Mexico City and Los Angeles, approximately 45 % of the total VOC emissions result from gasoline-related emissions, including a substantial portion of aromatic compounds

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such as benzene and toluene (Brown et al. 2007). These compounds are known to be toxic, genotoxic, and carcinogenic and play an important role in tropospheric chemistry due to their active participation in photochemical reactions. They are ozone precursors (Lu et al. 2006; Katsoyiannis et al. 2006; Hoque et al. 2008) and have multiple and diverse sources in urban areas (motor vehicle exhaust, incomplete combustion of fossil fuels and biomass, oil, and gas service stations, cooking and heating processes, household products, and other industrial and human activities). In Mexico, there is little information about BTEX levels in ambient air. Most of the studies have been focused on Mexico City (Arriaga et al. 1997; Bravo et al. 2002; Mugica et al. 2002; Cerón- Bretón et al. 2013a). Here, we focus on San Nicolás de Garza, one of the 12 municipalities of the metropolitan area of Monterrey (MAM), which is the third largest city in Mexico and one of the country's most important urban and industrial centers. MAM is characterized by the presence of important education and research centers, business activities, and industrial settlements. In this work, we present BTEX measurements obtained in San Nicolás de los Garza during summer and autumn 2013. The purpose of this field campaign was to characterize the BTEX present in the ambient air and identify the relationships among the measured variables using a principal component analysis (PCA) analysis (including criteria air pollutant concentrations and meteorological parameters), in order to infer the sources that could contribute to the BTEX observations.

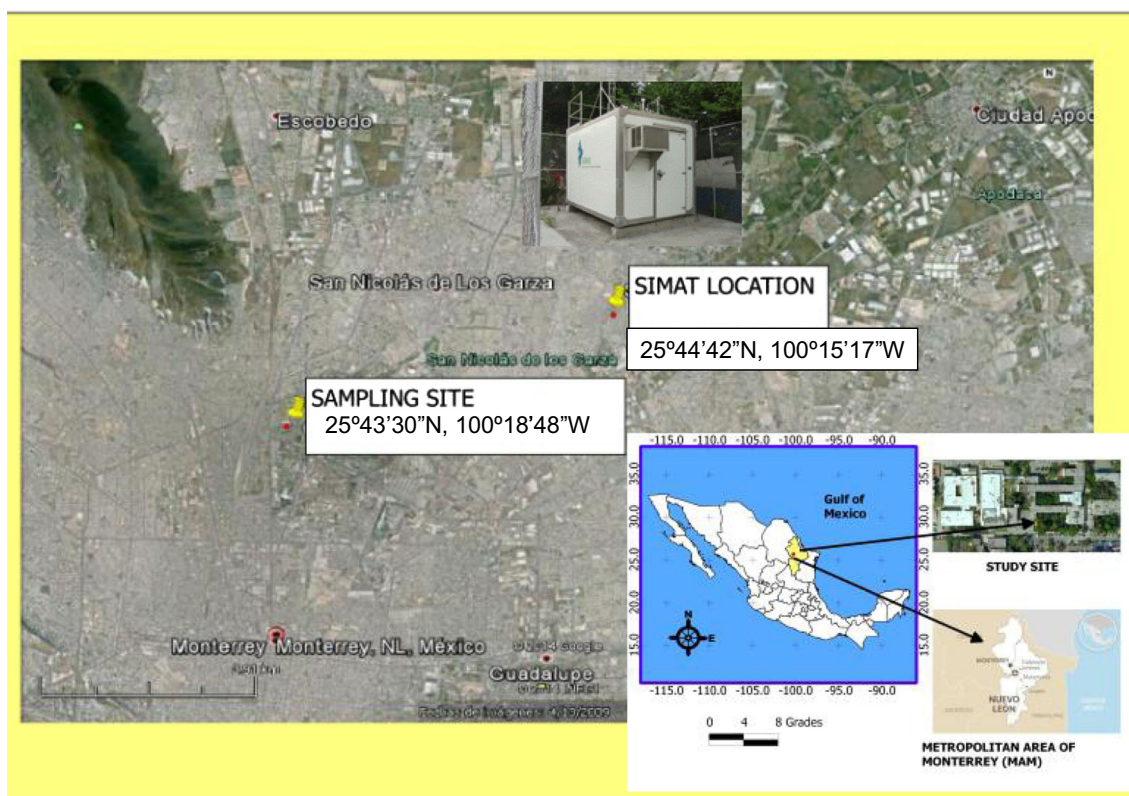
## Materials and methods

### Observation site

The observation site is located near the urban center of Monterrey, Nuevo Leon, Mexico, inside the Chemistry School (Postgraduate Division building) of the Autonomous University of Nuevo Leon ( $25^{\circ} 43' 30''$  N;  $100^{\circ} 18' 48''$  W), at 500 masl. A detailed map of the site is presented in Fig. 1. This municipality is located at the northeast of the MAM and has a semiarid warm climate (Bsh) according to the Köppen climatic classification modified by García (García 1990). Frontal systems coming from the north are common in this area. The specific observation site is located within an industrial, residential, educational, and commercial area where there also are several avenues with high vehicular traffic volume.

### Sampling method

A total of 60 samples were collected from July 3 to November 14, 2013, half during the summer season and half during autumn. Benzene (B), ethyl benzene (Ebz), toluene (T), and *p*-xylene (X) were determined in all ambient air samples. Samples were collected using glass tubes containing 226–01 Anasorb CSC (SKC) with the following features: length of 70 mm, inner diameter of 4.0 mm, and outer diameter of 6 mm packed in two sections with 100 and 500 mg of active carbon,



**Fig. 1** Location of the sampling site and the SIMAT air quality northeast station

separated by a glass wool section (Method INSHT MTA/MA-030/A92) (INSHT 1992; Cerón et al. 2013b). The downstream end of the glass tube was connected to a calibrated flow meter. Ambient air was passed through the glass tubes at a flow rate of  $200 \text{ ml min}^{-1}$  at 1.5-h intervals. Samples with a sampling volume lower than 5 l were discarded. Sampling was carried out using a Universal XR pump model PCXR4 (SKC), at three sampling periods (local time): B1 (morning, from 0900 to 1030 h), B2 (midday, from 1200 to 1330 h), and B3 (afternoon, from 1500 to 1630 h). Prior to the main study, several pilot experiments were conducted to evaluate the suitability of the sampling procedure described here. These pilot experiments included the determination of appropriate sampling times. In addition, desorption efficiency (DE) was calculated for each glass tubes lot and for each analyte, and tubes with ED lower than 75 % were discarded. After the exposure time, the adsorption tubes were labeled and capped tightly with PTFE caps and transferred to the laboratory in cold boxes. This procedure was applied to both clean and sample tubes for storage prior to use or analysis. Field blanks were transported to the field along with samplers and stored in the laboratory during the sampling period. Samples were analyzed within 3 weeks after sample collection.

#### Analytical method

Samples were extracted with 1 ml of  $\text{CS}_2$  for each section of the sample tubes and shaken for 30 s to assure maximum desorption. Extracted samples were analyzed using a TRACE GC Ultra gas chromatograph (Thermo Scientific) and one flame ionization detector (FID; Thermo Scientific Technologies, Inc) (Method INSHT MTA/MA-030/A92) (INSHT 1992). The analytical column used was a capillary column (57 m, 0.32 mm i.d., 0.25- $\mu\text{m}$  film thickness). The oven temperature program was initially set to 40 °C for 4 min, then increased at a rate of 5 °C  $\text{min}^{-1}$  up to 100 °C, and finally maintained for 10 min at 100 °C. The FID temperature was set to 250 °C using a hydrogen/air flame with constant flows of 35 and 350  $\text{ml min}^{-1}$  for ultra-pure hydrogen and extra-dried air, respectively. The ultra-pure nitrogen carrier (99.999 %) gas flow rate was 1  $\text{ml min}^{-1}$  (INSHT 1992). Four BTEX were investigated: benzene (B), *p*-xylene (X), ethylbenzene (Ebz), and toluene (T). Five-point calibration was performed using 99.98 % Sigma-Aldrich analytical reagents at a concentration of 2 ppm for each BTEX. The established calibration curves for the four investigated BTEX were found to have *R*-square values of 0.999. Method detection limits (MDL) for each compound were calculated by multiplying the standard deviation obtained from seven replicate measurements of the first level of calibration by 3.14 (Student's *t* test). The analytical results showed that the MDLs for B, Ebz, X, and T were 0.0517, 0.0566, 0.0600, and 0.025  $\mu\text{g m}^{-3}$ , respectively. The

amount of BTEX in blank samples was below the limit of detection for all compounds studied.

#### Monitoring of meteorological parameters and criteria air pollutants

Wind conditions (speed and direction), relative humidity, temperature, and barometric pressure were monitored from July 3 to November 14 using a Davis Vantage Pro II portable meteorological station located at the BTEX observation site. Wind frequency statistics were determined using WRPLOT software (Lakes Environmental). Criteria air pollutant ( $\text{O}_3$ , NO,  $\text{NO}_2$ ,  $\text{NO}_x$ , CO, and  $\text{SO}_2$ ) concentrations measured by API Teledyne automatic analyzers were obtained from the Integrated System of Environmental Monitoring of the MAM (SIMAT) Northeast Station, located 5 km away at 25° 44' 42" N, 100° 15' 17" W, 500 masl. The BTEX and criteria pollutant sites are essentially collocated in terms of meteorological characteristics and air masses being sampled, pollution sources, population density, traffic volume, and topography. Figure 1 shows both locations.

#### Correlation and PCA

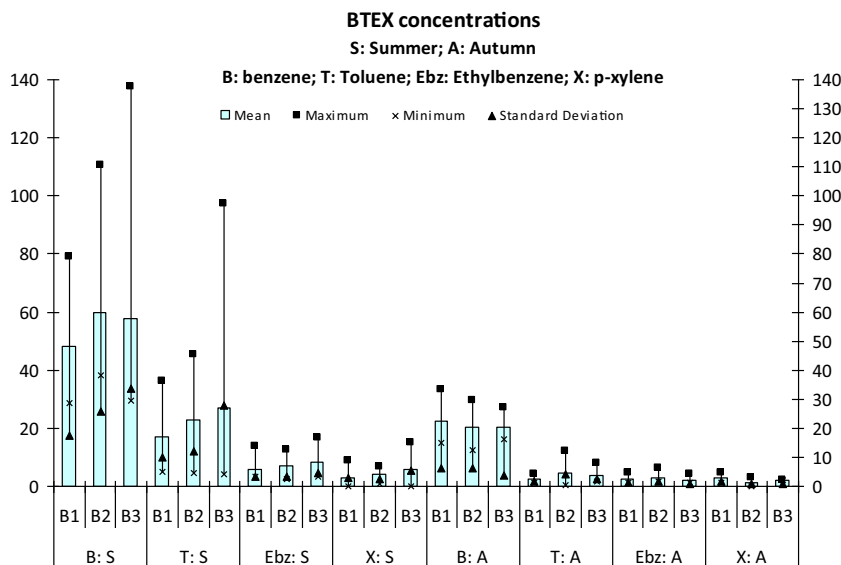
Pearson correlation analysis was applied to all data collected at the sampling site. To assess the relationships between BTEX concentrations, meteorological parameters, and criteria air pollutants, a factor analysis (principal component analysis) was applied using XLSTAT software (Statistics Package for Microsoft Excell).

## Results and discussion

#### Diurnal and seasonal variation

Diurnal variation and descriptive statistics for the summer and autumn seasons can be observed in Fig. 2. During the summer period, T, Ebz, and X showed similar diurnal patterns related to the prevailing ESE and ENE winds (see Meteorological influence). The highest concentrations occurred during the afternoon (B3), decreasing during the midday (B2), and reaching the lowest values during the mornings (B1). B exhibited maximum concentrations during the midday (B2), decreasing during the afternoon (B3), and reaching the lowest values during the mornings (B1). During autumn, all BTEX components presented different diurnal behavior, probably due to variable wind conditions occurring during this season and transporting air masses from different sources located in diverse directions (see Meteorological influence). BTEX concentrations during summer were higher than those during autumn, presumably due to seasonal differences in wind,

**Fig. 2** Diurnal variation and descriptive statistics for measured BTEX during the summer and autumn sampling periods. B1 (0900–1030 h), B2 (1200–1330 h), and B3 (1500–1630 h)



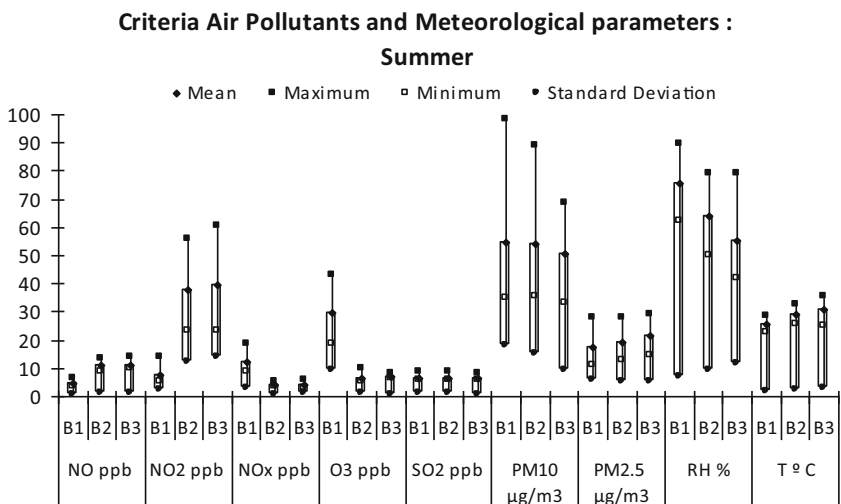
temperature (higher during summer), and relative humidity (higher during autumn). The relative abundance of BTEX exhibited the following order during both sampling periods: B > T > Ebz > X. During summer, the mean concentration levels were 55.24, 22.24, 6.94, and 4.17  $\mu\text{g m}^{-3}$ , respectively. During autumn, the respective mean concentrations were 21.079, 3.648, 2.521, and 2.115  $\mu\text{g m}^{-3}$ .

Descriptive statistics and diurnal variation for criteria air pollutants and meteorological parameters are shown in Figs. 3 and 4 for summer and autumn, respectively.  $\text{NO}_2$ ,  $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ ,  $\text{SO}_2$ , and RH showed higher levels during autumn, while NO and temperature were higher during summer. During summer season,  $\text{NO}_2$ ,  $\text{PM}_{2.5}$ , T, and  $\text{SO}_2$  showed a similar behavior with the highest levels during the afternoon (B3), decreasing during midday (B2), and showing the lowest values during the morning (B1).  $\text{NO}_x$ ,  $\text{PM}_{10}$ , and RH during summer showed the same diurnal pattern with the highest values during the morning period (B1) and the lowest levels

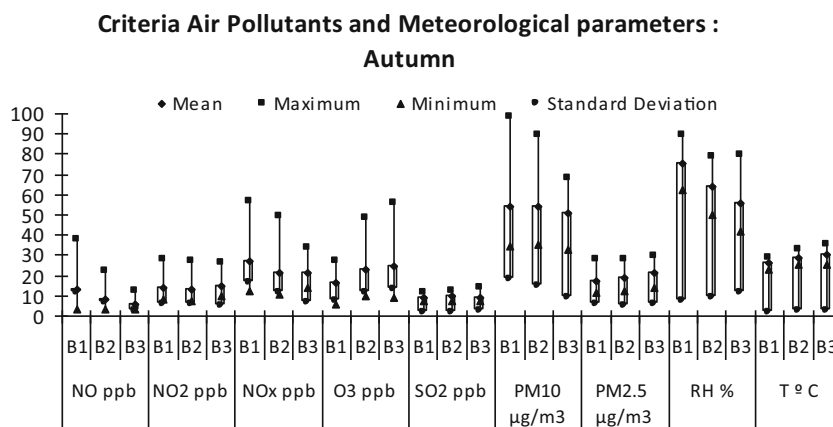
during the afternoon period (B3). NO concentrations were higher during B2 period, decreasing during the afternoon period (B3), and with the lowest levels during the morning period (B1). The highest levels of  $\text{O}_3$  were found during the mornings (B1). During autumn, NO,  $\text{NO}_x$ , and RH had the same pattern with the highest levels during the mornings (B1) and the lowest values during the afternoons (B3).  $\text{PM}_{10}$  and  $\text{SO}_2$  showed the highest concentrations during the midday period (B2) and the lowest values of concentration during the morning period (B1).  $\text{PM}_{2.5}$ , temperature, and  $\text{O}_3$  showed similar behavior with the lowest levels during the mornings, increasing during the midday, and registering the highest values during the afternoons.

All BTEX measurements were made only during weekdays and therefore were not possible to analyze the weekday/weekend effect. For criteria pollutants, a strong weekday/weekend signal was not evident except for an unexplained increase on November 9–10 (not shown) and a weekday when

**Fig. 3** Descriptive statistics and diurnal variation for criteria air pollutants and meteorological parameters during summer season



**Fig. 4** Descriptive statistics and diurnal variation for criteria air pollutants and meteorological parameters during autumn season



all criteria pollutants registered high values in comparison with the rest of weekdays of the period. This specific day was a holiday (November 1) which corresponds to an annual Mexican celebration called “Los Santos Difuntos.”

#### Meteorological influence

Wind speed, wind direction, and meteorological influences for each air pollution sample during summer and autumn can be observed in Table 1. The wind conditions are used to identify the probable sources of the measured BTEX compounds. Prevailing winds during the whole period were from ESE and ENE. During summer, BTEX levels were generally higher when winds blew from ESE. During this season, wind conditions were 50 % from ESE and 50 % from ENE during the B1 period with wind speed values from 3.51 to 12.5 km h<sup>-1</sup>, 70 % from ESE and 30 % from ENE during the B2 period with wind speed ranging from 3.73 to 11.38 km h<sup>-1</sup>, and 90 % from ESE during the B3 period with speed values from 6.45 to 11.51 km h<sup>-1</sup>. During autumn, wind conditions were variable and had the following characteristics: 40 % from ENE, 30 % from ESE, 20 % from NNW, 10 % from WSW during the B1 period (wind speed, 0.556–13.13 km h<sup>-1</sup>), 40 % from ENE, 30 % from ESE, 20 % from NNE, 10 % from NNW during the B2 period (2.37–11.92 km h<sup>-1</sup>), 60 % from ESE, 20 % from ENE, 10 % from NNW, and 10 % from NNE during the B3 period (3.57–12.71 km h<sup>-1</sup>).

On July 11, 2013 (Table 1), there was a peak for BTEX compounds during the B3 period (B 137.52 µg m<sup>-3</sup>, T 97.18 µg m<sup>-3</sup>, Ebz 14.32 µg m<sup>-3</sup>, and X 15.15 µg m<sup>-3</sup>), with prevailing winds from ESE (wind speed 10.67 m s<sup>-1</sup>). These wind conditions probably promoted pollutant transport from upwind sources. For the midday period (B2), B and T concentrations were higher when air masses came from the ENE, whereas Ebz and X levels were higher with ESE winds. During the summer afternoons, BTEX levels were generally higher when winds blew from ESE where the Guadalupe

municipality is located. Anthropogenic sources are located throughout the MAM, as is typical of a large urban and industrial center; however, industrial activities and roads with high vehicular traffic are concentrated in the northeast and southeast zones. On the morning of October 30, an air pollution episode occurred, with BTEX levels reaching the highest values of the autumn period (B 29.86 µg m<sup>-3</sup>, T 4.35 µg m<sup>-3</sup>, and Ebz 3.64 µg m<sup>-3</sup>) (see Table 1). Prevailing winds on this day were ENE. During the B1 period on this day, the highest BTEX concentrations occurred with ENE winds. During B2 period, high BTEX concentrations occurred on November 1 with ENE winds (B 27.45 µg m<sup>-3</sup>, T 11.99 µg m<sup>-3</sup>, Ebz 6.20 µg m<sup>-3</sup>, and X 3.05 µg m<sup>-3</sup>). On October 24 and November 14, high levels of afternoon (B3) BTEX were found when winds blew from the ESE and ENE, respectively.

#### Toluene to benzene ratio

The toluene to benzene (T/B) ratio has been commonly used as an indicator of traffic emissions. B and T are constituents of gasoline and are emitted into the atmosphere by motor vehicle exhaust. The T content of gasoline and motor vehicle exhaust is three to four times higher than the B content (Pekey and Yılma 2011). T/B values lower than 2–3 are characteristic of vehicular emissions in many urban areas worldwide (Elbir et al. 2007; Mugica et al. 2003; Rad et al. 2014), whereas values higher than 3 may indicate that BTEX levels could be associated with industrial facilities and area sources (evaporative emissions, painting, cooking processes, among others). During summer, this ratio was between 0.108 and 0.835, being higher during the afternoon sampling period. For the autumn period, this ratio was between 0.012 and 0.383. These values are in agreement with typical values of vehicular emissions reported for other urban areas, suggesting that this site was under the influence of mobile sources. The seasonal differences in T/B may be due to transport. In summer, winds were typically ESE. Winds were more variable in autumn, suggesting transport from sources in different directions. In

**Table 1** Meteorological conditions and BTEX concentrations for each air pollution sample during summer and autumn

SP	Summer 2013						Autumn 2013					
	Date	WD/MWS (km h <sup>-1</sup> )	BTEXC (μg m <sup>-3</sup> )				Date	WD/MWS (km h <sup>-1</sup> )	BTEXC (μg m <sup>-3</sup> )			
			B	T	Ebz	X			B	T	Ebz	X
<b>B1</b>	03/07	ESE/5.5.	30.5	16.7	3.8	0.9	22/10	NNW/13.1	23.9	ND	1.3	ND
<b>B2</b>		ESE/9.6	45.2	13.8	2.3	ND		NNW/10.2	12.6	ND	1.6	ND
<b>B3</b>		ES/10.4	34.6	11.8	3.4	0.1		NNW/6.9	19.3	1.7	1.6	ND
<b>B1</b>	05/07	ENE/4.3	47.3	16.5	7.6	1.8	<b>24/10</b>	ENE/4.4	21.2	2.4	4.4	4.7
<b>B2</b>		ESE/9.9	38.3	32.0	12.6	5.1		ESE/11.9	19.4	ND	2.0	ND
<b>B3</b>		ESE/10.0	93.3	49.2	16.5	12.0		<b>ESE/12.7</b>	<b>26.9</b>	<b>3.5</b>	<b>1.6</b>	<b>2.0</b>
<b>B1</b>	09/07	ENE/5.5	75.9	36.1	13.6	8.5	28/10	ESE/4.2	28.2	1.3	1.8	ND
<b>B2</b>		ESE/9.4	44.7	22.0	11.9	4.7		ESE/7.1	23.6	0.2	2.6	ND
<b>B3</b>		ESE/10.4	61.1	28.8	13.0	7.5		ESE/8.8	16.9	2.3	1.7	ND
<b>B1</b>	<b>11/07</b>	ENE/3.5	28.5	6.2	3.1	ND	<b>30/10</b>	<b>ENE/2.8</b>	<b>29.8</b>	<b>4.3</b>	<b>3.6</b>	<b>ND</b>
<b>B2</b>		ESE/11.0	38.9	13.4	3.6	ND		NNE/2.3	29.3	3.4	5.5	0.2
<b>B3</b>		<b>ESE/10.7</b>	<b>137.5</b>	<b>97.1</b>	<b>14.3</b>	<b>15.1</b>		ESE/6.3	18.0	ND	1.3	ND
<b>B1</b>	15/07	ESE/6.3	44.9	4.8	3.7	ND	<b>01/11</b>	WSW/0.5	33.3	ND	4.3	1.3
<b>B2</b>		ESE/11.4	40.8	4.6	7.4	6.6		<b>ENE/4.4</b>	<b>27.4</b>	<b>11.9</b>	<b>6.2</b>	<b>3.0</b>
<b>B3</b>		ESE/10.6	43.8	4.2	7.9	8.4		ESE/4.6	24.7	ND	4.1	ND
<b>B1</b>	17/07	ESE/9.5	79.0	26.2	6.0	2.7	05/11	NNW/4.1	15.5	ND	1.5	ND
<b>B2</b>		ENE/9.7	89.6	37.3	5.9	0.6		ENE/2.5	12.8	ND	1.9	ND
<b>B3</b>		ESE/11.1	31.6	13.2	4.9	1.3		ESE/8.9	16.1	ND	1.3	ND
<b>B1</b>	18/07	ENE/7.5	33.9	14.8	4.5	0.8	08/11	ENE/2.5	18.3	ND	1.33	ND
<b>B2</b>		ESE/10.5	52.0	20.5	4.6	0.7		ENE/5.1	12.6	ND	1.9	ND
<b>B3</b>		SE/6.5	29.6	13.7	3.8	1.0		ENE/4.9	16.0	ND	1.8	ND
<b>B1</b>	22/07	ENE/5.5.	43.0	8.9	3.6	ND	11/11	ENE/5.6	14.9	ND	2.9	ND
<b>B2</b>		ENE/3.7	110.4	45.4	8.3	5.0		ESE/7.1	19.9	0.9	2.3	ND
<b>B3</b>		ESE/11.5	50.5	18.2	6.2	3.2		ESE/6.4	21.2	2.3	2.6	ND
<b>B1</b>	23/07	ESE/4.6	44.1	11.2	4.1	0.1	12/11	ESE/12.7	18.4	1.7	1.8	ND
<b>B2</b>		ESE/7.3	87.7	21.5	6.2	2.8		NNE/4.2	22.7	4.5	2.3	ND
<b>B3</b>		ESE/11.3	41.4	12.9	4.2	0.6		NNE/4.5	23.5	3.3	1.8	ND
<b>B1</b>	26/07	ESE/12.5	54.4	26.6	6.1	5.3	<b>14/11</b>	ESE/5.3	20.5	3.4	2.1	ND
<b>B2</b>		ENE/4.5	51.2	19.4	6.9	6.1		ENE/2.7	23.7	7.4	2.5	0.5
<b>B3</b>		ESE/8.1	51.9	18.8	6.8	6.3		<b>ENE/3.5</b>	<b>20.5</b>	<b>7.8</b>	<b>2.7</b>	<b>ND</b>

Individual samples discussed in the text are highlighted in bold

SP sampling period, MWS mean wind speed, BTEXC BTEX concentrations, WD wind direction, ND non detected

addition, relative humidity (RH) was much higher during autumn, and its correlation with T was negative and higher than during summer. Higher RH levels could have a washout effect on T concentrations and cause a drop in the T/B ratios during this period.

#### *p*-Xylene to ethylbenzene ratio

The *p*-xylene to ethylbenzene (X/Ebz) ratio is commonly used as an indicator of the photochemical age of air masses. A value of 3.6:1 of this ratio has been established as a typical emission relation for these species (Keymeulen et al. 2001; Lee et al.

2002). This ratio is related to the atmospheric residence time of these pollutants: High values indicate aged air masses (old emissions), and low values indicate fresh air masses (recent emissions). Kuntasal et al. (2005) used a value of 3.8 for this ratio. Fresh gasoline emissions provide values between 3.8 and 4.4 for this ratio. In this study, the combined summer and autumn period registered low values for this ratio, indicating that most of the air masses correspond to “fresh emissions.” A mean value of 0.4849 for this ratio was obtained for summer (B1 0.4437, B2 0.570, B3 0.440). During autumn, the mean value was 0.7529 (B1 0.777, B2 0.207, B3 1.249). Taken together, T/B and X/Ebz ratios, it can be suggested that these

fresh emissions correspond to vehicular emission from mobile sources. The values for this ratio in the site under study are similar to those observed in other cities around the world such as Guangzhou in China (0.21) (Wang et al. 2003), Izmir in Turkey (0.45) (Muezzinoglu et al. 2001), Seoul in Korea (0.30) (Na and Kim 2001), and Valparaíso in Chile (0.33) (Toro et al. 2014).

#### Ozone photochemical sensitivity

The ozone photochemical sensitivity can be determined from an empirical approach based on the mean ambient mixing ratio of VOCs (in part per billion carbon) and NO<sub>x</sub> (in parts per billion by volume) (Geng et al. 2008; Jiménez and Baldasano 2004). According to EPA's empirical kinetic modeling approach (EKMA) (Whitten et al. 1985), maximum afternoon ozone levels are dependent on the morning concentrations and mixing ratios of VOC and NO<sub>x</sub>. The morning VOC to NO<sub>x</sub> ratio can provide a useful starting point for evaluating the relative effectiveness of cost-efficient ozone precursor control strategies. A VOC to NO<sub>x</sub> ratio of 8 to 1 is often cited as an approximate decision point for determining the relative benefits of NO<sub>x</sub> vs VOCs controls. At low VOC to NO<sub>x</sub> ratios (<about 4 to 1), an area is considered to be VOC-limited. VOC reductions will be most effective in reducing ozone, and NO<sub>x</sub> controls may lead to ozone increases. At high VOC to NO<sub>x</sub> ratios (>about 15 to 1), an area is considered NO<sub>x</sub> limited, and VOC controls may be ineffective. When VOC to NO<sub>x</sub> ratios are at intermediate levels (4 to 15), a combination of VOC and NO<sub>x</sub> reductions may be warranted. VOC to NO<sub>x</sub> ratios for the sampling site under study were 2.58 and 0.41 for summer and autumn seasons, respectively. According to these results, this site is in an ozone formation regime that is VOC-limited (Kang et al. 2004; Martilli et al. 2002; Neftel et al. 2002).

#### Reactivity and ozone production by individual VOCs

The reactivity of VOCs is normally evaluated by estimating the ozone formation potential or OFP (Carter 1994; Carter and Heo 2012). The OFP is defined as  $OFP_i = MIR_i \times C_i$ , where OFP<sub>i</sub> is calculated from the maximum incremental reactivity scale (MIR<sub>i</sub>), according to values obtained from Carter and Heo 2012 (B 0.69, T 3.88, Ebz 2.93, X 7.61) and the ambient concentration for each VOC (C<sub>i</sub>). The obtained values for OFP of each measured BTEX during summer season (expressed in  $\mu\text{g m}^{-3}$ ) were the following: B 38.11, T 86.29, Ebz 20.33, and X 31.73, whereas OFP values obtained during autumn season were the following: B 14.54, T 14.15, Ebz 7.8, and X 16.09. During summer season, the highest OFP values were obtained for B and T, whereas during autumn period, X and B showed the highest values of OFP. Other studies have reported that X is the largest contributor to ozone formation

potential (Alghamdi et al. 2014). These compounds could contribute significantly to the formation of ozone in the site under study. Summer showed higher OFP values than autumn, indicating that during this period, photochemical activity was higher.

#### PCA and Pearson correlation

The T/B ratios and X/Ebz ratios suggest that summer and autumn BTEX levels at the site under study were influenced in a dominant way by vehicular traffic emissions (see [Toluene to benzene ratio](#) and [p-Xylene to ethylbenzene ratio](#)). However, PCA analysis can reveal more detailed information about the behavior of the studied pollutants. While BTEX ratios are used as markers of fresh, local traffic emissions, different gasoline formulations can result in different T/B ratios. These ratios must therefore be used with caution. In addition, low values for the T/B ratio may indicate the presence of other benzene sources in this area in addition to motor vehicle emissions. It is well known that BTEX have multiple sources. In the MAM study area, road transportation and area sources (evaporative emissions from solvents, storage tanks, coatings, fuel marketing, and other miscellaneous sources) are the dominant sources of VOCs. The MAM Emissions Inventory for 2005 (SEMARNAT. INE 2008) reported that 48.3 % of the total VOC emissions come from mobile sources, 43.5 % from area sources, and 8.2 % from industrial fixed sources. Therefore, it is necessary to investigate the relationship among BTEX and other pollutants and meteorological parameters in order to infer their probable additional sources. In addition, Pearson correlation matrixes were constructed for each sampling period (B1, B2, and B3) for the summer and autumn seasons. Principal component analysis (PCA) was used to study the variability patterns present in this multivariate data set. A PCA model was developed for air pollutants (CO, NO<sub>x</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub>, PM10, PM2.5, B, T, Ebz, and X) and the meteorological parameters (temperature (Temp), barometric pressure (P), relative humidity (RH), wind direction (WD), and wind speed (WS)). Table 2 shows the PCA loadings obtained for the morning (B1), midday (B2), and afternoon (B3) sampling periods during summer and autumn.

The analysis of the summer data set for the B1 period gave three principal components (F1, F2, and F3) with eigenvalues greater than 0.5 expressing about 78.438 % of the total variance. The loadings for these factors are shown in Table 2. F1 showed high factor loadings among CO, NO<sub>x</sub>, SO<sub>2</sub>, and NO<sub>2</sub>, which could be associated with combustion sources (vehicular exhaust). F2 showed high factor loadings between O<sub>3</sub> and temperature, being an evidence of the photochemical activity during this period. BTEX had a poor correlation with the combustion tracers but good correlations on each other with high factor loadings in F3, indicating that they probably had common sources different from vehicular emissions.

**Table 2** Eigenvalues and factor loadings for the summer and autumn data set during the three sampling periods

Variables	B1 sampling period			B2 sampling period				B3 sampling period			
	F1	F2	F3	F1	F2	F3	F4	F1	F2	F3	F4
CO	0.7 <sup>S</sup> 0.6 <sup>A</sup>			0.5 <sup>S</sup> 0.5 <sup>A</sup>	0.7 <sup>S</sup>			0.6 <sup>A</sup>	0.6 <sup>S</sup>	0.6 <sup>S</sup>	
NO <sub>x</sub>	0.9 <sup>S</sup> 0.9 <sup>A</sup>			0.9 <sup>A</sup>	0.7 <sup>S</sup>			0.9 <sup>A</sup>			
NO	0.9 <sup>A</sup>			0.8 <sup>S</sup> 0.9 <sup>A</sup>				0.8 <sup>A</sup>			
O <sub>3</sub>		0.7 <sup>S</sup> −0.6 <sup>A</sup>						0.5 <sup>S</sup>	0.5 <sup>A</sup>	0.5 <sup>S</sup>	
NO <sub>2</sub>	0.9 0.8 <sup>A</sup>			0.9 <sup>A</sup>	0.8 <sup>S</sup>			0.8 <sup>A</sup>		0.7 <sup>S</sup>	
PM <sub>10</sub>	0.8 <sup>A</sup>	0.6 <sup>S</sup>		0.8 <sup>A</sup>		0.7 <sup>S</sup>		0.7 <sup>A</sup>	0.7 <sup>A</sup>	0.5 <sup>A</sup>	0.5 <sup>S</sup>
PM <sub>2.5</sub>	0.5 <sup>A</sup>			0.5 <sup>A</sup>		0.8 <sup>S</sup> −0.6 <sup>A</sup>		0.5 <sup>S</sup> 0.6 <sup>A</sup>	0.7 <sup>A</sup>		0.5 <sup>S</sup>
B		0.6 <sup>A</sup>	0.6 <sup>S</sup> 0.5 <sup>A</sup>		0.8 <sup>A</sup>		0.73 <sup>S</sup>	0.6 <sup>S</sup>	0.7 <sup>S</sup> −0.7 <sup>A</sup>		
T			0.7 <sup>S</sup>	0.8 <sup>A</sup>			0.75 <sup>S</sup>	0.7 <sup>A</sup>	0.7 <sup>S</sup>		
Ebz	0.6 <sup>A</sup>		0.7 <sup>S</sup>	0.6 <sup>A</sup>	0.6 <sup>A</sup>			0.5 <sup>S</sup> 0.7 <sup>A</sup>	0.7 <sup>S</sup>		
X			0.5 <sup>S</sup>	0.5 <sup>A</sup>		0.5 <sup>A</sup>		0.5 <sup>S</sup>	0.7 <sup>S</sup>		
SO <sub>2</sub>	0.9 <sup>S</sup> 0.8 <sup>A</sup>			0.5 <sup>A</sup>	0.9 <sup>S</sup> −0.5 <sup>A</sup>		0.19 <sup>S</sup>	0.5 <sup>S</sup> 0.6 <sup>A</sup>		0.7 <sup>S</sup>	
WS			0.5 <sup>A</sup>	0.9 <sup>S</sup>							
WD	0.5 <sup>S</sup>		0.7 <sup>A</sup>	0.7 <sup>S</sup>		0.7 <sup>A</sup>			−0.5 <sup>A</sup>		
Tempera-ture		0.9 <sup>S</sup>	0.6 <sup>A</sup>			0.7 <sup>A</sup>		0.9 <sup>S</sup>		0.8 <sup>A</sup>	
RH		0.4 <sup>A</sup>		0.6 <sup>S</sup>	0.5 <sup>A</sup>						

S summer, A autumn

Table 3 shows the Pearson correlation matrix for the B1 period during both summer and autumn. A significant positive correlation was found during summer among CO, NO<sub>x</sub>, NO<sub>2</sub>, SO<sub>2</sub>, and WD, indicating that these compounds likely had a common origin (vehicular emissions). O<sub>3</sub> showed a significant negative correlation with NO and WS, indicating that the air during this period was rich on NO<sub>x</sub> and that ozone probably originated via photochemical reaction of NO<sub>2</sub>. PM10 and PM2.5 showed a significant positive correlation, indicating common sources for these particulate pollutants. A good correlation between NO<sub>x</sub> and SO<sub>2</sub> indicates that these pollutants probably originated from common sources that implicate high temperature combustion processes of sulfur-containing fossil fuels. All BTEX showed no significant negative correlation with O<sub>3</sub> and good correlations among each other indicating that they may originate from common sources. BTEX did not have good correlations with temperature; this suggests that evaporative emissions were negligible during the summer period. However, BTEX did not correlate with either CO or SO<sub>2</sub>, indicating that neither vehicular emissions nor industrial sources contributed to the ambient levels of these compounds (this finding is not in agreement with the BTEX ratios analysis) and they may have originated from area sources.

During summer for the B2 period, four components expressed about 89.218 % of the total variance (Table 2). F1 was associated with ozone precursors, and F2 showed high factor loadings for CO, NO<sub>x</sub>, NO<sub>2</sub>, and SO<sub>2</sub>. These are all species emitted from combustion sources, i.e., vehicular exhaust in urban areas. F3 was associated with particulate matter with high factor loadings for PM10 and PM2.5. F4 was associated to B and T indicating that these compounds had common sources but different from vehicular emissions. It should be noted that BTEX can be emitted from either vehicular exhaust or solvent use and this can be evaluated using their correlation with the combustion tracer CO. During summer (B2), NO<sub>2</sub>, NO<sub>x</sub>, WD, and SO<sub>2</sub> showed a significant positive correlation with CO, evidence that these pollutants could originate from mobile sources (Table 4). NO<sub>x</sub> correlated well with SO<sub>2</sub> indicating that at least partially, this pollutant had its origin in industrial sources and from the combustion of sulfur-containing fossil fuel. During this period, T and B correlated positively ( $r=0.732$ ) indicating that they probably had common sources. A good correlation among temperature and X indicates that this hydrocarbon could originate from evaporative emissions, a conjecture supported by the occurrence, during this period, of the highest mean ambient



**Table 3** Pearson correlation matrix for B1 sampling period during summer and autumn seasons

Variables	CO	NO <sub>x</sub>	O <sub>3</sub>	NO	NO <sub>2</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	B	T	Ebz	X	SO <sub>2</sub>	WS	WD	RH	Temperature
CO	1.00															
NO <sub>x</sub>	<b>0.75<sup>S</sup></b> <b>0.58<sup>A</sup></b>	1.00														
O <sub>3</sub>	0.10 <sup>S</sup> -0.39 <sup>A</sup>	0.35 <sup>S</sup> 0.35 <sup>S</sup>	1.00													
NO	0.27 <sup>S</sup> <b>0.56<sup>A</sup></b>	0.35 <sup>S</sup> <b>0.97<sup>A</sup></b>	-0.53 <sup>S</sup> -0.31 <sup>A</sup>	1.00												
NO <sub>2</sub>	<b>0.72<sup>S</sup></b> <b>0.51<sup>A</sup></b>	<b>0.96<sup>S</sup></b> <b>0.88<sup>A</sup></b>	<b>0.53<sup>S</sup></b> -0.02 <sup>A</sup>	0.08 <sup>S</sup> <b>0.76<sup>A</sup></b>	1.00											
PM <sub>10</sub>	-0.58 <sup>S</sup> <b>0.59<sup>A</sup></b>	-0.11 <sup>S</sup> <b>0.78<sup>A</sup></b>	0.49 <sup>S</sup> -0.55 <sup>A</sup>	-0.14 <sup>S</sup> <b>0.80<sup>A</sup></b>	-0.078 <sup>S</sup> <b>0.60<sup>A</sup></b>	1.00										
PM <sub>2.5</sub>	0.10 <sup>S</sup> 0.26 <sup>A</sup>	0.34 <sup>S</sup> <b>0.54<sup>A</sup></b>	0.25 <sup>S</sup> -0.04 <sup>A</sup>	0.12 <sup>S</sup> 0.48 <sup>A</sup>	0.33 <sup>S</sup> <b>0.57<sup>A</sup></b>	<b>0.68<sup>S</sup></b> <b>0.55<sup>A</sup></b>	1.00									
B	-0.29 <sup>A</sup> 0.02 <sup>S</sup>	0.23 <sup>A</sup> -0.08 <sup>S</sup>	-0.62 <sup>A</sup> -0.02 <sup>S</sup>	0.20 <sup>A</sup> -0.13 <sup>S</sup>	0.26 <sup>A</sup> -0.05 <sup>S</sup>	0.44 <sup>A</sup> -0.15 <sup>S</sup>	-0.21 <sup>A</sup> -0.17 <sup>S</sup>	1.00								
T	0.04 <sup>A</sup> 0.07 <sup>S</sup>	0.02 <sup>A</sup> -0.25 <sup>S</sup>	-0.38 <sup>A</sup> -0.15 <sup>S</sup>	0.06 <sup>A</sup> -0.19 <sup>S</sup>	-0.07 <sup>A</sup> -0.12 <sup>S</sup>	0.20 <sup>A</sup> 0.006 <sup>S</sup>	-0.02 <sup>A</sup> 0.006 <sup>S</sup>	0.15 <sup>A</sup> <b>0.72<sup>S</sup></b>	1.00							
Ebz	0.26 <sup>A</sup> -0.30 <sup>S</sup>	<b>0.68<sup>A</sup></b> -0.49 <sup>S</sup>	-0.38 <sup>A</sup> -0.05 <sup>S</sup>	<b>0.68<sup>A</sup></b> -0.38 <sup>S</sup>	<b>0.57<sup>A</sup></b> -0.41 <sup>S</sup>	0.47 <sup>A</sup> -0.13 <sup>S</sup>	0.47 <sup>A</sup> -0.32 <sup>S</sup>	0.61 <sup>S</sup> <b>0.61<sup>S</sup></b>	0.28 <sup>A</sup> 0.61 <sup>S</sup>	1.00						
X	-0.13 <sup>A</sup> <b>0.76<sup>S</sup></b>	0.03 <sup>A</sup> <b>0.86<sup>S</sup></b>	0.06 <sup>A</sup> 0.49 <sup>S</sup>	0.22 <sup>A</sup> -0.11 <sup>S</sup>	-0.36 <sup>A</sup> <b>0.95<sup>S</sup></b>	0.01 <sup>A</sup> -0.19 <sup>S</sup>	-0.17 <sup>A</sup> 0.24 <sup>S</sup>	-0.45 <sup>A</sup> -0.39 <sup>S</sup>	-0.06 <sup>A</sup> -0.04 <sup>S</sup>	0.01 <sup>A</sup> -0.17 <sup>S</sup>	1.00					
SO <sub>2</sub>	<b>0.54<sup>A</sup></b> 0.31 <sup>S</sup>	<b>0.95<sup>A</sup></b> -0.14 <sup>S</sup>	-0.01 <sup>A</sup> <b>0.74<sup>S</sup></b>	<b>0.90<sup>A</sup></b> 0.34 <sup>S</sup>	<b>0.89<sup>A</sup></b> -0.25 <sup>S</sup>	0.63 <sup>A</sup> <b>0.56<sup>S</sup></b>	<b>0.63<sup>A</sup></b> -0.34 <sup>S</sup>	-0.02 <sup>A</sup> 0.24 <sup>S</sup>	-0.03 <sup>A</sup> 0.11 <sup>S</sup>	0.53 <sup>A</sup> 0.15 <sup>S</sup>	-0.35 <sup>S</sup> 0.02 <sup>A</sup>	1.00				
WS	0.004 <sup>A</sup> <b>0.71<sup>S</sup></b>	-0.40 <sup>A</sup> <b>0.57<sup>S</sup></b>	0.34 <sup>A</sup> -0.006 <sup>S</sup>	-0.34 <sup>A</sup> 0.08 <sup>S</sup>	-0.46 <sup>A</sup> <b>0.58<sup>S</sup></b>	-0.60 <sup>A</sup> -0.42 <sup>S</sup>	-0.65 <sup>A</sup> -0.03 <sup>S</sup>	-0.20 <sup>A</sup> -0.16 <sup>S</sup>	-0.23 <sup>A</sup> 0.06 <sup>S</sup>	-0.33 <sup>A</sup> -0.04 <sup>S</sup>	0.29 <sup>A</sup> -0.32 <sup>S</sup>	-0.14 <sup>S</sup> -0.34 <sup>A</sup>	1.00			
WD	0.39 <sup>A</sup> -0.38 <sup>S</sup>	0.03 <sup>A</sup> -0.48 <sup>S</sup>	0.32 <sup>A</sup> <b>0.57<sup>S</sup></b>	0.01 <sup>A</sup> 0.48 <sup>S</sup>	0.08 <sup>A</sup> <b>0.65<sup>S</sup></b>	-0.15 <sup>A</sup> -0.09 <sup>S</sup>	-0.25 <sup>A</sup> -0.33 <sup>S</sup>	0.07 <sup>A</sup> 0.17 <sup>S</sup>	-0.08 <sup>A</sup> -0.02 <sup>S</sup>	-0.20 <sup>A</sup> 0.040 <sup>S</sup>	-0.01 <sup>A</sup> 0.025 <sup>S</sup>	0.07 <sup>A</sup> -0.76 <sup>S</sup>	0.54 <sup>S</sup> 0.58 <sup>A</sup>	1.00		
RH	-0.60 <sup>A</sup> -0.40 <sup>S</sup>	-0.65 <sup>A</sup> -0.17 <sup>S</sup>	0.007 <sup>A</sup> <b>0.62<sup>S</sup></b>	-0.65 <sup>A</sup> -0.71 <sup>S</sup>	-0.54 <sup>A</sup> 0.02 <sup>S</sup>	-0.48 <sup>A</sup> 0.47 <sup>S</sup>	-0.23 <sup>A</sup> 0.16 <sup>S</sup>	-0.17 <sup>A</sup> 0.10 <sup>S</sup>	-0.07 <sup>A</sup> 0.09 <sup>S</sup>	-0.25 <sup>A</sup> 0.04 <sup>S</sup>	-0.14 <sup>A</sup> 0.36 <sup>S</sup>	-0.63 <sup>A</sup> 0.08 <sup>S</sup>	0.48 <sup>S</sup> -0.79 <sup>S</sup>	-0.27 <sup>S</sup> -0.70 <sup>A</sup>	1.00	
Temperature	0.05 <sup>A</sup>	0.03 <sup>A</sup>	0.008 <sup>A</sup>	-0.05 <sup>A</sup>	0.18 <sup>A</sup>	0.12 <sup>A</sup>	-0.45 <sup>A</sup>	<b>0.61<sup>A</sup></b>	-0.03 <sup>A</sup>	0.44 <sup>A</sup>	-0.29 <sup>A</sup>	-0.11 <sup>A</sup>	-0.09 <sup>A</sup>	0.17 <sup>A</sup>	-0.66 <sup>S</sup>	1.00

Correlation coefficients highlighted in bold are statistically significant at  $P < 0.05$

S summer, A autumn

**Table 4** Pearson correlation matrix for B2 sampling period during summer and autumn seasons

Variables	CO	NO <sub>x</sub>	O <sub>3</sub>	NO	NO <sub>2</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	B	T	Ebz	X	SO <sub>2</sub>	WS	WD	RH	Temperature
CO	1.00															
NO <sub>x</sub>	<b>0.64<sup>S</sup></b> <b>0.59<sup>A</sup></b>	1.00														
O <sub>3</sub>	-0.11 <sup>S</sup> -0.47 <sup>A</sup>	0.23 <sup>S</sup> -0.06 <sup>A</sup>	1.00													
NO	0.27 <sup>S</sup> <b>0.69<sup>A</sup></b>	0.40 <sup>S</sup> <b>0.98<sup>A</sup></b>	-0.72 <sup>S</sup> -0.19 <sup>A</sup>	1.00												
NO <sub>2</sub>	<b>0.56<sup>S</sup></b> 0.46 <sup>A</sup>	<b>0.87<sup>S</sup></b> <b>0.98<sup>A</sup></b>	<b>0.64<sup>S</sup></b> 0.09 <sup>A</sup>	-0.08 <sup>S</sup> <b>0.93<sup>A</sup></b>	1.00											
PM <sub>10</sub>	<b>-0.57<sup>S</sup></b> <b>0.57<sup>A</sup></b>	-0.03 <sup>S</sup> -0.04 <sup>A</sup>	0.41 <sup>S</sup> -0.04 <sup>A</sup>	-0.17 <sup>S</sup> <b>0.83<sup>A</sup></b>	0.05 <sup>S</sup> <b>0.73<sup>A</sup></b>	1.00										
PM <sub>2.5</sub>	-0.14 <sup>S</sup> 0.15 <sup>A</sup>	0.23 <sup>S</sup> <b>0.51<sup>A</sup></b>	0.07 <sup>S</sup> 0.14 <sup>A</sup>	0.21 <sup>S</sup> 0.47 <sup>A</sup>	0.13 <sup>S</sup> <b>0.54<sup>A</sup></b>	<b>0.77<sup>S</sup></b> <b>0.52<sup>A</sup></b>	1.00									
B	<b>-0.61<sup>S</sup></b> 0.11 <sup>A</sup>	-0.28 <sup>S</sup> 0.40 <sup>A</sup>	0.20 <sup>S</sup> <b>-0.52<sup>A</sup></b>	-0.21 <sup>S</sup> 0.44 <sup>A</sup>	-0.19 <sup>S</sup> 0.34 <sup>A</sup>	0.24 <sup>S</sup> 0.33 <sup>A</sup>	-0.20 <sup>S</sup> -0.16 <sup>A</sup>	1.00								
T	-0.27 <sup>S</sup> <b>0.53<sup>A</sup></b>	-0.14 <sup>S</sup> <b>0.84<sup>A</sup></b>	0.16 <sup>S</sup> 0.13 <sup>A</sup>	-0.14 <sup>S</sup> <b>0.82<sup>A</sup></b>	-0.07 <sup>S</sup> <b>0.83<sup>A</sup></b>	-0.05 <sup>S</sup> <b>0.65<sup>A</sup></b>	-0.36 <sup>S</sup> 0.33 <sup>A</sup>	<b>0.73<sup>S</sup></b> 0.19 <sup>A</sup>	1.00							
Ebz	-0.10 <sup>S</sup> 0.12 <sup>A</sup>	<b>-0.54<sup>S</sup></b> <b>0.55<sup>A</sup></b>	-0.05 <sup>S</sup> -0.20 <sup>A</sup>	-0.37 <sup>S</sup> <b>0.55<sup>A</sup></b>	-0.39 <sup>S</sup> <b>0.53<sup>A</sup></b>	0.01 <sup>S</sup> <b>0.52<sup>A</sup></b>	-0.10 <sup>S</sup> -0.007 <sup>A</sup>	-0.04 <sup>S</sup> <b>0.78<sup>A</sup></b>	0.37 <sup>S</sup> 0.49 <sup>A</sup>	1.00						
X	-0.09 <sup>S</sup> 0.29 <sup>A</sup>	-0.38 <sup>S</sup> <b>0.64<sup>A</sup></b>	0.27 <sup>S</sup> <b>0.56<sup>A</sup></b>	-0.89 <sup>S</sup> <b>0.56<sup>A</sup></b>	0.05 <sup>S</sup> <b>0.70<sup>A</sup></b>	0.06 <sup>S</sup> 0.32 <sup>A</sup>	-0.20 <sup>S</sup> 0.09 <sup>A</sup>	-0.19 <sup>S</sup> 0.01 <sup>A</sup>	-0.15 <sup>S</sup> <b>0.57<sup>A</sup></b>	0.43 <sup>S</sup> 0.32 <sup>A</sup>	1.00					
SO <sub>2</sub>	<b>0.72<sup>S</sup></b> 0.34 <sup>A</sup>	<b>0.68<sup>S</sup></b> <b>0.56<sup>A</sup></b>	<b>0.56<sup>S</sup></b> 0.07 <sup>A</sup>	-0.26 <sup>S</sup> <b>0.56<sup>A</sup></b>	<b>0.88<sup>S</sup></b> <b>0.54<sup>A</sup></b>	-0.19 <sup>S</sup> 0.42 <sup>A</sup>	-0.06 <sup>S</sup> <b>0.67<sup>A</sup></b>	-0.41 <sup>S</sup> -0.22 <sup>A</sup>	-0.22 <sup>S</sup> <b>0.52<sup>A</sup></b>	-0.19 <sup>S</sup> -0.09 <sup>A</sup>	0.32 <sup>S</sup> 0.30 <sup>A</sup>	1.00				
WS	<b>0.61<sup>S</sup></b> -0.06 <sup>A</sup>	0.24 <sup>S</sup> <b>-0.59<sup>A</sup></b>	-0.71 <sup>S</sup> 0.03 <sup>A</sup>	0.63 <sup>S</sup> <b>-0.57<sup>A</sup></b>	-0.06 <sup>S</sup> -0.59 <sup>A</sup>	<b>-0.60<sup>S</sup></b> <b>-0.71<sup>A</sup></b>	-0.25 <sup>S</sup> -0.72 <sup>A</sup>	-0.20 <sup>S</sup> -0.42 <sup>A</sup>	-0.14 <sup>S</sup> -0.35 <sup>A</sup>	-0.15 <sup>S</sup> <b>-0.61<sup>A</sup></b>	-0.54 <sup>S</sup> -0.09 <sup>A</sup>	0.06 <sup>S</sup> -0.27 <sup>A</sup>	1.00			
WD	<b>0.74<sup>S</sup></b> 0.12 <sup>A</sup>	0.44 <sup>S</sup> -0.23 <sup>A</sup>	-0.28 <sup>S</sup> 0.27 <sup>A</sup>	0.30 <sup>S</sup> -0.26 <sup>A</sup>	0.32 <sup>S</sup> -0.20 <sup>A</sup>	-0.48 <sup>S</sup> -0.27 <sup>A</sup>	-0.24 <sup>S</sup> -0.39 <sup>A</sup>	-0.32 <sup>S</sup> -0.46 <sup>A</sup>	-0.35 <sup>S</sup> 0.12 <sup>A</sup>	-0.28 <sup>S</sup> -0.17 <sup>A</sup>	-0.16 <sup>S</sup> 0.20 <sup>A</sup>	0.46 <sup>S</sup> -0.40 <sup>A</sup>	0.78 <sup>S</sup> 0.49 <sup>A</sup>	1.00		
RH	-0.23 <sup>S</sup> -0.38 <sup>A</sup>	-0.21 <sup>S</sup> -0.18 <sup>A</sup>	-0.70 <sup>S</sup> -0.11 <sup>A</sup>	<b>0.60<sup>S</sup></b> -0.23 <sup>A</sup>	<b>-0.55<sup>S</sup></b> -0.11 <sup>A</sup>	-0.17 <sup>S</sup> -0.37 <sup>A</sup>	-0.22 <sup>S</sup> -0.12 <sup>A</sup>	0.47 <sup>S</sup> 0.40 <sup>A</sup>	0.39 <sup>S</sup> -0.43 <sup>A</sup>	-0.03 <sup>S</sup> 0.03 <sup>A</sup>	-0.71 <sup>S</sup> -0.24 <sup>A</sup>	<b>-0.69<sup>S</sup></b> <b>-0.55<sup>A</sup></b>	0.13 <sup>S</sup> -0.04 <sup>A</sup>	0.52 <sup>S</sup> -0.67 <sup>A</sup>	1.00	
Temperature	-0.35 <sup>S</sup> -0.04 <sup>A</sup>	-0.25 <sup>S</sup> 0.02 <sup>A</sup>	<b>0.64<sup>S</sup></b> 0.18 <sup>A</sup>	<b>-0.68<sup>S</sup></b> 0.01 <sup>A</sup>	0.09 <sup>S</sup> 0.02 <sup>A</sup>	0.48 <sup>S</sup> 0.27 <sup>A</sup>	0.30 <sup>S</sup> -0.40 <sup>A</sup>	-0.16 <sup>S</sup> 0.20 <sup>A</sup>	-0.14 <sup>S</sup> 0.05 <sup>A</sup>	0.28 <sup>S</sup> <b>0.52<sup>A</sup></b>	0.72 <sup>S</sup> 0.36 <sup>A</sup>	0.15 <sup>S</sup> -0.38 <sup>A</sup>	<b>-0.86<sup>S</sup></b> -0.09 <sup>A</sup>	-0.19 <sup>A</sup> 0.24 <sup>A</sup>	<b>-0.78<sup>S</sup></b> -0.26 <sup>A</sup>	1.00

Correlation coefficients highlighted in bold are statistically significant at  $P < 0.05$ *S* summer, *A* autumn

temperature (28.8 °C). A negative correlation among O<sub>3</sub> with NO, CO, and Ebz indicates that these last compounds could be precursors of tropospheric ozone in the site under study. O<sub>3</sub> is produced when primary pollutants such as NO<sub>x</sub> and VOCs (including BTEX) interact under the action of sunlight. The main atmospheric sink process for CO is by reaction with OH, and this mechanism also makes CO a major precursor to photochemical ozone (Crutzen 1974). Negative correlations between B-CO, Ebz-NO<sub>x</sub>, and X-NO can be evidence of photochemical activity and secondary pollutant production from reaction between BTEX and OH radicals.

Four components were found for the summer data set during B3 period, expressing 88.106 % of the total variance (Table 2). F1 is associated with photochemical activity with high factor loadings of O<sub>3</sub>, PM2.5, B, T, Ebz, X, SO<sub>2</sub>, and temperature. F2 included high factor loadings of CO (combustion tracer) and the four BTEX compounds, indicating that during this period, these VOCs could originate from combustion sources related to vehicular traffic. F3 included the pollutants CO, O<sub>3</sub>, NO<sub>2</sub>, and SO<sub>2</sub>, and F4 was associated with particulate matter with high factor loadings of PM10 and PM2.5. Table 5 shows the Pearson correlation matrix for B3 period during both summer and autumns. During summer (B3), BTEX components showed significant positive correlations, evidence that these compounds probably originated from common sources. NO correlated positively in a significant way with NO<sub>x</sub>, indicating that these pollutants also could have a common origin. NO<sub>2</sub> and NO<sub>x</sub> showed a significant positive correlation with CO, indicating that they probably had their origin in vehicular sources. NO, NO<sub>x</sub>, CO, and BTEX showed a negative significant correlation with O<sub>3</sub>, indicating that during this period, all these compounds were ozone precursors. B, T, Ebz, and X showed moderate correlations with SO<sub>2</sub> during this period suggesting that at least partially, industrial sources could influence the BTEX levels in the study area. Ebz was negatively correlated with relative humidity, indicating that the washout phenomenon could be the most important removal process for this compound as MAM typically receives about 300 mm of rain during the summer.

During the B1 period for autumn, three principal components were found, which explained 70.931 % of the total variance (Table 2). F1 was associated with combustion sources (vehicular exhaust) with high factor loadings for CO, NO<sub>x</sub>, NO, NO<sub>2</sub>, PM10, PM2.5, Ebz, and SO<sub>2</sub>. F2 showed high factor loadings for B and O<sub>3</sub>, indicating that this compound could act as an ozone precursor during this period. Finally, F3 suggested that B could originate from evaporative emissions. Table 3 shows the Pearson correlation matrix for the B1 period during autumn. CO, NO, NO<sub>2</sub>, PM10, and SO<sub>2</sub> correlated with each other, indicating that this group of pollutants probably had a common origin, i.e., gasoline and fuel containing sulfur vehicle emissions. Ebz had good

correlations with NO<sub>x</sub> ( $r=0.686$ ), NO ( $r=0.684$ ), NO<sub>2</sub> ( $r=0.578$ ), PM10 (0.532), and SO<sub>2</sub> ( $r=0.539$ ) but did not show a good correlation with CO. This suggests that Ebz might have source contributions different than vehicle emissions. PM10 and PM2.5 showed an influence of wind speed ( $r=-0.606$  and  $r=-0.658$ ) indicating that particulate matter could be associated with nearby sources (WS for this period ranged from 0.55 to 13.12 km h<sup>-1</sup>). B correlated significantly with temperature ( $r=0.617$ ), indicating that this hydrocarbon could originate from evaporative emissions. RH was negatively correlated with all measured air pollutants. This behavior suggest that high concentrations of water vapor partially remove pollutants from the atmosphere by means of chemical reaction (acid rain) or condensation (promoting deposition) (Felipe-Sotelo et al. 2006).

The analysis of the autumn data set for B2 period gave three principal components, explaining 73.884 % of the total variance (Table 2). F1 was associated to combustion tracers (vehicular exhaust) with high factor loadings of CO, NO<sub>x</sub>, NO, NO<sub>2</sub>, PM10, PM2.5, T, Ebz, X, and SO<sub>2</sub>. F2 included B and Ebz, and F3 showed high factor loadings for X, WD, and temperature, indicating that probably this compound could also originate from evaporative emissions. The following correlations: T-CO ( $r=0.530$ ), T-NO<sub>x</sub> ( $r=0.844$ ), T-NO ( $r=0.827$ ), Ebz-NO<sub>x</sub> ( $r=0.555$ ) Ebz-NO ( $r=0.551$ ), X-NO<sub>x</sub> ( $r=0.640$ ), X-NO ( $r=0.561$ ), X-NO<sub>2</sub> ( $r=0.703$ ) and T-PM10 ( $r=0.659$ ) indicate that this group of pollutants originated from common sources (vehicular emissions) (Table 4). CO and B were negatively correlated with ozone indicating that both played an important role in the formation of tropospheric ozone during this period. B-Ebz and T-X showed significant correlations suggesting that they probably had sources in common (Table 4). WS showed negative correlation with NO<sub>x</sub>, NO, PM10, PM2.5, and Ebz, indicating that all these pollutants may be associated with nearby sources. Once again, RH played an important role in the washout of pollutants in the site under study during this sampling period as MAM typically receives nearly 400 mm of rain during the autumn. During B3 period for autumn (Table 2), three components were necessary to explain 72.117 % of the total variance in the data set. F1 was associated with combustion sources (vehicular exhaust) with high factor loadings for CO, NO<sub>x</sub>, NO, NO<sub>2</sub>, PM10, PM2.5, Ebz, and SO<sub>2</sub>. F2 showed high factor loadings for B, T, RH, and temperature indicating that at least during this period, these BTEX could originate from evaporative emissions. F3 showed the highest loadings for B, wind speed, and wind direction; this could indicate that probably B could have been transported from regional sources. The Pearson correlation matrix for the B3 period during autumn is shown in Table 5. Once again, the influence of vehicular emissions was evident from the

**Table 5** Pearson correlation matrix for the B3 sampling period during summer and autumn seasons

Variables	CO	NO <sub>x</sub>	O <sub>3</sub>	NO	NO <sub>2</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>	B	T	Ebz	X	SO <sub>2</sub>	WS	WD	RH	Temperature
CO	1.00															
NO <sub>x</sub>	<b>0.50<sup>S</sup></b> <b>0.69<sup>A</sup></b>	1.00														
O <sub>3</sub>	-0.23 <sup>S</sup> -0.44 <sup>A</sup>	<b>-0.50<sup>S</sup></b> -0.16 <sup>A</sup>	1.00													
NO	0.33 <sup>S</sup> <b>0.73<sup>A</sup></b>	<b>0.85<sup>S</sup></b> <b>0.81<sup>A</sup></b>	<b>-0.86<sup>S</sup></b> -0.42 <sup>A</sup>	1.00												
NO <sub>2</sub>	0.44 <sup>S</sup> <b>0.57<sup>A</sup></b>	<b>0.60<sup>S</sup></b> <b>0.95<sup>A</sup></b>	0.35 <sup>S</sup> -0.01 <sup>A</sup>	0.10 <sup>S</sup> <b>0.60<sup>A</sup></b>	1.00											
PM <sub>10</sub>	-0.37 <sup>S</sup> <b>0.50<sup>A</sup></b>	-0.26 <sup>S</sup> <b>0.66<sup>A</sup></b>	0.43 <sup>S</sup> 0.03 <sup>A</sup>	-0.37 <sup>S</sup> 0.46 <sup>A</sup>	0.05 <sup>S</sup> <b>0.67<sup>A</sup></b>	1.00										
PM <sub>2.5</sub>	-0.43 <sup>S</sup> -0.04 <sup>A</sup>	-0.29 <sup>S</sup> 0.49 <sup>A</sup>	-0.05 <sup>S</sup> 0.26 <sup>A</sup>	-0.07 <sup>S</sup> 0.34 <sup>A</sup>	-0.45 <sup>S</sup> <b>0.50<sup>A</sup></b>	<b>0.60<sup>S</sup></b> <b>0.67<sup>A</sup></b>	1.00									
B	0.16 <sup>S</sup> 0.47 <sup>A</sup>	-0.32 <sup>S</sup> 0.22 <sup>A</sup>	-0.05 <sup>S</sup> -0.16 <sup>A</sup>	-0.13 <sup>S</sup> 0.08 <sup>A</sup>	-0.41 <sup>S</sup> 0.27 <sup>A</sup>	0.41 <sup>S</sup> -0.05 <sup>A</sup>	0.41 <sup>S</sup> -0.44 <sup>A</sup>	1.00								
T	0.21 <sup>S</sup> 0.46 <sup>A</sup>	-0.18 <sup>S</sup> 0.62 <sup>A</sup>	-0.11 <sup>S</sup> -0.17 <sup>A</sup>	-0.01 <sup>S</sup> <b>0.80<sup>A</sup></b>	-0.32 <sup>S</sup> 0.44 <sup>A</sup>	-0.14 <sup>S</sup> 0.46 <sup>A</sup>	0.45 <sup>S</sup> 0.32 <sup>A</sup>	<b>0.97<sup>S</sup></b> 0.08 <sup>A</sup>	1.00							
Ebz	0.27 <sup>S</sup> <b>0.74<sup>A</sup></b>	-0.37 <sup>S</sup> <b>0.86<sup>A</sup></b>	-0.17 <sup>S</sup> -0.21 <sup>A</sup>	-0.12 <sup>S</sup> <b>0.60<sup>A</sup></b>	-0.51 <sup>S</sup> <b>0.86<sup>A</sup></b>	-0.15 <sup>S</sup> <b>0.60<sup>A</sup></b>	0.24 <sup>S</sup> 0.35 <sup>A</sup>	<b>0.83<sup>S</sup></b> 0.45 <sup>A</sup>	<b>0.75<sup>S</sup></b> 0.27 <sup>A</sup>	1.00						
X	0.16 <sup>S</sup> -	-0.31 <sup>S</sup> -	-0.19 <sup>S</sup> -	-0.07 <sup>S</sup> -	-0.48 <sup>S</sup> -	-0.18 <sup>S</sup> -	0.24 <sup>S</sup> -	<b>0.89<sup>S</sup></b> -	<b>0.80<sup>S</sup></b> -	<b>0.91<sup>S</sup></b> -	1.00					
SO <sub>2</sub>	0.44 <sup>S</sup> 0.27 <sup>A</sup>	-0.30 <sup>S</sup> <b>0.61<sup>A</sup></b>	0.49 <sup>S</sup> -0.006 <sup>A</sup>	-0.52 <sup>S</sup> <b>0.65<sup>A</sup></b>	0.21 <sup>S</sup> <b>0.50<sup>A</sup></b>	-0.02 <sup>S</sup> 0.29 <sup>A</sup>	-0.13 <sup>S</sup> <b>0.56<sup>A</sup></b>	0.49 <sup>S</sup> 0.03 <sup>A</sup>	0.41 <sup>S</sup> <b>0.54<sup>A</sup></b>	0.49 <sup>S</sup> 0.39 <sup>A</sup>	0.49 <sup>S</sup> -	1.00				
WS	<b>0.61<sup>S</sup></b> -0.16 <sup>A</sup>	0.10 <sup>S</sup> <b>-0.70<sup>A</sup></b>	<b>-0.50<sup>S</sup></b> -0.01 <sup>A</sup>	0.29 <sup>S</sup> -0.49 <sup>A</sup>	-0.23 <sup>S</sup> <b>-0.71<sup>A</sup></b>	-0.42 <sup>S</sup> <b>-0.65<sup>A</sup></b>	-0.27 <sup>S</sup> <b>-0.73<sup>A</sup></b>	0.24 <sup>S</sup> 0.33 <sup>A</sup>	0.24 <sup>S</sup> 0.33 <sup>A</sup>	0.34 <sup>S</sup> -0.45 <sup>A</sup>	0.28 <sup>S</sup> -	0.06 <sup>S</sup> -0.28 <sup>A</sup>	1.00			
WD	<b>0.82<sup>S</sup></b> -0.04 <sup>A</sup>	<b>0.53<sup>S</sup></b> -0.30 <sup>A</sup>	-0.30 <sup>S</sup> -0.12 <sup>A</sup>	0.42 <sup>S</sup> -0.35 <sup>A</sup>	0.36 <sup>S</sup> -0.23 <sup>A</sup>	-0.13 <sup>S</sup> <b>-0.60<sup>A</sup></b>	-0.40 <sup>S</sup> <b>-0.71<sup>A</sup></b>	-0.07 <sup>S</sup> 0.10 <sup>A</sup>	-0.03 <sup>S</sup> <b>-0.52<sup>A</sup></b>	0.07 <sup>S</sup> -0.24 <sup>A</sup>	-0.07 <sup>S</sup> -	0.07 <sup>S</sup> -0.47 <sup>A</sup>	<b>0.70<sup>S</sup></b> 0.36 <sup>A</sup>	1.00		
RH	0.11 <sup>S</sup> -0.13 <sup>A</sup>	<b>0.59<sup>S</sup></b> 0.06 <sup>A</sup>	-0.30 <sup>A</sup> -0.02 <sup>A</sup>	<b>0.78<sup>S</sup></b> 0.02 <sup>A</sup>	-0.06 <sup>S</sup> 0.07 <sup>A</sup>	<b>-0.55<sup>S</sup></b> -0.21 <sup>A</sup>	-0.21 <sup>S</sup> 0.40 <sup>S</sup>	-0.37 <sup>S</sup> 0.39 <sup>S</sup>	-0.24 <sup>S</sup> 0.01 <sup>A</sup>	-0.32 <sup>S</sup> 0.15 <sup>A</sup>	-0.37 <sup>S</sup> -	-0.67 <sup>S</sup> -0.33 <sup>A</sup>	0.21 <sup>S</sup> 0.02 <sup>A</sup>	0.21 <sup>S</sup> 0.02 <sup>A</sup>	1.00	
Temperature	-0.48 <sup>S</sup> -0.10 <sup>A</sup>	<b>-0.71<sup>S</sup></b> -0.35 <sup>A</sup>	<b>0.63<sup>S</sup></b> 0.15 <sup>A</sup>	<b>-0.74<sup>S</sup></b> <b>-0.58<sup>A</sup></b>	-0.22 <sup>S</sup> -0.18 <sup>A</sup>	<b>0.56<sup>S</sup></b> 0.30 <sup>A</sup>	0.40 <sup>S</sup> -0.06 <sup>A</sup>	0.39 <sup>S</sup> -0.06 <sup>A</sup>	0.24 <sup>S</sup> -0.54 <sup>A</sup>	0.34 <sup>S</sup> -0.08 <sup>A</sup>	0.43 <sup>S</sup> -	0.44 <sup>S</sup> -0.55 <sup>A</sup>	-0.47 <sup>S</sup> 0.19 <sup>A</sup>	<b>-0.54<sup>S</sup></b> 0.01 <sup>A</sup>	<b>-0.88<sup>S</sup></b> -0.33 <sup>A</sup>	1.00

Correlation coefficients highlighted in bold are statistically significant at  $P < 0.05$ *S* summer, *A* autumn

high correlations with CO: NO<sub>x</sub>-CO ( $r=0.695$ ), NO-CO ( $r=0.731$ ), NO<sub>2</sub>-CO ( $r=0.579$ ), PM10-CO ( $r=0.506$ ), Ebz-CO (0.742), B-CO ( $r=0.47$ ), and T-CO ( $r=0.46$ ). In addition, high correlations between T-NO, T-NO<sub>x</sub>, Ebz-NO<sub>x</sub>, and Ebz-NO<sub>2</sub> were found. O<sub>3</sub> correlated in a moderate way with CO and NO, indicating that these pollutants could act at least partially as ozone precursors during this period. NO<sub>x</sub>, PM10, PM2.5, and T showed a moderate influence of the wind conditions ( $r>-0.5$ ), indicating that nearby sources could influence their levels during this period (WS, 3.5–12.72 km h<sup>-1</sup>; prevailing WD, ESE (60 %)).

## Conclusion

B and T showed the highest concentrations in the study site. B concentrations were higher than those reported in other large cities, whereas the levels of T, Ebz, and X were similar to those reported for other cities around the world. All measured BTEX compounds showed a clear diurnal and seasonal pattern with the highest concentrations during summer. Diurnal patterns for BTEX were similar during summer but changed in autumn. The seasonal change in diurnal pattern was due to meteorology: Summer winds were predominantly ESE, while autumn winds were more variable. Other meteorological differences include lower temperatures and higher relative humidities in autumn. According to the prevailing winds, the municipalities of Apodaca and Guadalupe (which contain important industries, high traffic volume, many oil and gas service stations, and the biggest airport in the region) could influence BTEX concentrations found in this site during the sampling period. According to the VOC to NO<sub>x</sub> ratio analysis, the study area is VOC-limited. This implies that VOCs are sparse and NO<sub>x</sub> is abundant. Calculated OFP values showed that benzene, toluene, and *p*-xylene were the BTEX species that could contribute to the formation of ozone in the study area, especially during high solar radiation (higher photochemical activity) periods. T/B and X/Ebz ratios showed that BTEX were influenced by fresh vehicular emissions; however, BTEX ratios must be used with caution. PCA analysis confirmed the relative importance of vehicular sources only for the autumn season. During summer, this analysis suggested that additional sources beyond traffic-related emissions could influence the levels of BTEX. The ratios, Pearson correlations, and PCA analysis reported here provide preliminary information about the probable sources of VOCs in the study area but do not provide conclusive evidence about the source types and their contributions. A more complete understanding of BTEX source identification requires the application of a more robust tool such as receptor modeling.

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