International Interdisciplinary Congress on Renewable Energies, Industrial Maintenance, Mechatronics and Informatics
Booklets

RENIECYT 1702902 CONACYT

RENIECYT - LATINDEX - Research Gate - DULCINEA - CLASE - Sudoc - HISPANA - SHERPA UNIVERSIA - Google Scholar DOI - REDIB - Mendeley - DIALNET - ROAD - ORCID

Title: Diurnal variation and health risk of atmospheric aromatic hydrocarbons concentrations in an urban site located in Nuevo Leon, Mexico

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Editorial label ECORFAN: 607-8695
BCIERMMI Control Number: 2022-01
BCIERMMI Classification (2022): 261022-0001

Pages: 17
RNA: 03-2010-032610115700-14

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INTRODUCTION

- The deterioration of air quality either by anthropogenic or natural causes, can generate negative effects on human health and ecosystems (Torres et al., apud Valls, 2017).
- The use of fossil fuels, operation of coal-fired power plants, the increased dependency of motor vehicles for private transport, inefficient use of energy in buildings and the use of biomass burning to cook food and for space heating, produce the called Volatile Organic Compounds (VOC's) (World Health Organization-WHO, 2014).
- Within this group of compounds exists a sub-group named as BTEX, that includes to benzene and its alkyl-derivatives: benzene, toluene, ethylbenzene and xylenes. These compounds can cause both carcinogenic and non-carcinogenic (cardiovascular and respiratory diseases) and they are tropospheric ozone precursors (Marć et al., 2014).
- Many cities around the world commonly monitor the levels of BTEX in ambient air, but in Mexico, even when the risks and consequences of the inhalation of these compounds are well known, neither there is an air quality standard that regulates the maximum levels in ambient air nor a continuous monitoring is carried out in the air quality stations belonging to the Mexican air quality network, excepting in Mexico City.

Objetive

- The general objective of this study was to evaluate the atmospheric levels of aromatic hidrocarbons (BTEX: benzene, toluene, ethylbenzene and p-xylene), their origin and their relationship with criteria pollutants, as well as their impact on health in an urban site located within the Metropolitan Area of Monterrey during the Norths season 2020.

Justification

There are not enough studies about the levels and distribution of BTEX in big cities of Mexico. Thus, the Metropolitan Area of Monterrey in Nuevo Leon State, is one of the biggest population centers in the country. This Metropoli is constituted by 12 municipalities (Guadalupe, Apodaca, San Nicolás de los Garza, General Escobedo, Santa Catarina, Benito Juárez, García, San Pedro Garza García, Cadereyta Jiménez, Santiago, Salinas Victoria, El Carmen) and Monterrey city, according to the National Institute of Statistics and Geography (INEGI) is the second most populous metropolitan area in Mexico with 5,341,171 inhabitants and the second with the largest territorial extension (7657 km^2), being the 84^{th} largest metropolitan area in the world.

ANTECEDENTES

According to the INEM (Criteria Pollutant Emissions Inventory) for the Metropolitan Area of Monterrey 2016, VOC emissions for these municipalities are largely due to the use and consumption of products containing volatile organic compounds.

These emissions are mainly due to work in mining, the construction industry, based on electricity consumption, transportation, fossil fuel industries, industrial processes, waste management, agriculture, treatment of hazardous waste, and other anthropogenic factors. Table 1 shows the results for the emissions inventory 2016 for VOC's in Nuevo Leon State.

In the 2016 emissions inventory, the municipality of Monterrey, where Obispado is located, stands out with the main contribution to VOC (Volatile Organic Compound) emissions, being the municipality with higher emissions, this is due to the contribution of area sources such as commercial and light industrial sources, poor waste management and the use of solvents. But above all, the main contaminant for the distribution of VOCs in the metropolitan area is the use of petroleum derivatives for transportation.

Table 1. Results for the emissions inventory 2016 for VOC's in Nuevo Leon State.

Source Distribution	Municipalities	COV's (tons/year)
Area Sources	Sabinas Hidalgo, Salinas Victoria, General Zuazua, General Zuazua, Apodaca, García, Santa Catarina Monterrey, San Nicolás de los Garza, Pesquería, Cadereyta Jiménez, Santiago, Montemorelos, Allende, Linares, Galeana, Doctor Arroyo.	> 6,750.00 - 12,197.72
Fixed sources	Salinas Victoria, Ciénega de Flores, El Carmen, Abasolo, Apodaca, García, General Escobedo Monterrey, Cadereyta Jiménez, Santa Catarina, Juárez, Montemorelos, Linares, Agualeguas.	> 1,155.30 - 2,060.77
Mobile Sources	Sabinas Hidalgo, Apodaca, García, San Nicolás de los Garza, Monterrey, Cadereyta Jiménez, Santa Catarina, Montemorelos, Allende, Linares, Santiago	> 3,098.94 - 7,047.72
Natural Sources	Vallecillo, Sabinas Hidalgo, Villaldama, Bustamante, General Treviño, Cerralvo, Melchor Ocampo, los Herreras, General Bravo, Doctor Coss, Los Ramones, Cadereyta Jiménez, Santa Catarina, Juárez, Montemorelos, Linares, Galeana, Aramberri, Doctor Arroyo, Mier y Noriega, Hualahuises, General Terán, El Carmen, Juárez.	> 2,088.05 - 4,881.98

METHODOLOGY

Study Area description and Sampling Method

Samples were collected in Obispado site, within an air quality monitoring station of the government of Nuevo Leon State. It is located within the coordinates 25°40’24”N 100°20’32”W / 25.67347222, -100.34217778. It is located at the tip of the Loma de la Chepe Vera, so called because the lands of José Vera were in its surroundings. This hill is currently known as the Cerro del Obispado and the palace is also known as the Palacio del Obispado.

Figure 1. Location of the Metropolitan Area of Monterrey

Figure 2. Location of Obispado sampling site

Ambient air samples were collected using Anasorb CSC 226-01 brand glass tubes, 70mm long by 4.0mm internal diameter and 6mm external diameter, divided into two sections: 50 mg and 100 mg of activated carbon in each (Figure 3a), connected to a GAST-type vacuum pump operating at a controlled flow of 200 ml/min according to the Method MTA/MA-030/A92 (INSHT, 1992) (Figure 3.b). Three periods of sampling were considered: morning (07:00 - 8:30 h), noon (14:00 - 15:30 h) and afternoon (17:30 - 19:00 h), with 1.5 hours of duration, from October 20 to November 18, 2020.

Figure 3 a) Anasorb CSC 226-01 brand activated carbon glasses

Figure 3 b) GAST type vacuum pump

Analytical Method

The desorption of each sample was carried out with 1 ml of carbon disulfide (CS_2) in amber vials of 2 ml. then the vial was shaken for a period of approximately 5 minutes to ensure that the desorption was completed, and it was refrigerated for 24 hours until its analysis. 1 µL of the vial's content was analyzed by gases chromatograpy using a TRACE GC Ultra Gas Chromatographs Thermoscientific brand equipment in splitless mode with flame ionization detector (Figure 4). According to MTA/MA-030/A92 method (INSHT, 1992).

Figure 4. TRACE GC Ultra gas chromatograph.

BTEX Ratios

T/B ratio: an indicator of emissions from vehicular traffic. Benzene and toluene are constituents of gasoline and are emitted into the atmosphere from motor vehicle exhaust. The toluene content in gasoline is 3 to 4 times higher than the benzene content (Pekey and Yilma, 2011).

Values of this ratio < 2-3: Vehicle emissions (reported in this range for many urban areas around the world) (Elbir et al. 2007; Mugica et al. 2003);

Values >3 : BTEX levels are associated with sources other than vehicular sources (industrial facilities and area sources: evaporative emissions, automotive paint shops, food cooking processes, screen printing shops; dry cleaners, among others).

X/E ratio: an indicator of the photochemical age of air masses at a given site (Keymeulen et al. 2001; Lee et al. 2002). **High values of X/E:** are associated to old air masses. **Low values of X/E:** indicate that the air masses are fresh (recent emissions). Kuntasal et al. (2005) used a value of X/E =3.8 and values from 3.8 to 4.4 have been associated to fresh gasoline.

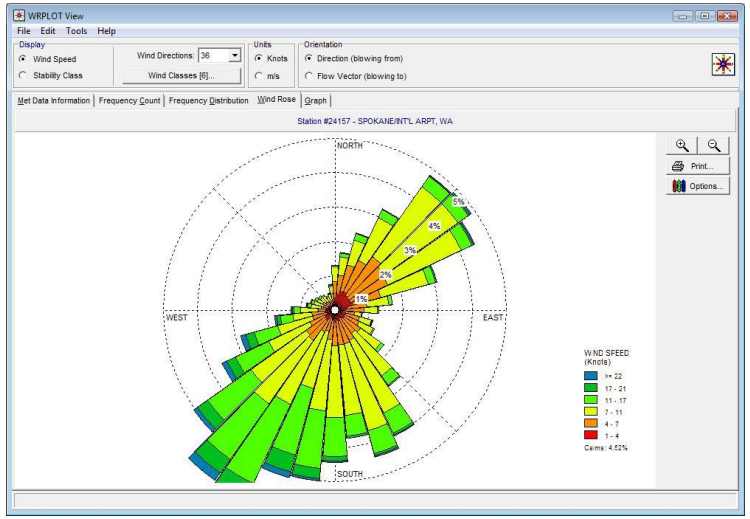
Descriptive Analysis: to identify the diurnal variation and box plots were made .

Bi-variate analysis: in order to know the Pearson correlation coefficient and the relation between each pair of BTEX and its grade of significance.

Principal component analysis (multivariate analysis: PCA): in order to determine the relation among the studied variables using XLSTAT 2016 (https://www.xlstat.com/es/). Cosines of the variables, factor loadings were used to identify groups of related compounds. Origin of compounds was inferred from tracer compounds present in each group and a biplot of the two principal components was constructed.

Meteorological Analysis

Wind speed and wind direction were examined simultaneously using a wind rose analysis. These graphs show the distribution of the direction and speed of the wind in a specific place. The wind rose model for each sampling site was made with the WRPLOT (Wind Rose Plots for Meteorological Data) software, which simulates the direction and speed of the prevailing winds in the sampling period (Software developed by Lakes Environmental, available in: https://www.weblakes.com/products/wrplot/index.html).



Health Risk Assessment

We determined the daily exposure (E) (USEPA, 2008), the lifetime risk of cancer (ILTCR) and the potential non-cancer risk (HQ), that is, the risk of developing diseases other than cancer (respiratory and cardiovascular diseases) (Zhang et al. 2015). The daily exposure (mg/kg per day) of an individual by inhalation can be calculated as :

$$E=(C\times IRa\times Da)/BW$$

Where C (mg/m^3) is the average concentration of benzene, IRa is the inhalation rate of an adult (0.83 m^3/h), Da is the duration of exposure of an adult (24 h/day), and Bw is the body weight of an average adult (65 kg)

The lifetime cancer risk (LTCR) is then calculated as:

$$LTCR=E\times SF$$

Where SF is the risk slope factor for toxic inhalation when the carcinogenic effect of exposure is considered linear. SF for benzene is of 0.029 mg/kg per day.

The non-cancer risk of BTEX will be measured as a hazard quotient (HQ):

$$HQ=C/RfC$$

Where C is the average concentration received daily and RfC is the inhalation reference concentration proposed by the United States Environmental Protection Agency (USEPA, 2005) for each pollutant (Table 3).

Table 3. Reference concentration (RfC) used for BTEX

Reference Concentration			
Benzene	**Toluene**	**Ethylbenzene**	**p-xylene**
(mg/m^3) ATSDR, 2005	(mg/m^3) USEPA, 2005	(mg/m^3) USEPA, 2005	(mg/m^3) USEPA, 2003
0.03	5	1	0.1

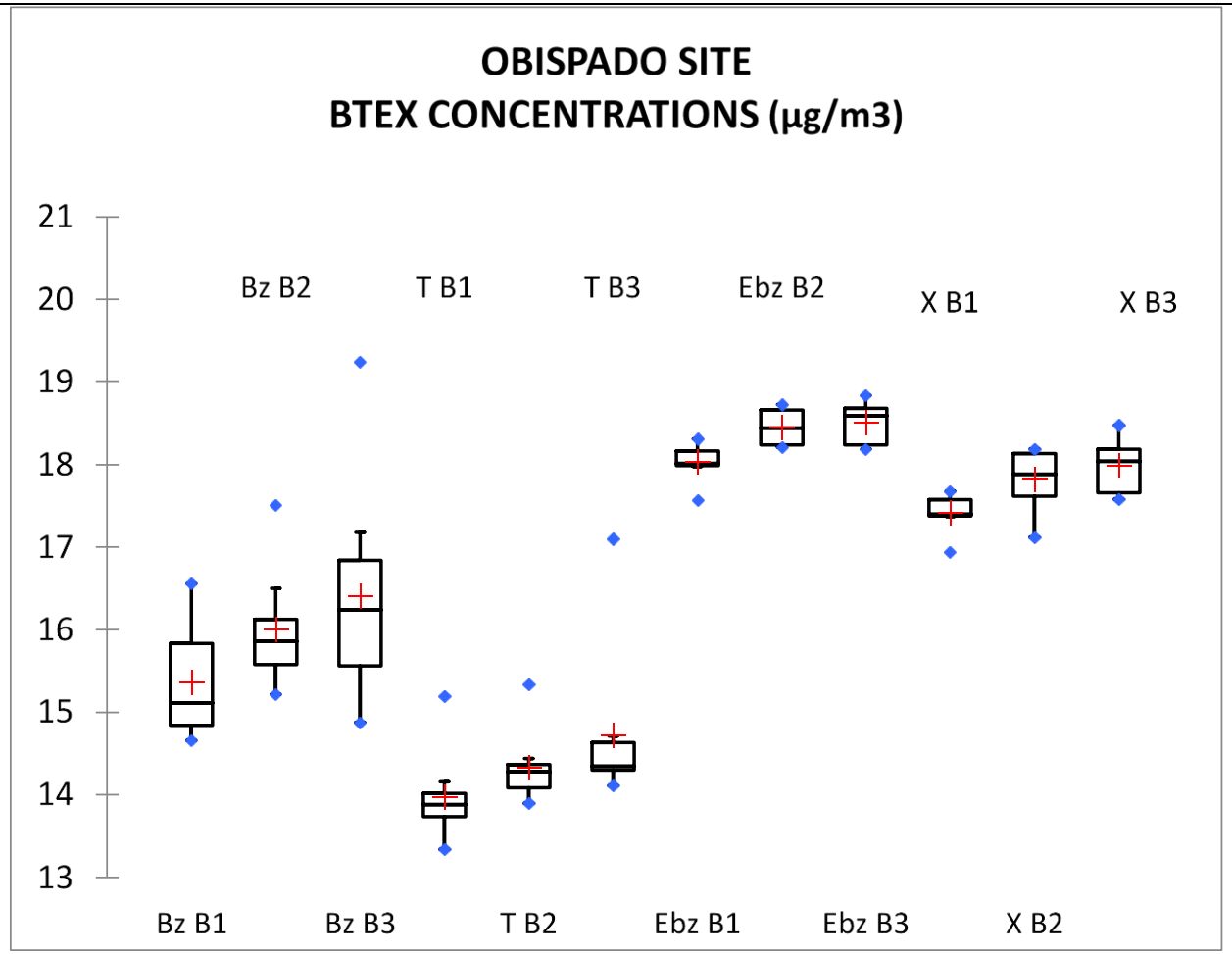
The accepted values proposed by EPA and WHO for and for HQ for inhalation of BTEX are 1x 10^{-6} and 1.0, respectively. If LTCR and HQ values are higher than these reference values, indicate a probable risk in the population health

RESULTS

BTEX Concentrations

DESCRIPTIVE STATISTIC FOR BTEX CONCENTRATIONS IN OBISPADO SITE ($\mu g/m^3$)												
Parameter	**Bz B1**	**Bz B2**	**Bz B3**	**T B1**	**T B2**	**T B3**	**Ebz B1**	**Ebz B2**	**Ebz B3**	**X B1**	**X B2**	**X B3**
Minimum	14.660	15.220	14.880	13.340	13.900	14.110	17.570	18.210	18.190	16.940	17.120	17.580
Maximum	16.560	17.510	19.240	15.190	15.340	17.100	18.310	18.730	18.840	17.680	18.190	18.480
1° Quartil	14.840	15.578	15.563	13.735	14.085	14.300	17.988	18.238	18.240	17.378	17.620	17.660
Median	15.115	15.860	16.240	13.880	14.280	14.345	18.015	18.440	18.595	17.400	17.885	18.040
3° Quartil	15.833	16.125	16.843	14.018	14.365	14.635	18.168	18.660	18.683	17.578	18.133	18.185
Mean	15.363	16.010	16.410	13.980	14.338	14.723	18.034	18.456	18.509	17.423	17.824	17.995
Typical Deviation (n-1)	0.672	0.714	1.397	0.545	0.443	0.980	0.225	0.234	0.249	0.232	0.380	0.346

BTEX showed the same diurnal pattern: higher mean concentration levels during the afternoon (B3 sampling period). This behavior can be explained due to the fact that during the afternoon occurs a peak on vehicular traffic originated by a higher population mobility that commuting from their workplaces to their homes, producing higher emissions of air pollutants from automobile exhaust. Ethylbenzen and p-xylene were the dominant BTEX in Obispado site.



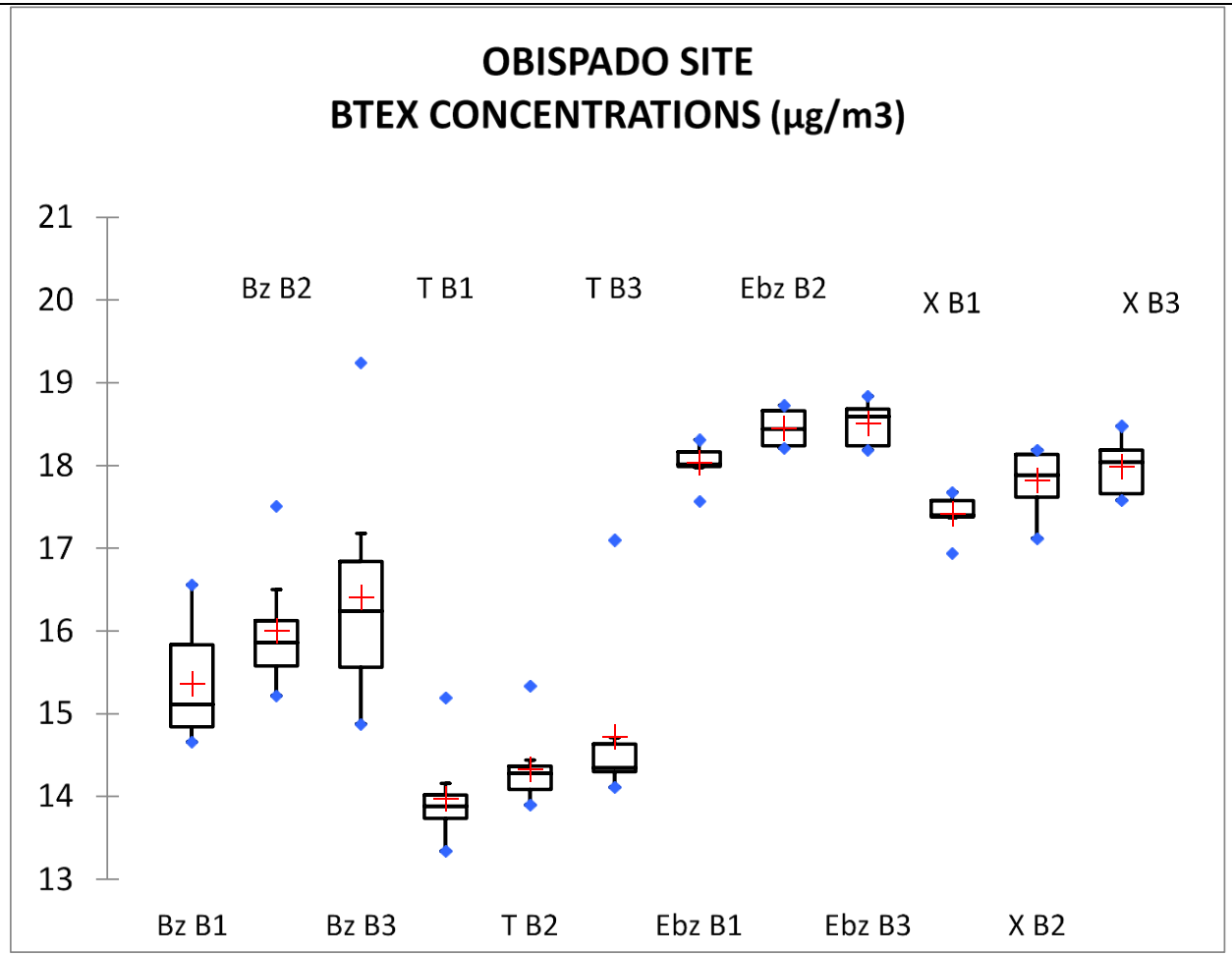
+ are the mean values of BTEX concentrations, ♦ are the maximum and minimum values of BTEX concentrations and the edges of the box are the 1° and 3° quartiles, the box does not have a statistic mean only is represented for better visualization. Bz: benzene; T: toluene; Ebz: ethylbenzene; X: p-xylene. B1: morning sampling period (08:00– 09:30 h); B2: midday sampling period (13:00 – 14:30 h); and B3: afternoon sampling period (17:30 – 19:00 h).

Figure 5. Box plot for BTEX concentrations measured in Obispado site during the sampling period.

A Friedman test at a significance level of $\alpha = 0.05$ was applied to the data set in order to investigate if there were significant differences among the different sampling periods along the day.

The results showed that there were significant differences in BTEX concentrations among the different sampling periods, which means that the measured BTEX had a clear diurnal variation in both sampling periods.

Comparing both sampling sites, we found that there were not significant differences between sampling sites, indicating that B TEX are homogeneously distributed in the study area and that the sources are the same in both locations.



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The results showed that there were significant differences in BTEX concentrations among the different sampling periods, which means that the measured BTEX had a clear diurnal variation.

We found that BTEX are homogeneously distributed in the study area and that the sources are the same in entire zone.

Meteorological conditions and influence of winds

Table 5 shows the average values for meteorological parameters, considering wind speed (WS), wind direction (WD), temperature (T), relative humidity (RH), solar radiation (SR) and barometric pressure (P). It can be observed that wind blowed predominantly from ESE with an average wind speed of 11.8 m/s, showing higher values of wind speed during the midday and afternoon sampling periods.

Figure 7 Concentration-wind roses for measured BTEX in Obispado during: a) morning sampling period (B1), b) midday sampling period (B2) and c) afternoon sampling period (B3).

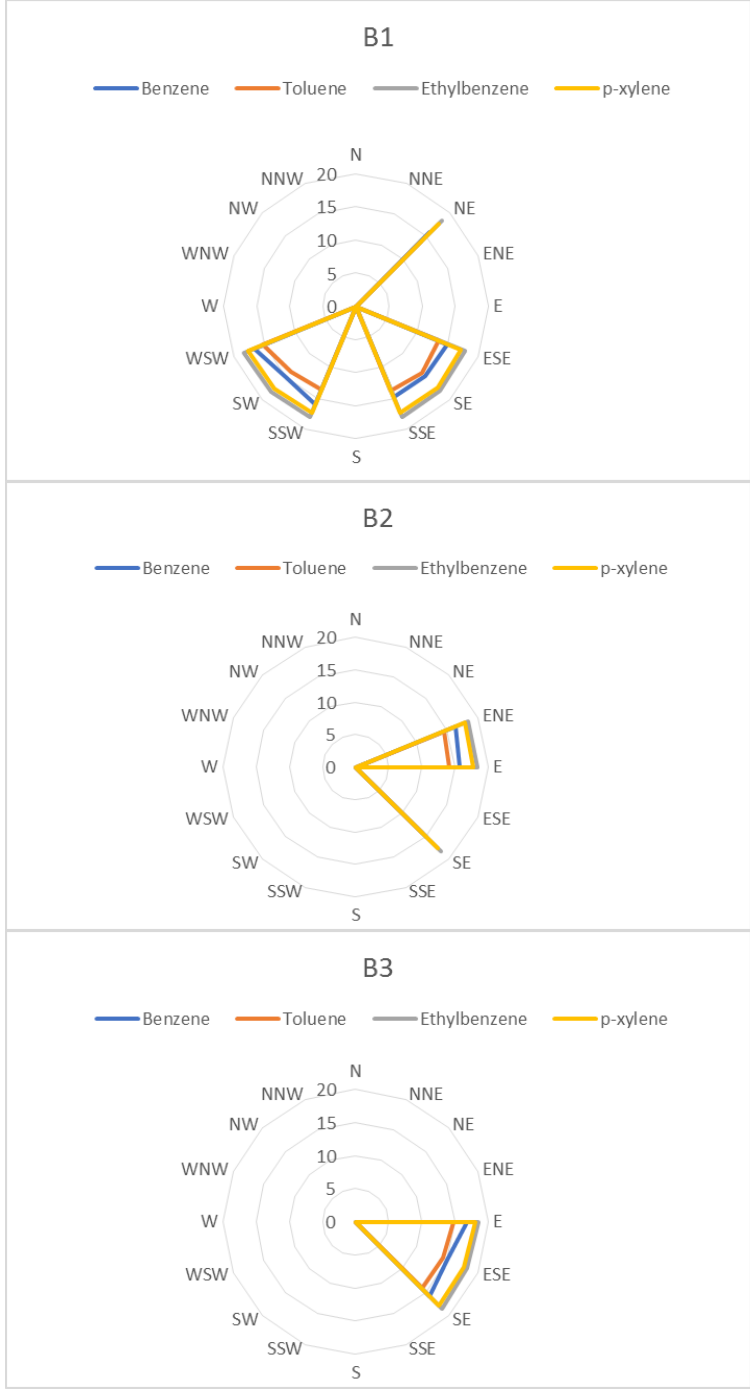

Table 5 Meteorological parameters for both sampling sites. B1: morning sampling period (08:00– 09:30 h); B2: midday sampling period (13:00 – 14:30 h); and B3: afternoon sampling period (17:30 – 19:00 h).

Obispado site							
Meteorological parameters		WS	WD	T	RH	SR	P
		m/s		°C	%	W/m^2	mm Hg
Sampling periods	B1	6.9	SSE	18.88	62.75	167.63	715.74
	B2	14.6	E	24.18	46.13	169.13	712.73
	B3	13.9	ESE	21.65	55.5	148.22	713.56
	Mean Value	11.8	ESE	21.57	54.79	161.66	714.01

BTEX concentrations in Obispado (Figure 7) site were higher when winds blowed from WSW, SSW, SW, SSE, ESE and NE during the B1 period. During midday (B2 period), BTEX concentrations were higher when winds blowed from ENE, E and SE. During the afternoon (B3 period) BTEX concentrations were higher with winds blowing from E, ESE and SE. The municipalities of Juárez and Apodaca are located in these directions, as well as numerous avenues with high vehicular traffic with emissions that could have contributed to the BTEX levels measured at the study site.

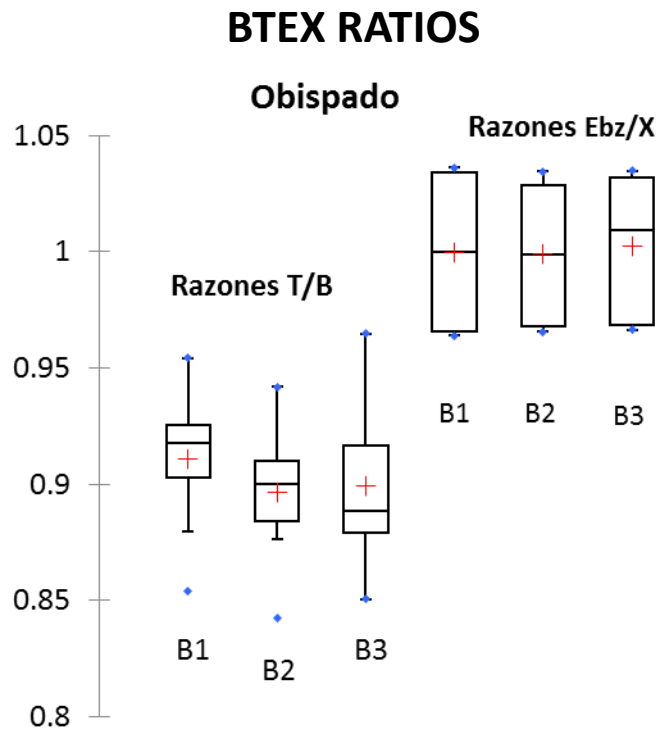

Figure 6 Box plot for BTEX ratios during the sampling period.

The T/B ratio values found in this study (<2) are within the typical range reported for urban sites with a strong influence of vehicle emissions. T/B ratios found in Obispado were higher during the morning sampling period (B1), when a peak of vehicular traffic occurs due to the mobility of population to their work centres and school.

X/E ratios were low: most of the air masses corresponded to "fresh or local emissions". These values are within the typical range reported for fresh emissions with little or almost no photochemical processing (emissions from primary and local sources). X/E ratios remained constant throughout the day: the influence of vehicular traffic on this site is also a constant. There were no significant differences in BTEX ratios indicating that the sources of these compounds (mainly vehicle-type emissions) are homogeneously distributed in the study area.

HEALTH RISK ASSESSMENT

Table 6 shows the average of the non-cancer risk coefficients that represent the BTEX measured in the study site for both, adult and children population. The non-cancer risk coefficient (HQ: Hazard Quotient) was higher for benzene, having the following behavior: benzene> p-xylene> ethylbenzene> toluene. HQ values were below the maximum permissible limit established by the EPA and the WHO (HQ < 1.0): there is no risk of developing diseases different than cancer (respiratory and cardiovascular diseases) by inhalation of BTEX at the study site.

Table 6 Non-cancer risk coefficients (HQ) in Obispado site during the sampling period for a) Adult population, and b) Children population.

a) Non cancer risk coefficients (HQ) for Adult population	
Air Pollutant	**Obispado Site**
Benzene	0.536
Toluene	0.003
Ethylbenzene	0.018
p-Xylene	0.178
THQ= ΣHQ =	**0.735**
b) Non cancer risk coefficients (HQ) for Children population	
Non-cancer Risk	
Air Pollutant	**Obispado site**
Benzene	0.5309
Toluene	0.0029
Ethylbenzene	0.0018
p-Xylene	0.1777
THQ= ΣHQ =	**0.7126**

Health Risk Assessment

Table 7 shows the life-time cancer risk coefficients in children and adult population for both sampling sites due to benzene inhalation. According to WHO and EPA, the established permissible limit is (1 $x10^{-6}$). The values obtained exceeded the maximum permissible levels almost by two orders of magnitude, therefore is a possible risk of developing cancer in the life-time due to the inhalation of benzene at the concentrations found at the study sampling site.

Table 7 Life-time cancer risk coefficients (LTCR) in Obispado site during the sampling period for a) Adult population, and b) Children population.

a) Adult population	
Life-time Cancer Risk (LTCR)	
Air Pollutant	OBISPADO
Benzene	1.445×10^{-4}
b) Children population	
Life-time Cancer Risk (LTCR)	
Air Pollutant	OBISPADO
Benzene	2.575×10^{-4}

Bi-variate and multi-variate analysis

During the morning sampling (B1) (Table 8): Benzene presented positive correlation coefficients close to linearity with ethylbenzene (0.898) and with p-xylene (0.892). Ethylbenzene presented a significant linear positive correlation with P-xylene (0.999). These compounds could have originated from common sources. Ethylbenzene and p-xylene presented a linear and significant negative correlation with PM2.5: these hydrocarbons could have participated in photochemical reactions of secondary organic aerosol formation (SOA). Positive correlations between CO with PM2.5 (0.885), with O3 (0.717), and with SO2 (0.798), indicating that these pollutants could have originated from emissions of vehicular sources, since CO is a tracer of combustion emissions in motor vehicles.

Table 8 Pearson correlation coefficients for the morning sampling period (B1) in Obispado.

Variables	CO	NO_2	O_3	PM10	PM2.5	SO_2	Benzene	Toluene	Ethyl-benzene	p-xylene
CO	**1**									
NO_2	0.646	**1**								
O_3	0.717	0.903	**1**							
PM10	0.079	0.074	-0.317	**1**						
PM2.5	0.885	0.218	0.380	0.023	**1**					
SO_2	0.798	0.695	0.489	0.623	0.579	**1**				
Benzene	-0.910	-0.340	-0.365	-0.317	-0.948	-0.792	**1**			
Toluene	-0.142	0.605	0.275	0.395	-0.563	0.311	0.330	**1**		
Ethylbenzene	-0.723	0.058	-0.098	-0.100	**-0.957**	-0.451	0.898	0.707	**1**	**0.999**
p-xylene	-0.732	0.046	-0.127	-0.052	**-0.964**	-0.433	0.892	0.721	**0.999**	1

Bi-variate and multi-variate analysis

During the midday sampling period (B2) (Table 9) significant linear correlations could be observed between CO and PM2.5 (0.957), NO_2 and PM10 (0.962) and NO_2- SO_2 (0.973), indicating that these air pollutants could be originated from emissions of vehicular sources since CO is a tracer of emissions related to vehicular traffic and from high temperature combustion sources. PM10 and PM2.5 showed a significant linear positive correlation (0.944), indicating that particulate matter had their origin in common sources during this study. Negative linear correlations of CO with ethylbenzene (-0.963) and p-xylene (-0.998) can be explained from the following atmospheric reactions that carry out during the midday, when solar radiation is intense and that cause the production of highly reactive OH radicals which is the main trajectory of depletion of BTEX in air.

Negative correlations between ethylbenzene and p-xylene with NO_2 during the midday evidence photochemical process of depletion of BTEX in ambient air in high solar radiation conditions. SO_2 showed linear positive correlations with PM10 and PM2.5 (0.925 and 0.918, respectively), indicating that these particles could be originated from combustion processes that use high sulfur fuels as diesel. Toluene and Ozone showed a significant positive linear correlation (0.837), indicating that these compounds could be originated from photochemical reactions.

Table 9 Pearson correlation coefficients for the midday sampling period (B2) in Obispado.

Variables	CO	NO_2	O_3	PM10	PM2.5	SO_2	Benzene	Toluene	Ethyl-benzene	p-xylene
CO	**1**									
NO_2	0.859	**1**								
O_3	0.013	-0.081	**1**							
PM10	0.924	**0.962**	-0.239	**1**						
PM2.5	**0.957**	0.938	-0.207	**0.994**	**1**					
SO_2	0.905	**0.97**3	0.128	0.925	0.918	**1**				
Benzene	-0.151	-0.635	0.108	-0.451	-0.355	-0.525	**1**			
Toluene	-0.405	-0.246	0.837	-0.483	-0.504	-0.123	-0.196	**1**		
Ethylbenzene	**-0.963**	-0.722	-0.220	-0.788	-0.844	-0.826	-0.046	0.276	**1**	
p-xylene	**-0.998**	-0.828	-0.062	-0.895	-0.935	-0.889	0.097	0.380	**0.979**	**1**

Significant positive linear correlations can be observed between NO_2 and PM2.5 (0.998) and between benzene and toluene (0.976): these compounds could have originated from common sources. Positive linear correlations can be observed that, although not significant, suggest that these compounds could have originated from common sources: CO-PM10 (0.860), CO-SO_2 (0.939), NO_2-PM10 (0.806) and SO_2-PM10 (0.840), indicating that the levels of these pollutants could be influenced by vehicle emissions derived from intense vehicular traffic on avenues surrounding the sampling site.

Benzene-xylene (0.936), ethylbenzene-xylene (0.807) and toluene-xylene (0.837) presented correlations close to linearity, although not significant: these hydrocarbons could have originated at least partially from common sources. The negative correlations between CO with benzene, ethylbenzene and xylene indicate that in presence of high levels of CO, photochemical reactions of OH radical production occur, causing the depletion of BTEX in the study site.

Table 10 Pearson correlation coefficients for the afternoon sampling period (B3) in Obispado.

Variables	CO	NO_2	O_3	PM10	PM2.5	SO_2	Benzene	Toluene	Ethyl-benzene	p-xylene
CO	**1**									
NO_2	0.548	**1**								
O_3	0.713	0.919	**1**							
PM10	0.860	0.806	**0.962**	**1**						
PM2.5	0.596	**0.998**	0.924	0.826	**1**					
SO_2	0.939	0.380	0.660	0.840	0.423	**1**				
Benzene	-0.031	-0.066	-0.362	-0.366	-0.040	-0.324	**1**			
Toluene	0.169	0.118	-0.160	-0.154	0.150	-0.146	**0.976**	**1**		
Ethylbenzene	-0.812	-0.682	-0.913	**-0.973**	-0.698	-0.872	0.551	0.357	**1**	
p-xylene	-0.350	-0.356	-0.652	-0.669	-0.342	-0.576	0.936	0.837	0.807	**1**

MULTIVARIATE ANALYSIS: For the morning sampling period (B1), two principal components were required to explain 84.30% of the total variability of the data. Figure 8 shows the loadings of the factors representing the groups of variables that were related to each other. Group F1 : CO, PM2.5, SO_2, Benzene, Ethylbenzene and p-xylene → the compounds in this group are related to emissions from motor vehicle exhaust. F2 group: Ozone, NO_2 and Toluene: →These compounds had a high influence on photochemical activity. F3 group: PM10 → this pollutant could have a different origin, probably re-suspension of dust from the quarries and companies dedicated to the manufacture of ceramic and glass products.

In Figure 8 also it can be observed that benzene, ethylbenzene and p-xylene are in the same quadrant: these compounds could have originated from common sources. It can observed that NO_2 and Ozone are very close to each other: these compounds were influenced by photochemical activity. SO_2, CO, and PM2.5 showed proximity to each other as well as vectors with the same intensity: these compounds were influenced by vehicular combustion sources.

In Figure 9 it can be observed that two principal components were required to explain 86% of the variability in the data. Group F1: CO, NO_2, PM10, PM2.5, SO_2, ethylbenzene and p-xylene → these compounds were influenced by vehicle emissions. F2 group: ozone and toluene → these compounds were influenced by photochemical activity. F3 group: benzene → this hydrocarbon could have had a different source than the rest of the BTEX.

	F1	F2	F3
CO	0.193	**0.626**	0.181
NO_2	**0.884**	0.001	0.115
O_3	0.271	**0.706**	0.023
PM10	**0.738**	0.112	0.150
PM2.5	**0.777**	0.208	0.015
SO_2	0.010	**0.989**	0.000
Benzene	**0.536**	0.459	0.005
Toluene	**0.993**	0.002	0.005
Ethylbenzene	**0.911**	0.015	0.074
p-xylene	**0.843**	0.005	0.152

The values in bold correspond for each variable to the factor for which the squared cosine is the highest.

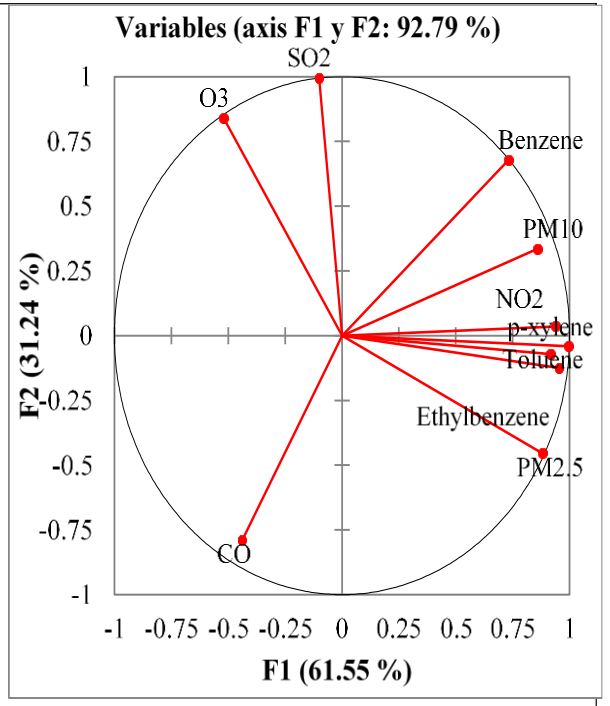

Figure 8 Principal Component Analysis for the measured variables during the morning sampling period (B1) in Obispado.

During the afternoon sampling period (Figure 10), two principal components (F1 and F2) were required to explain 89.57% of the total variability of the data. F1 group: CO, NO_2, O_3, PM10, PM2.5, ethylbenzene and p-xylene: → these compounds were influenced by vehicle emissions and photochemical activity. F2 group: benzene and toluene → likely originating from area sources such as solvent use, paints and coatings, biomass burning, and petrochemical industry.

	F1	F2	F3
CO	0.096	**0.887**	0.017
NO_2	**0.574**	0.221	0.205
O_3	**0.889**	0.003	0.108
PM10	**0.705**	0.274	0.021
PM2.5	**0.528**	0.405	0.067
SO_2	**0.897**	0.020	0.083
Benzene	0.218	**0.751**	0.031
Toluene	0.373	0.220	**0.407**
Ethylbenzene	**0.821**	0.000	0.179
p-xylene	**0.755**	0.011	0.234

The values in bold correspond for each variable to the factor for which the squared cosine is the highest.

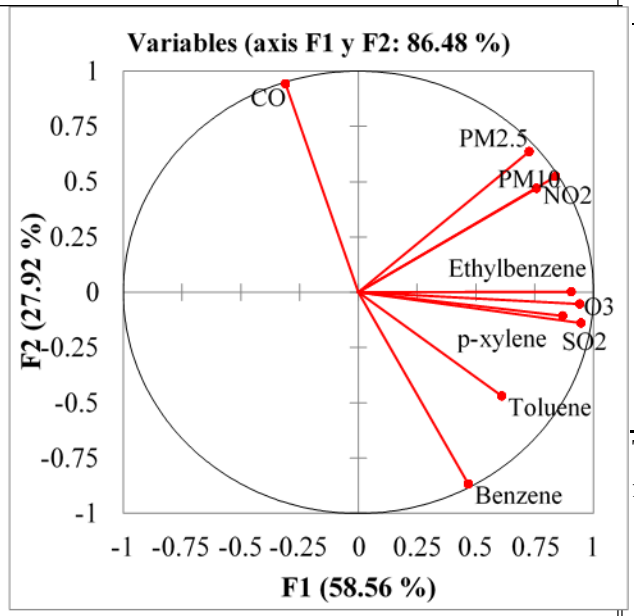

Figure 9 Principal Component Analysis for the measured variables during the midday sampling period (B2) in Obispado.

	F1	F2	F3
CO	**0.826**	0.166	0.008
NO_2	0.130	0.216	**0.654**
O_3	**0.734**	0.010	0.256
PM10	0.167	**0.783**	0.049
PM2.5	0.323	**0.646**	0.031
SO_2	0.418	0.059	**0.522**
Benzene	**0.550**	0.358	0.092
Toluene	**0.944**	0.018	0.038
Ethylbenzene	**0.984**	0.002	0.014
p-xylene	**0.965**	0.022	0.013

The values in bold correspond for each variable to the factor for which the squared cosine is the highest.

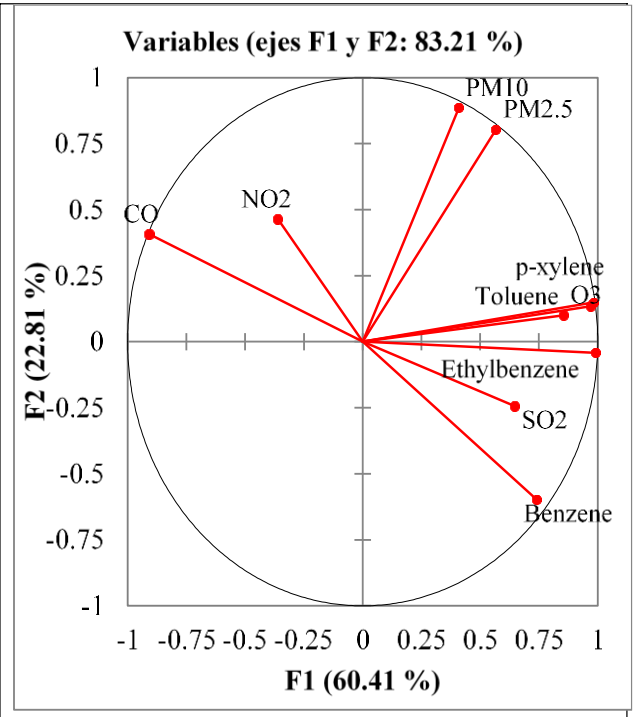

Figure 10 Principal Component Analysis for the measured variables during the afternoon sampling period (B3) in Obispado

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