Diurnal variation of BTX levels in ambient air of one urban site located at the southwest of Mexico City during two seasons in 2013

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Abstract—BTX (benzene, ethylbenzene, toluene and pxylene), criteria air pollutants (O_3, NO_2, NO_x, NO, CO, and SO_2) and meteorological parameters were measured in ambient air of an urban site located at the southwest of Mexico City during winter and spring 2013. A total of 82 samples were collected for BTX and analyzed by Gas Chromatography with Flame Ionization detection (GC-FID). Meteorological parameters were measured by a portable station. A marked diurnal variation was found for all measured BTX. During spring, the highest concentrations occurred during afternoon (15:00-16:30 h) for benzene and ethylbenzene, during the midday (12:00-13:30 h) for toluene and during the mornings (08:00-09:30 h) for p-xylene. During winter, higher concentrations were found in the afternoons for Benzene and Toluene, and during the mornings for ethylbenzene and p-xylene. Mean concentrations for benzene, ethylbenzene, toluene and p-xylene were: 32.78, 13.58, 36.25 and 14.51 $\mu g/m^3$, respectively. BTX abundance showed the following order during the whole study period: toluene > benzene > p-xylene > ethylbenzene. During spring BTX maximum concentrations were found when winds blowed from SSW and ENE. During winter time, in the mornings BTX levels were higher when winds blowed from E, in the midday, Toluene and p-xylene showed higher levels when wind blowed from WSW, benzene and ethylbenzene had higher concentrations when winds blowed from E and NNW, respectively. In the winter afternoons toluene showed higher levels when dominant winds blowed from SE and benzene, ethylbenzene and p-xylene showed higher levels when winds came from SSW. Local area sources and avenues with high vehicular traffic are located at these directions. These sources could contribute to the levels of BTX in this site.

Keywords— Air pollution, BTX, Mexico City, Ozone, Volatile organic compounds.

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I. INTRODUCTION

CURRENTLY document Currently volatile organic compounds (VOCs) constitute a serious concern due to their effects on public health. Their spatial and temporal outdoors concentrations patterns are complex, due to they are ubiquitous, have diverse sources [1], [25], and contribute to tropospheric photochemical ozone formation and enhancement of the global greenhouse effect [2]-[3], [30].

VOCs includes a series of compounds named as BTX, comprising mainly benzene and its alkyl derivatives (toluene, ethylbenzene, 1, 2 4- trimethyl-benzene, m,p-xylene and o-xylene) which are hazardous to human health due to their carcinogenic properties [4].

The determination of their concentrations in ambient air, the understanding of their role in the tropospheric ozone formation and their diurnal- seasonal variations, and the identification of their main sources can help in the development of efficient air pollution abatement strategies for Ozone and BTX in urban areas [5]-[7].

Over the world many studies have been carried out in order to know the levels of BTX in ambient air of important urban areas [3]-[11]. However, in Mexico there are not enough studies about VOCs patterns in the atmosphere [8-11], and most of them are focused to benzene and formaldehyde and comprise short sampling periods. Mexico City is the most important urban centre in the country with the highest vehicular fleet, with high traffic density within the metropolitan area and the presence of multiple and diverse sources contributing to the BTX levels in the atmosphere.

The objective of this research was to determine the atmospheric concentrations of some BTX (benzene, toluene, ethylbenzene and p-xylene) at one site located at the southwest of Mexico City during two seasons of 2013 (winter and spring) and to try to infer their probable sources from a PCA analysis

and their relation with meteorological parameters and other criteria air pollutants.

II. METHODOLOGY

A. Site Description

Mexico City is the capital of Mexico and one of the largest cities in the world with a population of more than 20 million. The city is situated at an altitude of more than 2,000 meters in the Valley of Mexico and is surrounded by volcanoes and mountains. Because of its situation warm air remains stationary. This causes high temperatures; especially during the winter it is much warmer in the city than in its direct surroundings.

According to the Köppen climate classification Mexico City has a moderate savannah climate (type Cwb) with two distinct seasons. A dry season from the second part of October till the second part of May and a wet period from the second part of May or the beginning of June till the second part of October. Large amounts of rain are not uncommon during this period.

The study was conducted in a site located at the southwest of Mexico City (Lat. 19°21'46.61" N, Long. 99°09'7.28"W) (Fig. 1).

Figure 1: Location of the sampling site.

B. Sampling Method

A total of 82 samples were collected, 42 were collected during spring from March 21 to April 3, 2013 and 40 were collected during winter from February 6 to February 18, 2013. Benzene, ethyl benzene, toluene and p-xylene were measured in ambient air. Samples of air were collected within glass tubes containing 226-01 Anasorb CSC (SKC): length 70 mm; inner diameter 4.0 mm; outer diameter 6 mm packed in the first section with 100 mg of actived carbon and 500 mg in the second one, separated by a glass wool section (Method INSHT

MTA/MA-030/A92) [13]. 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 ml min-1 at 1.5-hour intervals (day, midday and afternoon). Sampling was carried out using a Universal XR pump model PCXR4 (SKC), at three sampling periods: B1(from 08:00 to 09:30 h), B2 (from 12:00 to 13:30 h) and B3 (from 15:00 to 16:30 h).

During sampling, the Swagelok® fitting was removed from the marked end, and a diffusion cap was fitted to the end of the sampling tube. Prior to the main study, several pilot experiments were conducted to evaluate the suitability of the sampling procedure intended for use in the main study. This procedure included determining appropriate sampling times. Sampler's tubes were protected from bad weather conditions by aluminum shelters. 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 along with samplers to the field and stored in the laboratory during the sampling period. Samples were analyzed within three weeks after sample collection at the Environmental Sciences Laboratory in the Autonomous University of Carmen City (UNACAR).

C. Analytical Method

All Samples were extracted with 1 ml of CS_2 for each section of the samplers tubes, shaking during 30 s to assure a maximum desorption. Extracted samples were analyzed using a TRACE GC Ultra gas chromatograph (Thermoscientific) and one flame ionization detector (FID; Thermoscientific Technologies, Inc) (Method INSHT MTA/MA-030/A92) [13]. The analytical column used was a capillary column (57 m, 0.32 mm i.d., 0.25 μm film thickness). Operation of the instrument was controlled using a Trace Chemstation data system. The oven temperature program was initially set to 40 °C for 4 min, which was then increased at a rate of 5 °C/min up to 100 °C, and was 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 ml/ min and 350 ml/ min for ultra-pure hydrogen and extra-dried air, respectively. The ultra-pure nitrogen carrier (99.999%) gas flow rate was 1 ml/ min [14]. Four BTX that included benzene, p-xylene, ethyl benzene, and toluene, were investigated. Five-point calibration was performed using 99.98% Sigma-Aldrich anaytical reagents at a concentration of 2 ppm for each BTX.

The established calibration curves for the four investigated BTX were found to have R-square values of 0.999. Method detection limit (MDL) for each compound was calculated by multiplying the standard deviation obtained from seven replicate measurements of the first level of calibration by 3.14 (Student's t-value). The analytical results showed that the MDLs for the four VOC compounds of benzene, ethyl benzene, p-xylene, and toluene, were 0.0517; 0.0566; 0.0600; 0.025; μg/m^3, respectively. The amount of BTX in blank

samples was below the limit of detection (LOD) for all studied compounds.

D. Monitoring of Meteorological parameters and Criteria air pollutants

Wind conditions (direction and speed), relative humidity, temperature, and barometric pressure were monitored from March 21 to April 3, 2013 (spring) and from February 6 to February 18, 2013 (winter). A portable meteorological station Davis Vantage Pro II model was used in order to measure the meteorological parameters. Wind roses were constructed for each day using the software WRPLOT (from Lakes Environmental) [15]. 24 hr back air masses trajectories were calculated for the studied period using HYSPLIT model from the NOAA (National Oceanic Administration Agency, USA) in order to identify the probable origin of the air masses.

Criteria air pollutants (O_3, NO, NO_2, NOx, CO, SO_2, PM_{10}, $PM_{2.5}$) were monitored during the sampling period using API Teledyne automatic analyzers. Data were collected from the SIMAT-GDF Air Quality Station located in Miguel Hidalgo Delegation in Mexico City denoted as HGM. The specific location of this station is shown in Fig. 2.
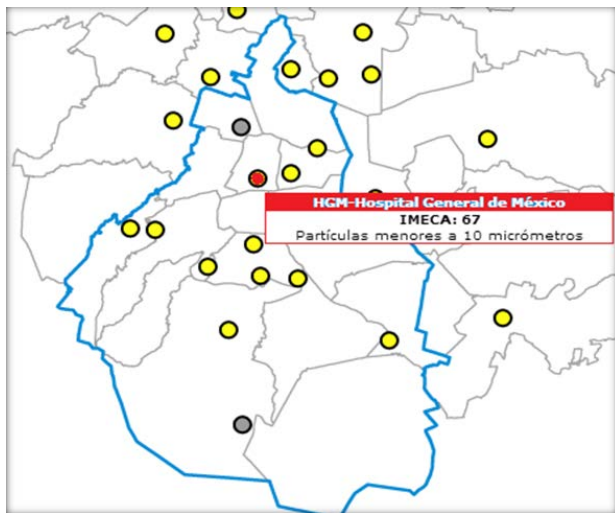

Figure 2: Specific location of the HGM Air Quality Station.

III. RESULTS

A. Diurnal and Seasonal Variation of BTX

During spring, Benzene (B) and EBz (Ethylbenzene) showed the same diurnal pattern registering the highest concentrations during the afternoon (B3) decreasing during the midday (B2) and showing the lowest values during the mornings (B1).   Toluene (T) showed the maximum concentrations during the midday (B2) decreasing during the afternoon (B3) and showing the lowest values during the mornings (B1). p-X showed the highest concentrations during the mornings (B1) and the lowest concentrations during the afternoons (B3). Diurnal variation and descriptive statistics

can be observed in Fig. 3 for spring period. Abundance of BTX followed the same order during spring time: Toluene > Benzene> Ethylbenzene> p-Xylene. During winter time, the diurnal pattern was the following: Benzene and Toluene had their higher concentrations during the afternoons (B3) decreasing during the mornings and showing the lowest values during the midday (Fig. 4). On the other hand, ethylbenzene and p-xylene had their higher levels during the mornings decreasing during the afternoons and showing their lowest values during the midday (Fig. 4). The relative abundance during winter time followed this order: toluene > benzene> p-xylene> ethylbenzene.
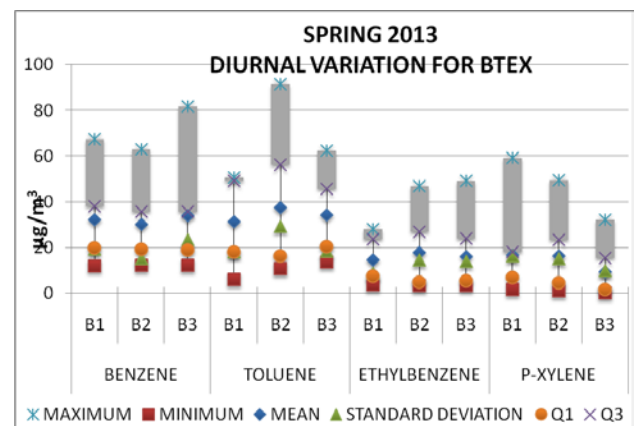

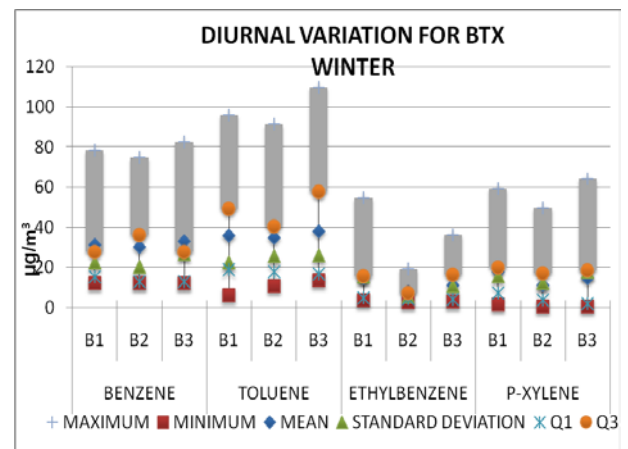Figure 3: BTX Diurnal variation during spring time for this study.

Figure 4: BTX Diurnal variation during winter time for this study.

In Table 1 is shown the comparison of the results of this study with ambient air concentrations found in other sites around the world. It can be observed that Bz levels found in this study are higher than those reported for cities like Hong Kong, Izmir, Fuji and Pamplona [18], [1],[20], [21] and lower than those measured in Rome [16]. BTX levels in this study were higher than those found in Izmir, Fuji and Pamplona

[18], [20], [21] but lower than those registered for Rome and Hong Kong [16], [18]. Ebz and p-X levels were higher than those reported for cities like Izmir, Fuji and Pamplona [18], [20], [21] but higher than those reported for Rome and Hong Kong [16], [18].

Table 1. Comparison of atmospheric concentrations of BTX ($\mu g/m^3$) found in this study with data of other studies around the world.

Location	Bz	T	Ebz	p-X
Kocaely, Turkey (urban)[1]	2.2994	36.1304	9.8905	37.5035
Rome [16]	36.1200	101.4415	17.9093	55.0282
Belgium (busy road) [17]	3.1238	7.6003	1.5060	3.9566
Hong Kong (industrial) [18]	15.3331	141.7844	25.1134	28.3590
Izmir (urban) [18]	3.3678	15.6587	3.7137	7.6289
Fuji (industrial) [20]	2.0957	14.2449	1.5466	1.8615
Pamplona (urban) [21]	2.8895	13.4914	2.1879	3.4382
Mexico City (urban) [8, 22]	21.2648 [8]	121.2828 [22]	19.0285 [8]	69.2702 [8]
This study (urban)	32.78	36.25	13.58	14.51
Bz: Benzene; T: Toluene; Ebz: Ethylbenzene; p-X: p-Xylene				

In Fig. 5 and Fig. 6 it can be observed the parametric statistics for the whole sampling period and the seasonal variation, respectively. It can be observed that all measured BTX did not show a clear seasonal pattern, mean concentrations remain without changes during spring and winter.

B. Toluene to Benzene ratio (T/Bz ratio)

T/Bz ratio has been commonly used as an indicator of traffic emissions. Bz and T are constituents of gasoline and are emitted into the atmosphere by motor vehicle exhausts. The toluene content of gasoline and motor vehicle exhaust is 3-4 times higher than Bz content [16].
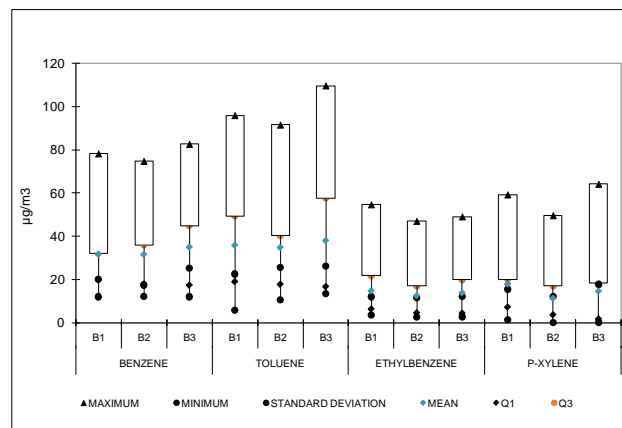

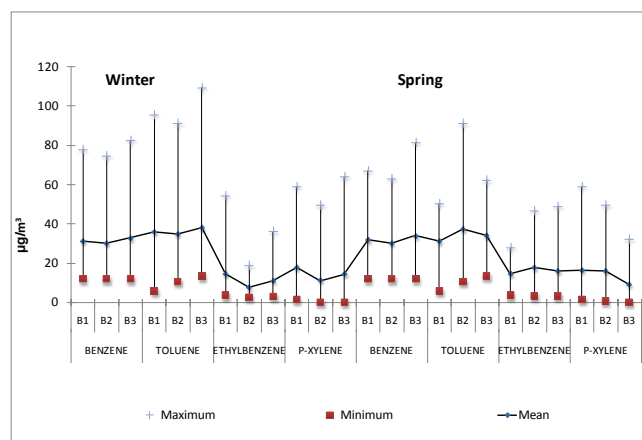Figure 5:   Parametric statistics for BTX during the whole sampling period.

Figure 6:   Seasonal variation for BTX during the whole sampling period.

A value of around 2-3 is characteristic of vehicular emissions in many urban areas worldwide [15], [22]. The range for the study site during spring time was between 0.1287 and 2.6963 being higher during the afternoon sampling period as it can be observed in Table 2.   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 values for this ratio during winter time were between 0.1965 and 4.5459 as it can be observed in Table 3. 4 days during the mornings and 2 days during the afternoons showed values of this ratio higher than 2, indicating that at least in these days there was a contribution from other sources different from the vehicular sources (probably industrial and area sources).

Table 2. Toluene/Benzene Ratios during spring 2013.

T/Bz Ratio			
Date	B1	B2	B3
	µg/m³	µg/m³	µg/m³
21.03.2013	1.0335	0.8561	0.7732
22.03.2013	0.2487	0.2233	0.1287
23.03.2013	1.5647	0.4730	0.4766
24.03.2013	0.7396	1.9880	0.4382
25.03.2013	0.5647	0.5806	0.2892
26.03.2013	0.5063	2.3494	0.5474
27.03.2013	2.6964	0.8508	0.7919
28.03.2013	0.7335	1.5768	0.5126
29.03.2013	0.4653	0.9297	0.1400
30.03.2013	0.7012	0.4929	0.6762
31.03.2013	0.3034	0.5345	0.5871
01.04.2013	0.7381	0.8601	0.7723
02.04.2013	0.7382	0.8377	0.8000
03.04.2013	0.6036	0.9402	0.8019

(Spring 2013)

Table 3. Toluene/Benzene Ratios during winter 2013.

T/Bz Ratio			
Date	B1	B2	B3
	µg/m³	µg/m³	µg/m³
06.02.2013	3.2192	1.7319	0.9676
07.02.2013	1.3933	1.0382	4.5459
08.02.2013	0.1856	0.7905	2.6055
09.02.2013	4.0457	0.5548	0.6762
10.02.2013	1.5402	0.7587	0.1097
11.02.2013	2.2239	1.7608	1.1959
12.02.2013	2.0463	0.7780	0.7919
13.02.2013	1.2266	0.1863	0.7022
14.02.2013	0.1965	1.7370	0.3497
15.02.2013	0.8761	1.0929	0.5708
16.02.2013	0.5235	0.7666	0.5272
18.02.2013	0.6660	0.7206	0.5786

(Winter 2013)

C. Pearsons correlation

Tables 4 and 5 show the Pearson's correlation coefficient matrix for the mean concentrations of BTX during spring and winter, respectively. A significant correlation between Bz, T and Ebz indicates that they were possibly originated from vehicular emissions. This behavior was evident during the three sampling periods during the day for spring time. p-X

showed a different pattern compared to the rest of BTX during the morning sampling period (B1). During the midday period, p-X and T showed a good correlation each other and with temperature, indicating that this BTX could be originated from evaporative emissions. EBz and p-X had a good correlation during the afternoon sampling period, indicating that both compounds probably had their origin from gasoline vehicles, petroleum plants and gasoline stations. T had the lowest coefficients in this work with EBz and p-X, suggesting that T had other additional sources.

During the morning and midday sampling periods in winter time, toluene and p-xylene and pxylene-ethylbenzene had good correlations, whereas, during the winter afternoons benzene had good correlations with ethylbenzene and p-xylene, and toluene had good correlations with ethylbenzene and p-xylene. These high correlations among the measured BTX indicate that these pollutants probably had sources in common.

According to the USEPA SPECIATE [22] data base, T, EBz and p-X are consistent with sources profiles given for "gasoline vehicle emissions".

Table 4. Pearson's correlation coefficient matrix for studied BTX during spring 2013.

BI			
	BZ	T	Ebz	p-X
BZ	1	0.526	0.658	0.004
T	0.526	1	0.613	0.394
Ebz	0.658	0.613	1	0.090
p-X	0.004	0.394	0.090	1
B2			
	BZ	T	Ebz	p-X
BZ	1	0.681	0.597	0.476
T	0.681	1	0.460	0.868
Ebz	0.597	0.460	1	0.435
p-X	0.476	0.868	0.435	1
B3			
	BZ	T	Ebz	p-X
BZ	1	0.945	0.545	0.439
T	0.945	1	0.601	0.461
Ebz	0.545	0.601	1	0.915
p-X	0.439	0.461	0.915	1

Bz: Benzene; T: Toluene; Ebz: Ethylbenzene; p-X: p-Xylene

B1: 08:00-09:30 H; B2: 12:00-13:30 H; B3: 15:00-16:30 H

Table 5. Pearson's correlation coefficient matrix for studied BTX during winter 2013.

BI				
	BZ	T	Ebz	p-X
BZ	**1**	0.122	-0.015	0.011
T	0.122	**1**	**0.702**	**0.797**
Ebz	-0.015	**0.702**	**1**	**0.514**
p-X	0.011	**0.797**	0.514	**1**
B2				
	BZ	T	Ebz	p-X
BZ	**1**	0.341	0.130	0.360
T	0.341	**1**	0.331	**0.947**
Ebz	0.130	0.331	**1**	**0.508**
p-X	0.360	**0.947**	0.508	**1**
B3				
	BZ	T	Ebz	p-X
BZ	**1**	0.374	**0.699**	**0.892**
T	0.374	**1**	**0.787**	**0.665**
Ebz	**0.699**	0.787	**1**	**0.897**
p-X	**0.892**	**0.665**	0.897	**1**
Bz: Benzene; T: Toluene; Ebz: Ethylbenzene; p-X: p-Xylene				
B1: 08:00-09:30 H; B2: 12:00-13:30 H; B3: 15:00-16:30 H				

D. Meteorological Analysis

BTX concentrations were correlated with meteorological parameter at surface level and 24 h backward air masses trajectories were calculated for maximum concentrations events using the HYSPLIT model from NOAA at 500, 700 and 1000 masl. The backward trajectories analysis helps to determine the origin of air masses and probable location of sources for the measured pollutants. In spring time, during the morning sampling period (B1) B had the highest concentrations when wind blowed from NW and SE; for T, the highest levels occurred when wind came from WSW and NW, for EBz and p-X the maximum concentrations were registered when wind blowed from ENE (Fig.7). For the midday sampling period (B2), B and T registered their maximum levels when wind came from ENE, for EBz when wind blowed from N and NNE and for p-X when wind blowed from E and WNW (Fig. 8). Finally, during the afternoon sampling period B and T had their maximum levels when wind blowed from N and SW and for EBz and p-X when wind blowed from SSE (Fig. 9). In winter time, during the mornings (B1) the highest concentrations were registered when winds came from ESE for benzene, from E for toluene and p-xylene and from ENE for

ethylbenzene (figure 10). During the midday in winter season (B2) (Fig. 11), benzene, toluene and p-xylene showed their maximum levels when winds blowed from WSW, whereas, ethlybenzene registered their highest values of concentration when winds came from NNW. Finally, during the afternoon sampling period (B3) (Fig. 12), all measured BTX showed their highest concentration values when winds blowed from SSW.
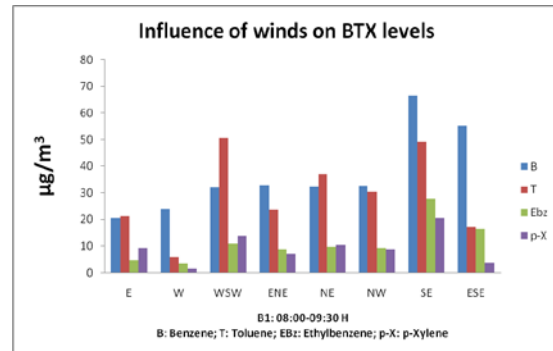

Figure 7: Wind direction influence on BTX concentrations for the morning sampling period during spring 2013.
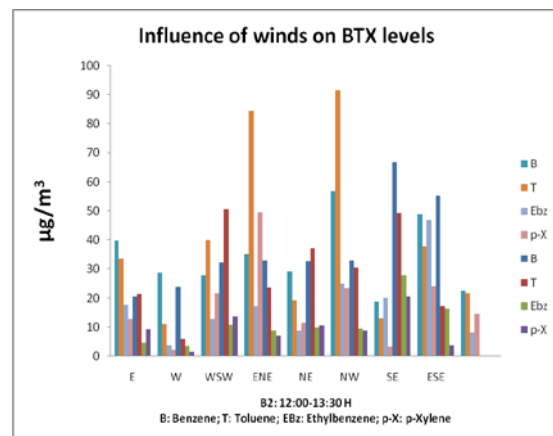

Figure 8: Wind direction influence on BTX concentrations for the midday sampling period during spring 2013.
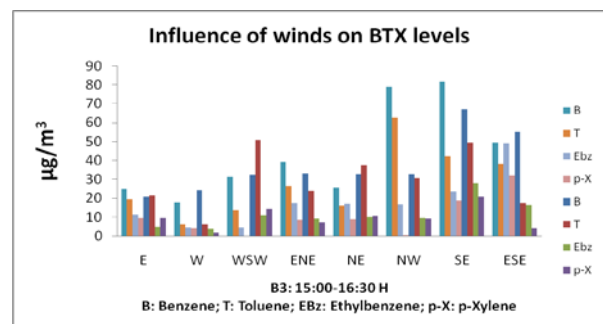

Figure 9: Wind direction influence on BTX concentrations for the afternoon sampling period during spring 2013.
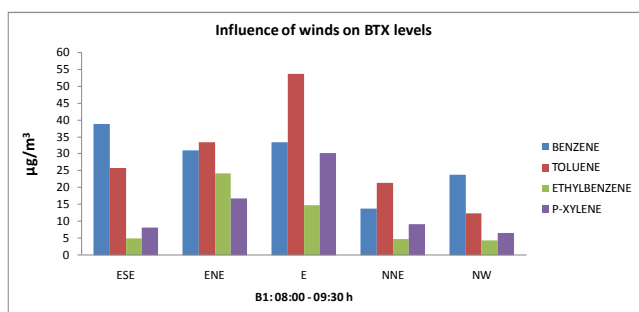
Figure 10: Wind direction influence on BTX concentrations for the morning sampling period during winter 2013.
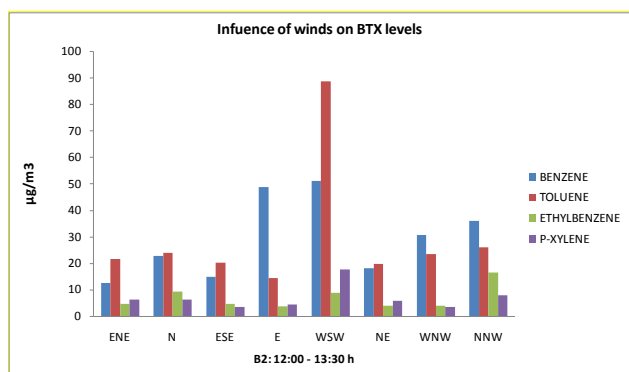

Figure 11: Wind direction influence on BTX concentrations for the midday sampling period during winter 2013.
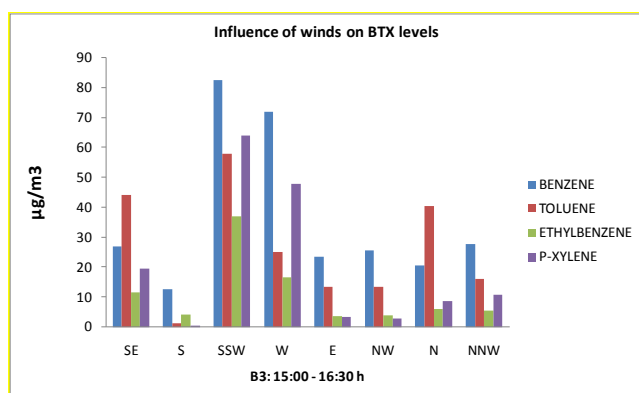

Figure 12: Wind direction influence on BTX concentrations for the afternoon sampling period during winter 2013.

E. p-Xylene to Ethylbenzene ratio (p-X/EBz ratio)

In Tables 6 and 7 are shown p-X/Ebz ratios for this study during spring and winter, respectively. This ratio is used commonly as indicator of the photochemical age of the air masses. A ratio of 3.6: 1 of (m+p-X/Ebz) has been established as a typical emission relation for these species [27], [28]. This ratio is useful to determine the staying of pollutants in the atmosphere, lower values of this ratio means that air masses have stayed a long time in the atmosphere (old emissions) and high values of this ratio indicate that air masses are recent (fresh emissions). Kuntasal *et al.* [29] used a value of 3.8 for this ratio. Gasoline fresh emissions have shown values

between 3.8 and 4.4 for this ratio. In this study, during spring 2013, only one day (March 24) during the morning sampling period (B1) showed high values for this ratio, indicating that most of the air masses correspond to "old emissions". During winter 2013 all values for this ratio correspond to "old emissions" showing values lower than the reference value.

Table 6. p-Xylene/Ethylbenzene Ratios for spring time.

		p-X/Ebz		
	Date	B1	B2	B3
		$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$
SPRING 2013	21.03.2013	1.9366	1.1069	0.8838
	22.03.2013	0.4246	0.3085	0.6818
	23.03.2013	1.2785	0.7141	1.2908
	24.03.2013	8.7551	1.8623	0.0660
	25.03.2013	0.6894	0.9256	0.1664
	26.03.2013	1.0260	2.8793	0.5227
	27.03.2013	2.5843	2.4897	0.0295
	28.03.2013	0.7745	0.9299	0.8078
	29.03.2013	0.7671	0.1495	0.2555
	30.03.2013	0.5151	0.4985	0.5191
	31.03.2013	0.5802	0.3590	0.3844
	01.04.2013	0.6691	0.5157	0.6575
	02.04.2013	0.7401	0.6741	0.6621
	03.04.2013	0.2391	1.8153	0.8469

Table 7. p-Xylene/Ethylbenzene Ratios for winter time.

		p-X/Ebz		
	Date	B1	B2	B3
		$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$
WINTER 2013	06.02.2013	2.0028	1.3677	0.4979
	07.02.2013	0.4370	0.5004	1.1905
	08.02.2013	1.1470	0.0885	2.4048
	09.02.2013	2.0015	1.0649	0.1270
	10.02.2013	1.9446	0.0728	0.1038
	11.02.2013	3.2314	1.3025	0.4154
	12.02.2013	2.6131	0.8572	2.8776
	13.02.2013	1.2152	0.5448	1.7664
	14.02.2013	1.1055	1.1589	2.9316
	15.02.2013	2.6605	0.8483	0.9665
	16.02.2013	1.5319	0.8810	0.7656
	17.02.2013	0.5580	1.4676	1.4460
	18.02.2013	1.7486	0.4777	2.0096

F. Principal component analysis (PCA)

A principal component analysis was carried out in order to study patterns in a multivariate data set for the three sampling

periods (08:00-09:30 h; 12:00-13:30 h; and 15:00-16:30 h). To assess the relationship between concentrations of the studied BTX, meteorological parameters and criteria air pollutants, a factor analysis (Principal Component Analysis) was applied using the software XLSTAT [32]. Varimax orthogonal rotation is widely used in atmospheric data manipulation to identify the principal components with clear pattern of factor loadings [31], [33]. The PCA analysis was applied for the BTEX concentrations (benzene, toluene, ethylbenzene and p-xylene), meteorological parameters (temperature: T, barometric pressure: P, relative humidity: RH, wind direction: WD and wind speed: WS).

Fig. 13, Fig. 14 and Fig. 15 show the result of the PCA for spring time whereas, Fig. 16, Fig. 17 and Fig. 18 show the PCA analysis for winter time.

Fig. 13 shows the principal compound analysis (PCA) among BTX, meteorological parameters and criteria pollutants during spring 2013 for the morning sampling period (B1). A significant positive correlation was found among NO_2, NO_X, NO and Ozone (O_3) indicating that probably these compounds had their origin in photochemical activity. Ozone showed a significant negative correlation with relative humidity, which is evidence that there was a partial elimination of this pollutant due to washout processes. PM_{10} and $PM_{2.5}$ showed a significant positive correlation with CO indicating that these particulate pollutants could be originated from vehicular emissions.   A good correlation between NO_X and SO_2 indicates that these pollutants were originated from industrial sources that implicate high temperature combustion processes.

All BTX excepting p-X showed a good correlation among each other indicating that B, T and EBz had the same emission sources probably local area sources. BTX did not show correlation with CO and SO_2, this is evidence that BTX measured in the study site in this period have not their origin neither vehicular emission nor industrial sources. All BTX showed a non significant negative correlation with Ozone indicating that ozone chemistry in this site was more sensible to changes in VOCs than NO_x.

Fig. 14 shows the principal component analysis (PCA) among BTX, meteorological parameters and criteria pollutants during spring 2013 for the midday sampling period (B2). Toluene, p-Xylene, NO, NO_2 and NO_x showed a significant positive correlation with CO which is evidence that all these pollutants could be originated from mobile sources. NO_x showed a good correlation with SO2 indicating that at least partially, this pollutant had their origin in industrial sources. During this period, T and B correlated positively indicating that probably these pollutants had sources in common. A good correlation among T and p-X with CO and SO_2 was found being evidence that these BTX could be originated from vehicular and industrial sources. During this period there was not dominant role neither from VOCs nor NO_x in the tropospheric ozone formation and it can be suggested that

found levels in this period were due to residual or accumulate ozone.

In Fig. 15 it can be observed that BTX showed a significant positive correlation among each other excepting B with p-X, this is evidence that these compounds were originated from sources in common, probably local area sources.
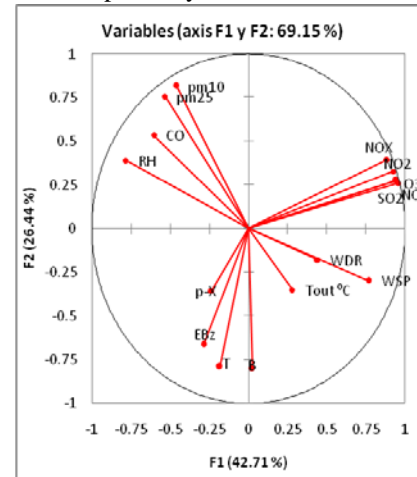

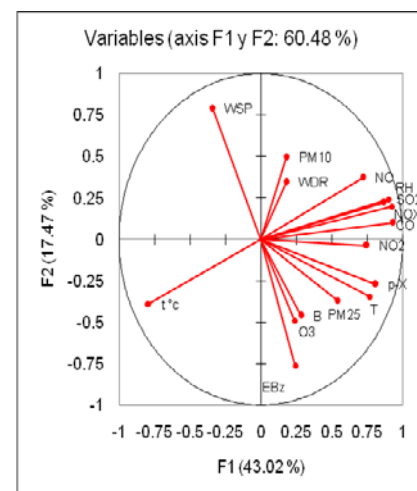Figure 13: PCA for spring season during the midday sampling period B1: 08:00-09:30 h.

Figure 14: PCA for spring season during the midday sampling period B2: 12:00-13:30 h.

NO correlated positively in a significant way with NO_2, indicating that these pollutants could be originated from photochemical reactions. $PM_{2.5}$, NO_2 and NO_x showed a significant positive correlation with CO, indicating that they had probably their origin in vehicular sources. NO showed a negative significant correlation with ozone, indicating that during this period NO was an ozone precursor.

Fig. 16 shows the ACP for winter season during the morning sampling period. In this figure it can be observed that CO, NO, NO_X, NO_2, PM_{10} and $PM_{2.5}$ showed a strong relation each

other, suggesting that these compounds probably had their origin in common sources (emissions from mobile sources derived from vehicular traffic and high temperatures combustion processes).

There was a negative correlation among NO, NO_X and O_3, it indicates that as NO and NO_X concentrations decreased, O_3 concentrations increased possibly due to photochemical reactions of NO and NO_X in order to produce ozone. In this period, ozone formation chemistry was more sensible to NO_X than VOCs. Toluene, ethylbenzene and p-xylene showed positive significant correlations among each other. Probably these pollutants had their origin in common sources. BTX did not show positive correlations neither with CO (vehicular emissions), Temperature (evaporative emissions), SO_2 (industrial sources) nor with O_3 (photochemical activity), indicating that these compounds probably were emitted from area sources.
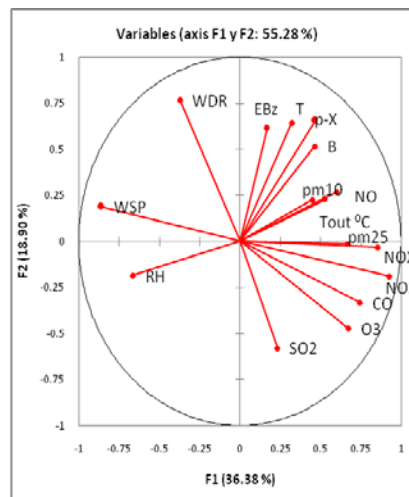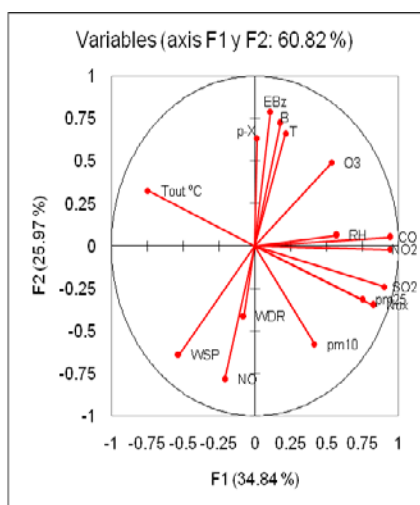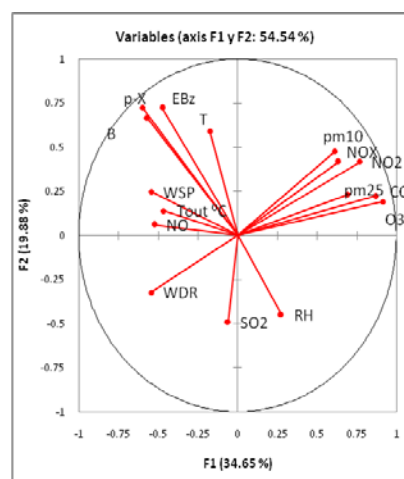

Figure 15: PCA for spring season during the morning sampling period B3: 15:00-16:30 h.

Figure 16: PCA for winter season during the morning sampling period B1: 08:00-09:30 h.

Figure 17: PCA for winter season during the midday sampling period B2: 12:00-13:30 h.

Figure 18: PCA for winter season during the afternoon sampling period B3: 15:00-16:30 h.
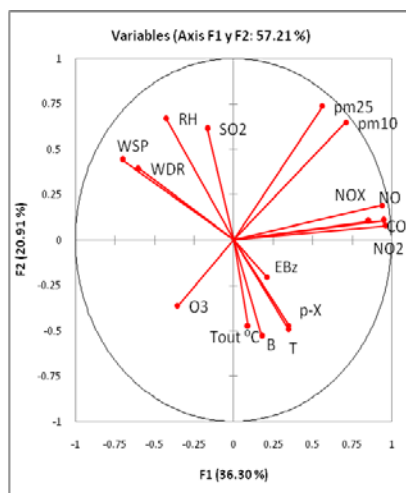
During midday sampling period in winter time (Fig. 17), NO, NO_X and NO_2 showed a negative correlation with relative humidity indicating that these compounds were eliminated at least partially by washout processes. NO_2, NO_X and CO showed good correlations among each other indicating that these compounds probably had their origin in vehicular sources. NO_2, toluene and p-xylene showed positive correlations with O_3, it suggests that these compounds probably were originated from photochemical activity. Toluene and p-xylene did not show significant positive correlations among each other indicating that these compounds had their origin in mixed and diverse sources. Toluene had a good correlation with ethylbenzene and temperature, suggesting that these BTX probably were originated from evaporative emissions. p-xylene probably was originated from mobile sources and high temperature combustion processes showing significant positive correlations with CO, NO_2 and NO_X.

In Fig. 18 is showed the ACP for the afternoon sampling period during winter time. It can be observed that positive correlations among CO, NO, NO_2, NO_X, PM_{10} and $PM_{2.5}$ were found, suggesting that all these pollutants could be originated from vehicular sources and high temperature combustion processes. Ozone had positive correlations with NO and NO_X indicating that photochemical activity could influence on the levels of these compounds. It is probably that during this period, BTX could be originated from area sources since they did not show positive correlations with tracers of vehicular emissions (CO), evaporative emissions (temperature) or industrial activity (SO_2).

IV. CONCLUSION

BTX concentrations in this work showed values comparable to those reported for cities like Mexico and Hong Kong. There was a clear diurnal pattern in the BTX concentrations in both seasons (winter and spring). However there was not a clear seasonal pattern, since BTX levels remain similar for both seasons. During spring, the highest levels during were found in the afternoons (B3) for Benzene and Ethylbenzene, during the midday for Toluene and during the mornings for p-X. According to T/Bz ratios and the meteorological analysis, was clearly under the influence of vehicular sources circulating in avenues located at NE and SW of the sampling site. On the other hand, the wind direction study showed that this site was under the influence of sources related to a gasoline station located at SSW of the sampling site. BTX abundance in the study site was: T > B> p-X > EBz. BTX concentrations during spring 2013 were influenced by vehicular sources (80%) and only in two days BTX levels were influenced by industrial sources during spring sampling period.

During winter, benzene and toluene showed their higher levels in the afternoon sampling period, whereas, ethylbenzene and p-xylene showed their higher concentrations during the mornings. Relative abundance of BTX during winter showed the following order: T> B> p-X>EBz. According to the ACP and meteorological analysis, BTX levels during this season were influenced by regional area sources located at E, WSW and SSW from the sampling site. p-X/EBz ratios for both season showed that air masses correspond to old emissions originated from regional sources.

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