



Concentrations, sources, and health risk associated with exposure to BTEX at ten sites located in an urban-industrial area in the Bajío Region, Mexico

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Abstract

The purpose of this study was to study the spatial and temporal variation of BTEX in the ambient air of Leon, Guanajuato, Mexico, to assess the inhalation health risk to the local population from exposure to these compounds. BTEX were monitored using passive samplers during two sampling seasons (rainy 2019 and cold dry 2020), and samples were analyzed by gas chromatography with flame ionization detection. BTEX ratios and meteorological analysis suggested that the concentrations were mainly influenced by vehicular and local sources located to the SE of the study area. The sum of average concentrations of BTEX in rainy and cold dry seasons were of $3.52 \pm 0.36 \mu\text{g m}^{-3}$ and $4.11 \pm 0.38 \mu\text{g m}^{-3}$, respectively. Mean concentrations were of 0.74, 1.59, 0.48, and $0.69 \mu\text{g m}^{-3}$, for benzene, toluene, ethylbenzene, and p-xylene, respectively. The highest levels of BTEX were found in sites with an urban land-use type of medium-intensity industrial zones with high population density. The lower BTEX concentrations found during the rainy season were probably due to higher solar radiation and temperatures that favored their photochemical degradation. Bi-variate and multivariate analysis showed that the BTEX species were strongly correlated with each other and with temperature and solar radiation, indicating that they originated from common sources. Benzene and toluene correlated strongly with CO and SO₂, indicating that they could originate from vehicular exhaust emissions and high-sulfur fuel combustion sources. The health risk assessment showed that the Leon city adult population is at possible risk of developing cancer in their lifetime due to exposure to the measured benzene levels, but indicated no risk of contracting respiratory and cardiovascular diseases due to inhalation of BTEX. The results suggest the need for BTEX emissions reduction policies in the study area, as well as the establishment of a Mexican standard that regulates the maximum permissible limit of these pollutants in ambient air in order to protect the health of the population.

Keywords BTEX · Passive samplers · Leon · Guanajuato · Mexico · Urban air · Air quality

Introduction

Volatile organic compounds (VOCs) are organic compounds with boiling points in the range of 50–100 to 240–260 °C at a pressure of 1013 hPa (Srivastava and Mazumdar 2011). VOCs include a vast array of aliphatic and aromatic hydrocarbons and their halogenated derivatives, alcohols, ketones, and aldehydes. The importance of this group of compounds is that they originate from multiple and diverse sources (both primary and secondary); they participate in photochemical reactions in the atmosphere that produce tropospheric ozone, contributing to the formation of photochemical smog, secondary organic aerosols (SOA) and reactive free radicals (Carter 1994); and they have direct adverse effects on ecology and human health. Within the VOCs family, there is a subgroup of compounds named BTEX that includes benzene and its alkyl derivatives

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(toluene, ethylbenzene, and xylenes). BTEX are of particular interest because they are the more dominant VOCs in urban and industrial areas (Shuai et al. 2018). Sources of BTEX include vehicle exhaust, painting, gasoline and diesel fuel evaporation, coke ovens, metallurgical operations, fuel stations (liquid fuel spills or leaks from distributor tanks), coal and biomass burning, and the petrochemical industry (Márc et al. 2015).

Exposure to aromatic VOCs is associated with respiratory effects such as asthma and reduced lung function (Kwon et al., 2006). The World Health Organization (1987) has reported that prolonged exposure to benzene is linked to adverse effects such as haematotoxicity and genotoxicity and that this compound has been classified as carcinogenic to humans by the Agency for Toxic Substances and Disease Registry (2007a, b). Toluene may affect the nervous system and cause headaches, dizziness or unconsciousness, and adverse renal, hepatic, and reproductive effects (ATSDR 2015). Short-term exposure to high levels of ethylbenzene can cause eye and throat irritation, vertigo, and dizziness, while long-term exposure to this air pollutant may cause cancer in humans (ATSDR 2010). Short- and long-term exposure to xylenes can cause irritation of the skin, difficulty in breathing, impaired lung function, and liver, kidney, and nervous system damage, among other adverse effects.

Despite the importance of these compounds for their effects on human health, knowledge of BTEX concentrations in Mexico is scarce, and continuous monitoring is only carried out in the metropolitan area of the Valley of Mexico (SMA-CDMX 2015) and for some isolated studies in the main cities of the country such as Monterrey (INECC 2015) and Guadalajara (INECC-CIATEJ 2014). However, in the center of the country, there are cities with great urban and industrial development where BTEX levels may be important and are not being measured. One of these areas is the Bajío, a geographic, historical, economic, and cultural region located in central Mexico. One of most important cities in this region is Leon, located in the state of Guanajuato, which is characterized by large industrial and commercial development. This has consequently caused a sustained urban growth in the last two decades as well as a degradation of air quality. The aim of this research was to study the temporal and spatial variation of BTEX concentrations at ten sites with different land-use types in Leon city during two seasonal periods (rainy and cold dry), using passive samplers. We then map the concentrations of isopleths using Krigging interpolation to study the relationships among BTEX levels, criteria of air pollutants, and meteorological parameters, in order to infer their probable sources of origin (using bi-variate and multivariate analysis). Finally, we assess the level of exposure to BTEX and the associated inhalation health risk of people living in this urban area, according to the methodology proposed by the US Environmental Protection Agency (1989, 2011).

Materials and methods

Sampling site description

The Leon metropolitan area (LMA) is an urban zone in Mexico's Bajío region. The region includes four urban cities in the state of Guanajuato: Leon, Silao de La Victoria, San Francisco del Rincon, and Purisima Del Rincon. Leon city has the highest demographic density in the LMA with 1,578,626 inhabitants (INEGI 2015), with growing commercial and industrial activity and mobility patterns and a large registered vehicle fleet of 373,069 automobiles, 7582 passenger trucks, and 67,681 motorcycles in circulation (INEGI 2017). Leon is located at 21°07' 44.7"N and 101°40'25.5"W. Its climate is temperate, with the subhumid subtropical variant with rains in summer. The annual average rainfall is 697.6 mm with an average annual temperature of 19.2 °C. Currently, the production of footwear and its related industries (tanning, cardboard, etc.) occupy a predominant place among the industrial activities carried out in Leon city. However, there are other industries such as the manufacturing of plastic containers, brickwork, chemistry, manufacturing of metallic cutlery, bodywork, automotive oils, steel wire products, and the automotive industry, among others, that have generated large economic and industrial growth. This study considered 10 sampling sites with different land-use types within Leon city: industrial, urban, and mixed. Three of these sites are co-located with air quality monitoring stations operated by the Direction of Air Quality Management of the Government of the State of Guanajuato (SEICA): CICEG-Fire Station, Faculty of Medicine Station, and T-21 Station. At these three sites, air criteria pollutants are continuously monitored (O₃, CO, NO₂, SO₂, PM₁₀, and PM_{2.5}). The location, coordinates, and land-use type of the 10 sampling sites are shown in Table 1. In the Supplementary Material Section, a figure showing the location of this study's 10 sampling sites has been included (Fig. S1). Land-use type classification was made according to the base cartography of the Municipal Planning Institute of the City of Leon, Guanajuato, for land-use allocations (IMPLAN 2017).

Sampling method

The samples were collected with Sigma Aldrich® brand passive devices, model Radiello® (cartridge adsorbent designed by Fondazione Salvatore Maugeri-IRCCS, Padova, Italy)(EN 14662–5:2005), 60 mm long by 5.8 mm diameter. Other studies have also used Radiello® passive samplers for monitoring BTEX in ambient air (Cruz et al. 2020; Márc et al. 2014, 2016; Buczynska et al. 2009; Villanueva et al. 2018; Parra et al. 2009). The cartridges are constructed of stainless steel (100 mesh, 5.8-mm diameter) and packed with activated carbon (30–50 mesh). These devices were placed inside a polyethylene container (60-mm high by 16-mm diameter diffusive body), with a 25-µm pore size diffusion membrane that allows

Table 1 Location, land-use type and characteristics of the 10 sampling sites included in this study

ID	Site	Coordinates	Sampling height (m)	Land-use type	Classification*
A	Municipal Institute for Women	21°6'4.70"N 101°36'44.19"W	3	High-density habitable zone	Type 1
B	CICEG	21°6'6.26" N 101°38'4.66"W	3.5	Medium-intensity industrial zone	Type 4
C	Technological Institute of Leon	21°6'29.57"N 101°37'44.44"W	3	Medium-intensity industrial zone	Type 4
D	IMSS-T21	21°6'31.28"N 101°41'16.48"W	4	High-density habitable zone	Type 1
E	Lomas blancas Neighborhood	21°6'42.32"N 101°42'58.33"W	2.5	High-density habitable zone	Type 1
F	CECYT	21°8'7.15"N 101°44'8.69"W	4	High-density habitable zone	Type 1
G	University of Guanajuato	21°9'13.14"N 101°42'23.34"W	3	Habitable zone, low-density residential and conditioned mixed uses	Type 2
H	School of Medicine	21°8'2.11"N 101°40'48.92"W	3.5	Habitable medium-density zone, mixed uses (commercial, service and industrial uses)	Type 3
I	Zoo	21°10'54.91"N 101°39'1.42"W	2.5	Urban consolidation zone	Type 5
J	Colinas de Jade Neighborhood	21°9'1.28"N 101°39'24.76"W	2.5	Habitable zone, low-density residential and conditioned mixed uses	Type 2

* Land-use type classification according to the base cartography of the Municipal Planning Institute of the City of Leon, Guanajuato (IMPLAN) for Land use allocations (IMPLAN 2017) and the Regulation of Zoning and land use of the Municipality of León Guanajuato (2000)

Type 1 (housing high density): it includes the various groups of single-family housing and multi-family subject to appropriate density standards for each type; population density: 900 inhabitants/ha and the properties in this area must meet a minimum size of 105 m²

Type 2 (housing low density and mixed use): this type of land use refers to a combination of different land uses within the same community, that is, where residential areas coexist with commercial areas and offices, even with hotels or cultural projects such as museums, galleries and small rooms or auditoriums; population density: 120 inhabitants/ha and the properties in this area must meet a minimum size of 300 m²

Type 3 (housing medium density and mixed uses of commerce, services and industry): this type of land use includes commercial use (private spaces for commercial use by a person or a private company) as well as those areas of the municipal district in which industrial polygons, factories, business parks, and in general, land for industrial use or secondary sector are housed; population density: 450 inhabitants/ha and the properties in this area must meet a minimum size of 140 m²

Type 4 (industrial medium intensity): this type of land use includes all those production activities that generate controllable medium impacts, which can be mitigated through environmental regulations. Such establishments must have a specific and concentrated location and its process requires buildings closed, up to 100 active people, maximum size of 2000 m² and loading and unloading services

Type 5 (urban consolidation zone): this type of land use consists of the part of the territory in which the municipality considers that it is possible that it will be inhabited in the future. Within the framework of the planning function, the municipality must anticipate the way in which population growth will take place and the housing needs that this implies (road improvement strategies, transportation, home public services, open areas and parks), in such a way that the expansion of the municipality in its urban area is orderly

controlled diffusion of polluting gases to the adsorbent tube at a diffusion rate of 80 mL min⁻¹. Exposure time was 2 weeks, with a passive sampler installed at each sampling site. Two different climatic seasons were considered: rains 2019 (June 10–June 24, 2019) and dry-cold 2020 (January 16–January 30, 2020).

The time-weighted average concentrations of benzene, toluene, ethylbenzene, and p-xylene were calculated using the following equation:

$$C = \frac{m}{Q_{298} \times \left(\frac{T}{298}\right)^{1.5} \times t} \times 10^6 \quad (1)$$

where m is the mass of the retained analyte on the sorbent bed (μg); t is the exposure time (minutes); C is the time-weighted average concentration of each BTEX compound in ambient air ($\mu\text{g m}^{-3}$); Q_{298} is the sampling rate of measured analytes at

298 K and a pressure of 1013 hPa (mL min^{-1}); and T is the temperature (K).

Q_{298} parameters (mL min^{-1}) and the associated uncertainty of determination (%) of each analyte collection rate from the gaseous medium by the Radiello® passive samplers for each BTEX compound by the manufacturer are the following: 26.8 mL min⁻¹ (7.5%) for benzene, 30 mL min⁻¹ (8.3%) for toluene, 25.7 mL min⁻¹ (9.1%) for ethylbenzene, and 26.6 mL min⁻¹ (11.3%) for p-xylene. An adjustment of these values was made to account for the mean values of temperature and pressure at the sampling sites since the Q values supplied by the manufacturer were evaluated under standard conditions (298 K and 1013 hPa). The obtained values for Q were the following: 35.8 mL min⁻¹ for benzene, 43.3 mL min⁻¹ for toluene, 37.7 mL min⁻¹ for ethylbenzene, and 36.6 mL min⁻¹ (11.3%) for p-xylene.

Sampling quality control/quality assurance (QA/QC)

Fields blanks and parallel duplicate samples were collected using additional Radiello® diffusive samplers located in each sampling site during the exposure period (14 days) for both sampling periods. Fields blanks were left unexposed during the sampling periods and were analyzed under the same conditions applied to the samples (Radiello® diffusive passive samplers which were exposed to ambient air). Results were corrected with the blank values.

Analytical method

The analytes were recovered from the Radiello® cartridges by chemical desorption with 1 mL of carbon disulfide (CS₂), and the extracts were stored in vials and subjected to an ultrasonic bath for 10 min at a temperature of 10 °C (EN 14,662–5:2005). Subsequently, the samples were kept in refrigeration until further analysis.

The chromatographic analysis of the samples was carried out according to the sampling and analysis Method MTA/MA-030/A92 from the National Institute of Safety and Hygiene of Spain (INSHT 1992). A gas chromatograph (TRACE GC Ultra Thermo Fisher Scientific Technologies, Inc., Waltham, MA, USA) coupled to a flame ionization detector (Thermo Fisher Scientific Technologies, Inc., Waltham, MA, USA) was used in splitless mode in order to analyze the collected samples. Analytical conditions were the following: (a) a fused silica methyl type capillary column was used (30 m × 0.32 mm ID, with a film thickness of 0.5 μm); (b) oven temperature program, 40 °C for 4 min, then temperature was increased at a rate of 5 °C/min up to 100 °C and maintained for 10 min; (c) carrier gas, ultra-pure nitrogen (99.999%) at 1 mL min⁻¹; and (d) flame ionization detector (FID) using ultra-pure hydrogen and extra-dried air at 35 mL min⁻¹ and 350 mL min⁻¹, respectively. Calibration with seven points was performed (from 0.05 to 100.00 μg mL⁻¹) using analytical reagents for each BTEX compound from Sigma Aldrich (99.98%). Limits of detection (LOD) were 0.05, 0.06, 0.06, and 0.05 μg mL⁻¹, for benzene, toluene, ethylbenzene, and p-xylene, respectively.

Measurements of criteria air pollutants and meteorological parameters

Meteorological parameters and hourly concentrations of criteria air pollutants (O₃, SO₂, CO, NO, NO₂, and PM₁₀) were measured during both sampling periods using a Doppler Sodar system (integrated with Met One weather stations, models: 010, 020, 083-E, 060A, 090-C, and solar radiation, respectively) and automatic analyzers installed at the CICEG-Fire Station (land-use type 4), School of Medicine (land-use type 3), and IMSS T-21 Station (land-use type 1)

sampling sites. Characteristics of the automatic analyzers are shown in Table S1 in the Supplementary Material Section.

Statistical analysis

Principal component analysis (PCA) and bi-variate statistical analysis were used in order to conduct exploratory data analysis and to identify relations among the measured variables. Correlations between the average concentrations of the measured BTEX and meteorological variables were evaluated at the three study sites with meteorological measurements. Pearson's correlation coefficients were used to identify relations between pairs of measured variables using XLSTAT software. PCA is a useful tool in multivariate data analysis, particularly for visualization, data reduction, and transformation of multivariate data. Bi-plots were constructed from two-dimensional projections of samples, using the axes as factors, for visual analysis emphasizing the components with greater contributions to the total data variability. Each principal component is a linear combination of the original responses, and these components are orthogonal to each other. PCA was performed using the XLSTAT tool (XLSTAT 2016). This tool constructs a new set of variables much better correlated for study and identifies the magnitude, sign and degree of significance of any correlation between two or more variables. From this analysis, groups of related compounds were identified considering their factor loads.

Mapping and Kriging interpolation

Kriging is a method of spatial inference which uses the information provided by the sample to estimate the values of a variable in places not sampled. The method is designed to give the best unbiased linear estimator with a minimum variance. Spatial variability for each climatic period was analyzed for the “rainy” and “cold dry” seasonal sampling periods. The coordinates of the measurement sites and the concentrations constitute the input data to derive the points from the maps. Contour maps were produced using the Kriging method by means of the Surfer tool version 14 (2017) in order to illustrate the spatial distribution of the BTEX concentrations.

Health risk assessment

Health risk assessment, considering BTEX intake through inhalation (EC), was calculated according to the US Environmental Protection Agency methodology (US EPA 1989, 2011). We determined the non-carcinogenic risk associated with BTEX exposure (HQ) and carcinogenic risk factors due to benzene exposure (LTCR) at each measurement site during both sampling periods. LTCR represents the probability of developing cancer over a lifetime as a result of exposure to benzene for a receptor exposed via inhalation. This

method has been applied in other studies by other authors (Bari and Kindzierski 2017; Feretti et al. 2014; De Donno et al. 2018; Nabizadeh et al. 2020a, b; Parvizimehr et al. 2020; Golkhorshidi et al. 2019; Baghani et al. 2019) to assess the health risk associated with air pollution in urban areas. The non-cancer risk was calculated for each BTEX species as a risk quotient (HQ) that determines the non-carcinogenic risk (cardiovascular and respiratory diseases) by inhalation. HQ has been defined as “the ratio of a single substance exposure level over a specified time period to a reference dose for that substance derived from a similar exposure period”. We calculated HQ according to the following equation:

$$HQ = \frac{EC}{Rfc} \quad (2)$$

where RfC (mg/m^3) is the inhalation reference concentration (defined as the estimate of a continuous inhalation exposure for the human population) that is likely to be without appreciable risk of deleterious effects during a lifetime. RfC values were taken from the Toxicological Review Profiles for each species (IRIS-US EPA): 0.03 mg m^{-3} for benzene (IRIS-USEPA 2002), 5 mg m^{-3} for toluene (IRIS-USEPA 2005), 1 mg m^{-3} for ethylbenzene (IRIS-USEPA 1999), and 0.1 mg m^{-3} for p-xylene (IRIS-USEPA 2003). EC ($\mu\text{g}/\text{m}^3$) is the chronic exposure concentration averaged over the exposure time for non-carcinogenic risk or over a lifetime for carcinogenic risk calculated according to the following equation:

$$EC = \frac{[CA \times ET \times EF \times ED]}{[AT]} \quad (3)$$

where CA ($\mu\text{g}/\text{m}^3$) is the air pollutant concentration, ET (h/day) is the exposure time, EF (days/year) is the exposure frequency, ED (years) is the exposure duration, and AT (years \times 365 days/year \times 24 h/day) is the averaging time of exposure. The values of exposure factors were taken from the Exposure Factor Handbook by taking into account the “residential” exposure, according the following information: $ET = 24$ h/day, $EF = 350$ days/year, and $ED = 24$ years for adults and 6 years for children. Consistent with ED , AT includes 24 years for non-carcinogenic risk (HQ) and 70 years for carcinogenic risk (LTCR).

LTCR was determined according to the following equation:

$$LTCR = IUR \times EC \quad (4)$$

where EC is the chronic exposure concentration averaged over the exposure time for carcinogenic risk over a lifetime, determined by Eq. 2, and considering $AT = ED = 70$ years; IUR ($\mu\text{g}/\text{m}^3$)⁻¹ is the inhalation unit risk defined as “the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of $1 \mu\text{g}/\text{m}^3$ in air”. The toxicity values were taken from the Integrated

Risk Information System’s (IRIS) toxicological database, which for benzene reports a RfC value of $3.00 \times 10^{-2} \text{ mg}/\text{m}^3$ and IUR from 2.2×10^{-6} to $7.8 \times 10^{-6} (\mu\text{g}/\text{m}^3)^{-1}$ (IRIS-USEPA 2002).

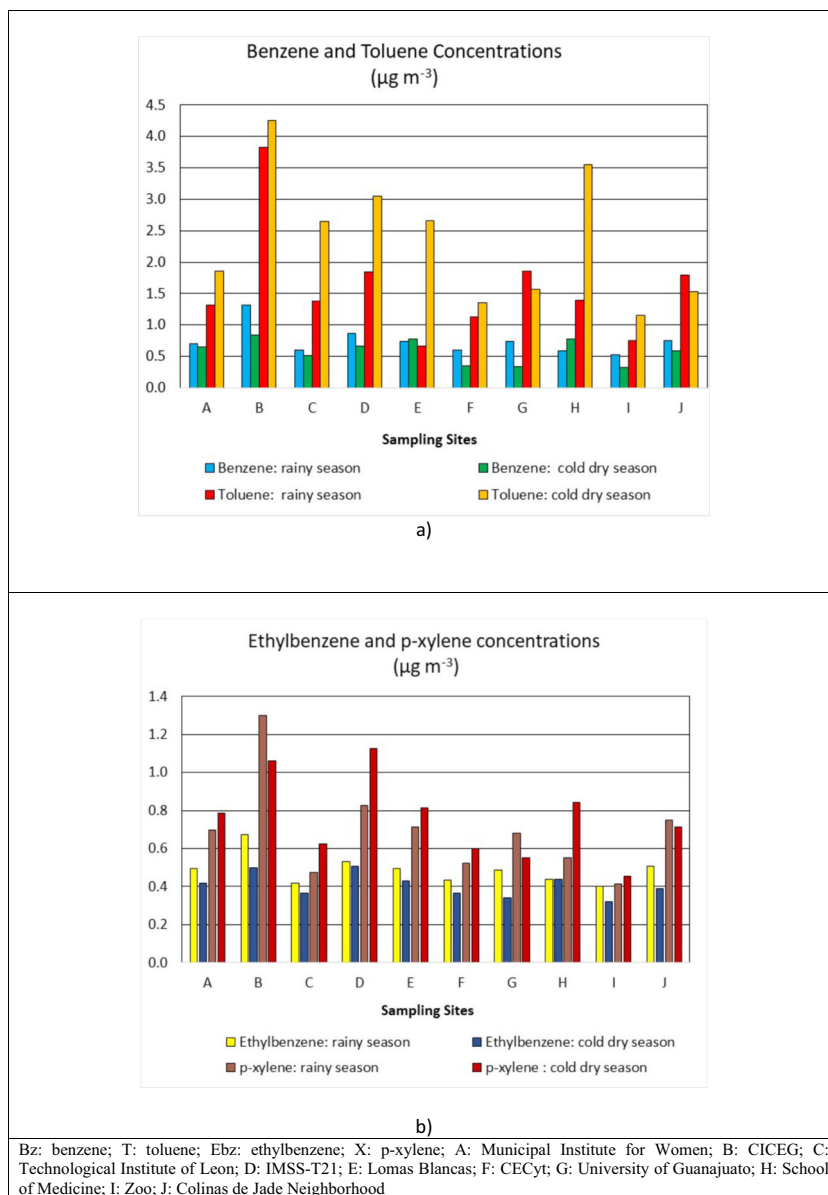
Results and discussion

Spatial and seasonal variations of BTEX concentrations

The relative abundance of BTEX in the ambient air of the study area, considering average concentrations in both seasonal periods, was the following: toluene ($1.98 \mu\text{g m}^{-3}$) > benzene ($0.66 \mu\text{g m}^{-3}$) > p-xylene ($0.75 \mu\text{g m}^{-3}$) > ethylbenzene ($0.45 \mu\text{g m}^{-3}$). These observations are consistent with a previous study where toluene was found to be the most important BTEX in Leon city, carried out by active sampling (Cérón Bretón et al. 2020) and with other studies where toluene has been reported as the dominant BTEX in urban areas (Parra et al. 2009; Yamamoto et al. 2000; Guo et al. 2004). Benzene and toluene have lower reactivities, with atmospheric lifetimes of 9.4 and 1.9 days, respectively, when reacting with the OH radical. They may thus reside longer in the atmosphere compared to the more reactive ethylbenzene and xylene, which have atmospheric lifetimes of 1.6 days and 20.3 h, respectively, considering their reaction with OH radical at concentration of 10^6 molecules cm^{-3} . This stability allows benzene and toluene to remain in the atmosphere and to be transported before their degradation, resulting in higher concentration levels. In addition, benzene and toluene are common constituents of gasoline, being emitted from the exhaust of mobile sources in urban areas, and they have been reported as the dominant BTEX species in compressed natural gas (CNG) stations (Baghani et al. 2019). Benzene concentrations ($0.74 \mu\text{g m}^{-3}$ and $0.58 \mu\text{g m}^{-3}$ for rainy and cold dry seasons, respectively) were below the maximum permissible levels established for air quality and cleaner air for Europe ($5 \mu\text{g m}^{-3}$), (European Environment Agency 2008) and by the Ambient Air Quality Criteria of the Ontario Ministry of Environment ($2.3 \mu\text{g m}^{-3}$) (OME 2012). Currently, toluene concentrations in ambient air are not regulated by the European legislation, but the World Health Organization (WHO) has established a value of $260 \mu\text{g m}^{-3}$ as a weekly average standard in order to protect population health. In this study, the measured levels of toluene were much lower than this benchmark value: $1.59 \mu\text{g m}^{-3}$ and $2.36 \mu\text{g m}^{-3}$ for rainy and cold dry seasons, respectively (WHO 1987).

BTEX concentrations for both sampling seasons are shown in Fig. 1. Benzene and toluene are highest at sampling site B (CICEG) during both sampling periods (Fig. 1a). The spatial variation for benzene and toluene is shown in Figs. 2a and 3a, and Figs. 2b and 3b, during the rainy and cold dry seasons,

Fig. 1 BTEX concentrations for both sampling seasons for each study site. Bz: benzene; T: toluene; Ebz: ethylbenzene; X: p-xylene; A: Municipal Institute for Women; B: CICEG; C: Technological Institute of Leon; D: IMSS-T21; E: Lomas Blancas; F: CECyt; G: University of Guanajuato; H: School of Medicine; I: Zoo; J: Colinas de Jade Neighborhood



respectively. Ethylbenzene and p-xylene showed the highest concentrations at sampling sites B and D during rainy and cold dry seasons, respectively (Fig. 1b). The spatial variation for ethylbenzene and p-xylene can be observed in Figs. 2c (rainy season) and 3c (cold dry season) for ethylbenzene and Figs. 2d (rainy season) and 3d (cold dry season) for p-xylene. Sampling site B (CICEG) corresponds to an industrial land-use type of medium intensity, while sampling site D (IMSS-T21) corresponds to an urban land-use type (high-density habitable zone). All measured BTEX compounds showed higher concentrations in the southern section of the study area. This area is characterized by multiple industries, avenues with dense vehicular traffic, and highways that connect the city with other municipalities including Silao de la Victoria and Guanajuato.

The seasonal variation of BTEX can be explained by the seasonal characteristics of the prevailing meteorology, source strengths, and the availability of OH radical and insolation on which the BTEX removal processes depend. Mean concentrations for benzene and toluene were $0.74 \mu\text{g m}^{-3}$ and $0.58 \mu\text{g m}^{-3}$ and $1.59 \mu\text{g m}^{-3}$ and $2.36 \mu\text{g m}^{-3}$, for rainy and cold dry seasons, respectively. Ethylbenzene and p-xylene mean values concentrations are of $0.49 \mu\text{g m}^{-3}$ and $0.41 \mu\text{g m}^{-3}$ and $0.69 \mu\text{g m}^{-3}$ and $0.76 \mu\text{g m}^{-3}$, for rainy and cold dry seasons, respectively. Benzene and ethylbenzene show similar concentrations during both rainy and cold dry seasons (Fig. 4), with similar spatial distributions. Toluene and p-xylene showed higher mean concentrations during the cold dry season; however, according to the Mann–Whitney test, these differences were not significant at a level of $\alpha =$

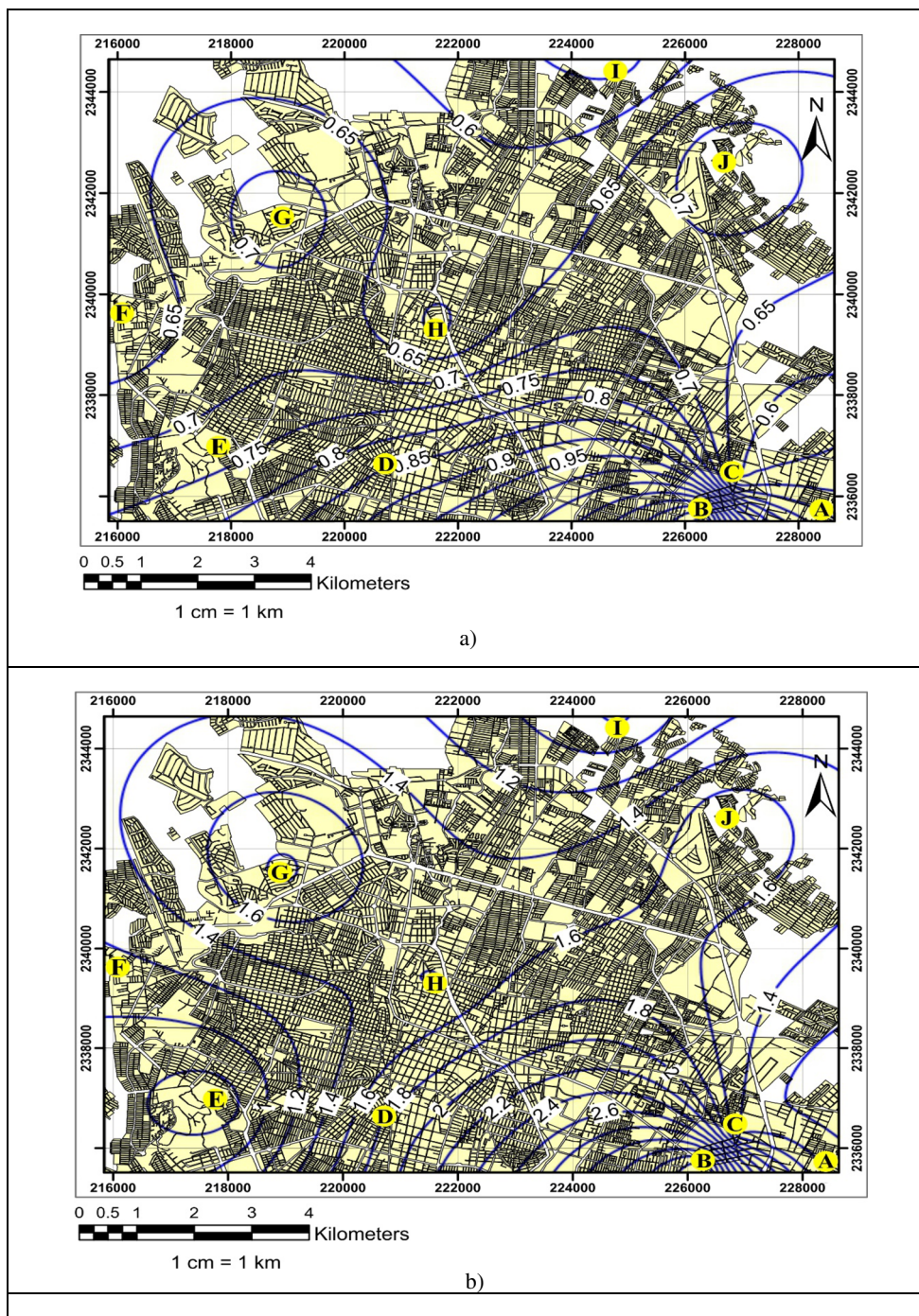


Fig. 2 Spatial variation of BTEX concentration ($\mu\text{g m}^{-3}$) during the rainy season. (a) benzene, (b) toluene, (c) ethylbenzene, (d) p-xylene. **A:** Municipal Institute for Women; **B:** CICEG; **C:** Technological Institute

of Leon; **D:** IMSS T-21; **E:** Lomas blancas neighborhood; **F:** CECyT; **G:** University of Guanajuato; **H:** School of Medicine; **I:** Zoo; **J:** Colinas de jade neighborhood

0.05. The sum of average concentrations of measured BTEX during the rainy and cold dry seasons were $3.52 \pm 0.36 \mu\text{g m}^{-3}$ and $4.11 \pm 0.38 \mu\text{g m}^{-3}$, respectively. The lower BTEX levels during the rainy sampling period are due to a greater degradation of BTEX by photochemical activity, as this period coincides with the summer months when temperature and solar radiation are higher ($23.5 \text{ }^\circ\text{C}$ and $16.7 \text{ }^\circ\text{C}$, and 400.8 W m^{-2}

and 178.1 W m^{-2} , for rainy and cold dry periods, respectively). In addition, during the rainy season, BTEX can be removed by wet deposition, further reducing the atmospheric concentrations. The lower intensities of solar radiation during the cold dry season is consistent with a decrease in photochemical activity and reduced concentration of atmospheric oxidants (OH), both serving to lengthen atmospheric BTEX

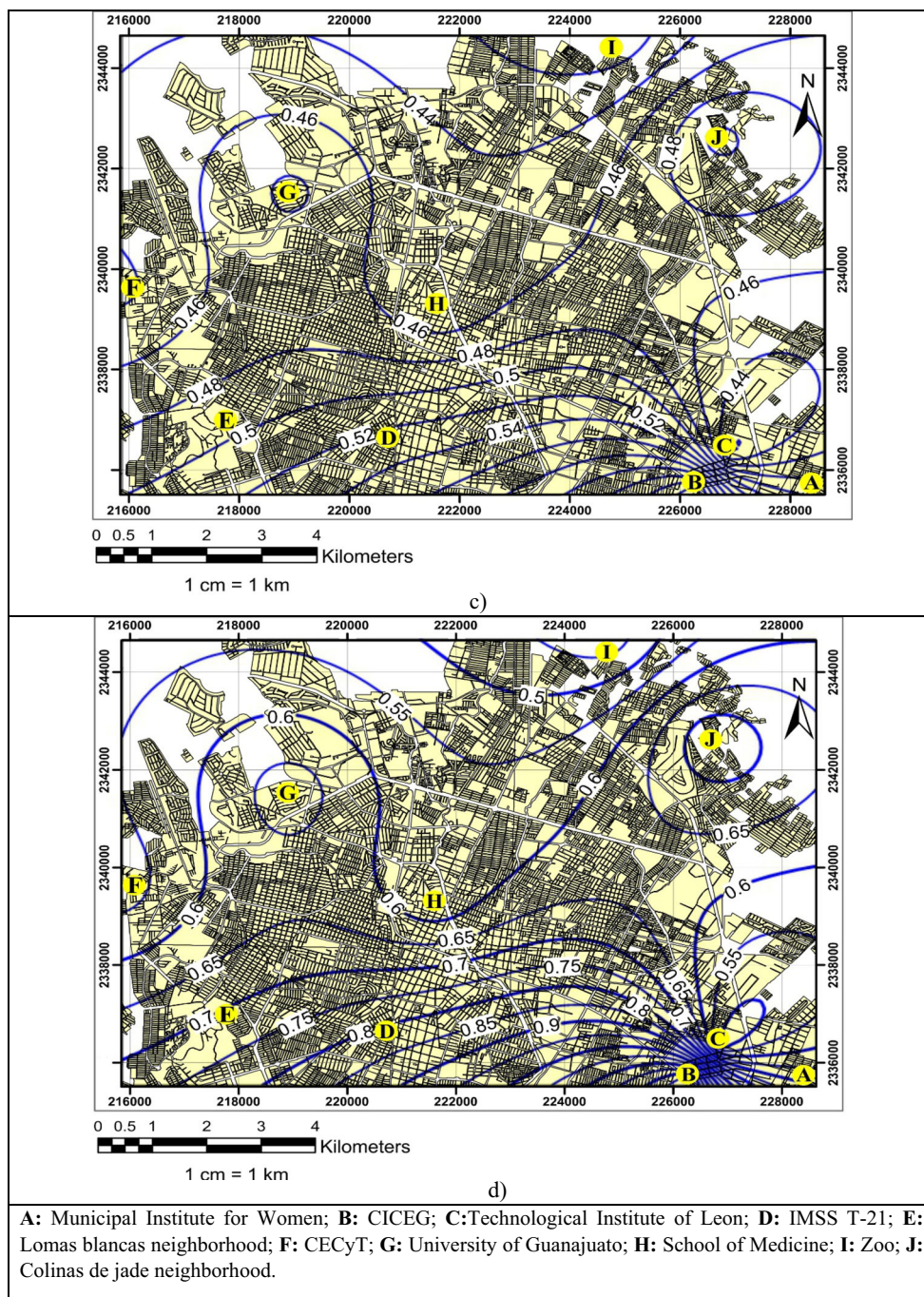


Fig. 2 (continued)

lifetimes (Monod et al. 2001). In addition, it is well known that the height of the boundary layer shows a seasonal behavior, being lower during winter months (cold dry season). A shallow boundary layer inhibits the dispersion of air pollutants, resulting in higher concentration levels.

The average wind speed and direction were similar during both seasons with a prevailing direction of SSE and an average speed of around 1.5 ms^{-1} . Wind roses for both sampling seasons in the study area are shown

in Fig. S2 in the Supplementary Material Section. The lack of large seasonal variability in wind characteristics is consistent with the similarity of mean seasonal concentrations of all BTEX species (Fig. 4). The average SSE winds, together with the observed spatial concentration gradient with higher BTEX concentrations to the south during both seasons (Figs. 2 and 3), suggest that the largest BTEX sources are located in the southern portion of the metropolitan area of Leon. These

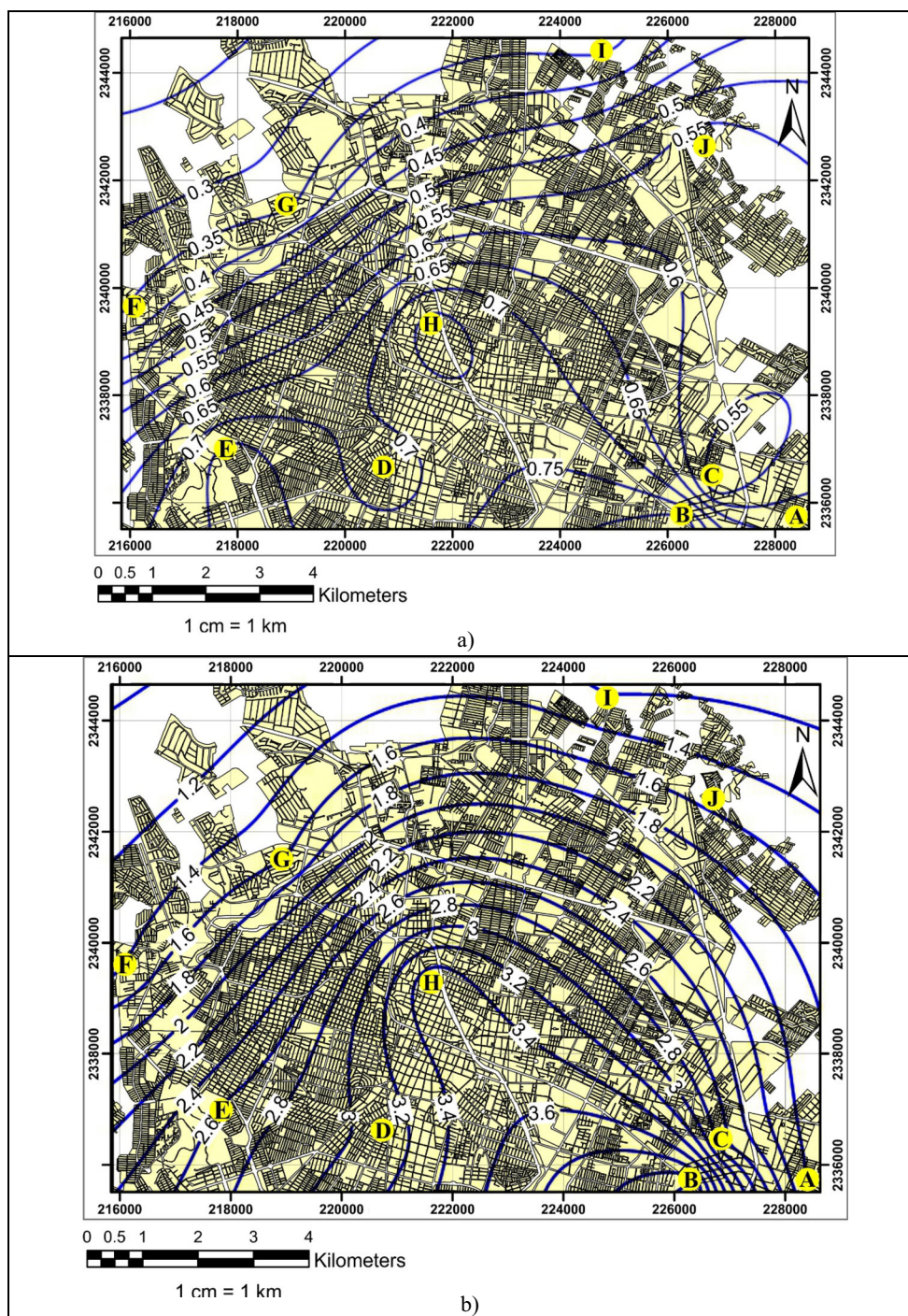


Fig. 3 Maps of the Spatial variation of BTEX concentration during ($\mu\text{g m}^{-3}$) the cold dry season. (a) benzene, (b) toluene, (c) ethylbenzene, (d) p-xylene. **A:** Municipal Institute for Women; **B:** CICEG; **C:** Technological

Institute of Leon; **D:** IMSS T-21; **E:** Lomas blancas neighborhood; **F:** CECyT; **G:** University of Guanajuato; **H:** School of Medicine; **I:** Zoo; **J:** Colinas de jade neighborhood

emissions are likely carried by local winds to the central and northern portions of the area during both seasons.

Mean benzene concentrations for each land-use type (according to the land-use classification of Leon city) were $0.73 \mu\text{g m}^{-3}$ (type 1), $0.75 \mu\text{g m}^{-3}$ (type 2), $0.59 \mu\text{g m}^{-3}$ (type 3), $0.96 \mu\text{g m}^{-3}$ (type 4), and $0.53 \mu\text{g m}^{-3}$ (type 5). Mean toluene concentrations for the different land-use types were

the following: type 1 ($1.24 \mu\text{g m}^{-3}$), type 2 ($1.83 \mu\text{g m}^{-3}$), type 3 ($1.39 \mu\text{g m}^{-3}$), type 4 ($2.60 \mu\text{g m}^{-3}$), and type 5 ($0.75 \mu\text{g m}^{-3}$). Mean concentration values for ethylbenzene and p-xylene according the different land-use types were $0.49 \mu\text{g m}^{-3}$ and $0.69 \mu\text{g m}^{-3}$, respectively, for type 1; $0.50 \mu\text{g m}^{-3}$ and $0.72 \mu\text{g m}^{-3}$, respectively, for type 2; $0.44 \mu\text{g m}^{-3}$ and $0.55 \mu\text{g m}^{-3}$, respectively, for type 3;

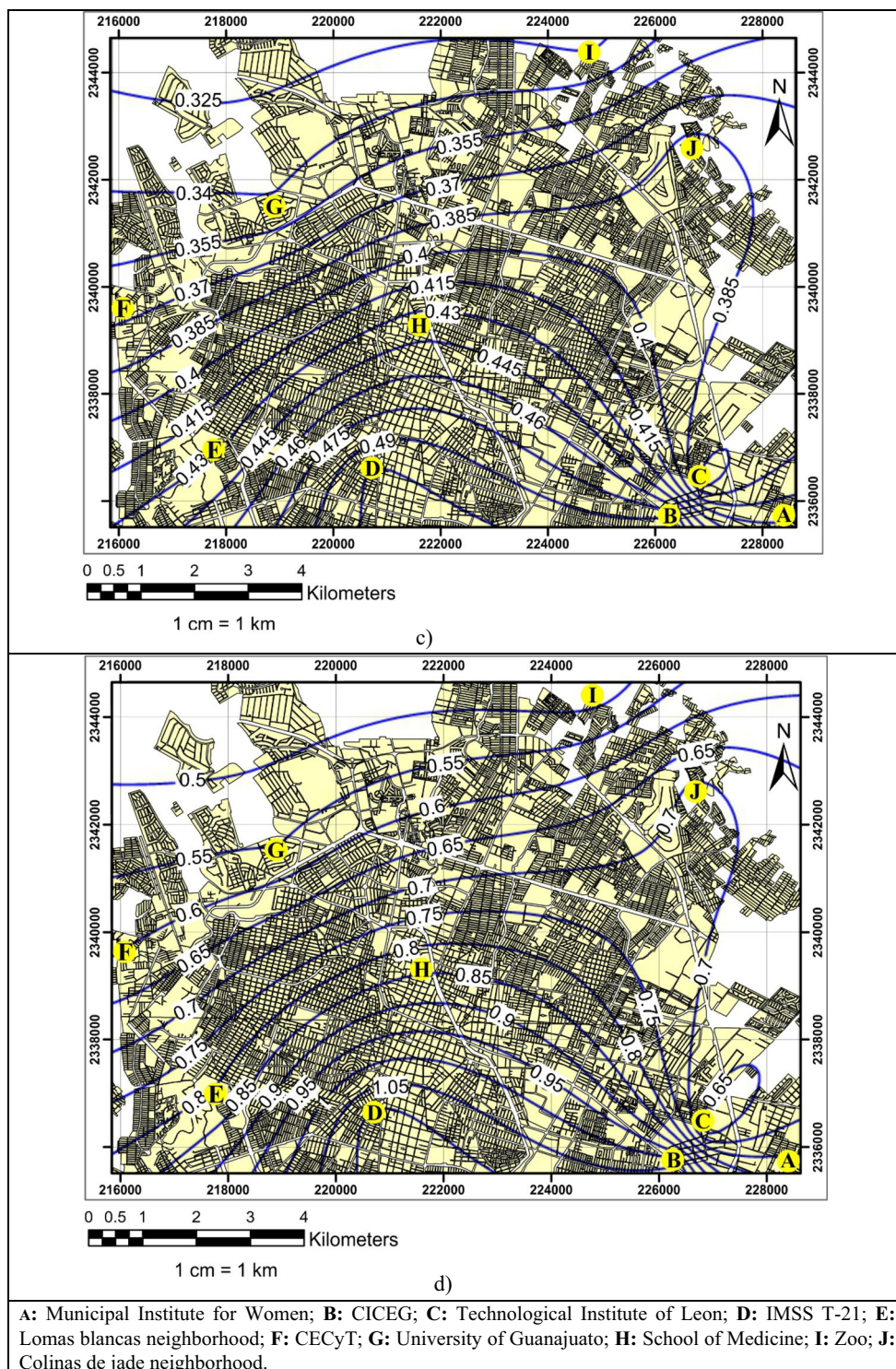
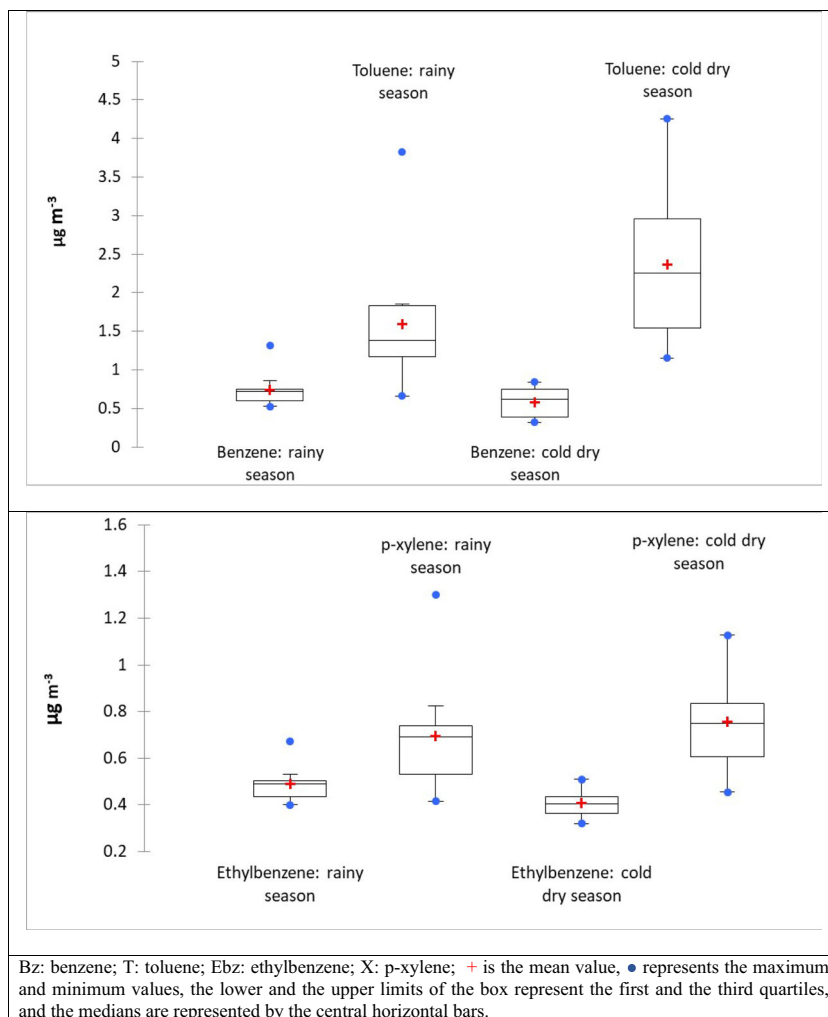


Fig. 3 (continued)

$0.55 \mu\text{g m}^{-3}$ and $0.89 \mu\text{g m}^{-3}$, respectively, for type 4; and $0.40 \mu\text{g m}^{-3}$ and $0.42 \mu\text{g m}^{-3}$, respectively, for type 5. The highest average BTEX concentrations were found for land-use type 4 (medium-intensity industrial zone), which includes sites B and C (CICEG and Technological Institute of Leon).

Both of these sites are located near one of the main avenues of the city (Boulevard Adolfo Lopez Mateos) which constitutes a principal exit towards the federal Leon-Silao-Guanajuato highway, suggesting the importance of vehicular sources.

Fig. 4 Descriptive statistics for BTEX during both sampling seasons (rainy and cold dry periods). Bz: benzene; T: toluene; Ebz: ethylbenzene; X: p-xylene; is the mean value, represents the maximum and minimum values, the lower and the upper limits of the box represent the first and the third quartiles, and the medians are represented by the central horizontal bars



Comparison with other studies

The BTEX concentrations reported in this study are compared to those reported in other cities around the world (Table 2). Benzene and toluene concentrations in Leon city were similar to those reported in Tri-City, Poland (Marć et al. 2014), and ethylbenzene and p-xylene concentrations found in this study were similar to those reported for Düzce, Turkey (Bozkurt et al. 2018). BTEX levels in Leon city were higher than those reported in southern Philadelphia, USA (Mukerjee et al. 2016), while BTEX concentrations in Modugno, Italy (Amodio et al. 2013), and Argiels, Algeria (Kerchich and Kerbachi 2012), were higher than those obtained in this study.

Criteria air pollutant concentrations

It is important to mention that we had criteria air pollutant measurements at only three of the sampling sites (CICEG, School of Medicine and IMSS T21), where stations belonging to the air quality network of Leon city are located. Criteria air

pollutant concentrations for both sampling periods showed the following mean values: 0.0076 ppm and 0.0076 ppm for SO_2 , 0.0314 ppm and 0.0186 ppm for O_3 , $32.58 \mu\text{g m}^{-3}$ and $39.99 \mu\text{g m}^{-3}$ for PM_{10} , 0.60 ppm and 1.08 ppm for CO, 0.0174 ppm and 0.0228 ppm for NO, and 0.0144 ppm and 0.0258 ppm for NO_2 , for rainy and cold dry seasons, respectively. SO_2 , PM_{10} , CO, NO, and NO_2 showed higher concentration values during cold dry season. This behavior is to be expected, since the cold dry season coincides with the winter months, when thermal inversions frequently occur in the study area, reducing the dispersion of pollutants and causing that their concentrations to remain higher due to a lower height of the mixed layer. O_3 was the air pollutant that showed higher concentrations during the rainy season. This can be explained by the fact that this sampling season coincides with the summer months, when solar radiation intensities are higher, favoring photochemical activity and increasing the photochemical production of tropospheric ozone. Concentration values for criteria air pollutants for each land-use type during both sampling periods are shown in Table S2 in the Supplementary Material Section.

Table 2 Comparison of results obtained in the present study with other studies around the world

Site	B	T	Ebz	X	Sampling site characteristics	Chemical analysis method	Author
Düzce, Turkey	2.09	3.29	0.61	1.08	377,610 inhabitants, 2574 km ² , urban-industrial area with high traffic flow	Passive sampling, glass tubes filled with Tenax TA, thermal desorption, GC/FID	Bozkurt et al. (2018)
South of Philadelphia, USA	0.52	0.64	0.11	0.4	1.5 millions of inhabitants, 367 km ² , urban-industrial area with high vehicular traffic	Passive sampling, Supelco® samplers, thermal desorption GC/SM	Mukerjee et al. (2016)
Modugno, Italy	1.38	3.05	0.69	2.13	38,443 inhabitants, 319 km ² , urban-industrial area with high vehicular traffic	Passive sampling, Radiello® cartridges, thermal desorption, GC-MS	Amodio et al. (2013)
Argiels, Algeria	11.1	27.7	4.53	4.3	3.5 millions of inhabitants, 273 km ² , urban-industrial area with high vehicular traffic	Passive sampling, Radiello® cartridges, chemical desorption with CS ₂ , GC/FID	Kerchich and Kerbachi (2012)
Tri-City, Poland	0.71	1.00	0.26	0.8	748,000 inhabitants, 414 km ² , urban-industrial area with high vehicular traffic	Passive sampling, Radiello® cartridges, thermal desorption GC-FID	Marć et al. (2014)
Leon, Guanajuato	0.74	1.59	0.48	0.69	1.57 millions of inhabitants, 1220 km ² , urban-industrial area with high vehicular traffic	Passive sampling, Radiello® cartridges, chemical desorption with CS ₂ , GC/FID	This Study

B benzene ($\mu\text{g m}^{-3}$); T toluene ($\mu\text{g m}^{-3}$); Ebz ethylbenzene ($\mu\text{g m}^{-3}$); X p-xylene ($\mu\text{g m}^{-3}$)

During the rainy season, concentrations of SO₂, O₃, NO₂, and NO were highest at the CICEG site (land-use type 4), decreasing at IMSS T-21 (land-use type 1), and lowest at the School of Medicine site (land-use type 3). CO showed the following behavior pattern: highest levels at the CICEG site (land-use type 4), decreasing at the School of Medicine site (land-use type 3), and lowest concentrations at IMSS T-21 (land-use type 1). PM₁₀ values showed a different behavior: School of Medicine site (land-use type 3) > CICEG site (land-use type 4) > IMSS T-21 site (land-use type 1). Higher levels of concentration were found for almost all air criteria pollutants during the rainy season at sampling sites with land-use type 4, except for PM₁₀ which showed higher concentrations at sampling sites with land-use type 3. Land-use type 4 included the CICEG and the Technological Institute of Leon sampling sites, both with industrial medium-intensity land-use (production activities with a specific and concentrated location, buildings closed, up to 100 active people) and located near busy avenues such as Avenida Adolfo Lopez Mateos and the highways that link the city of Leon with Silao and Guanajuato. All of these sources may have contributed to the higher levels of airborne contaminants at the study sites with land-use type 4.

During cold dry season, all measured criteria air pollutants (SO₂, PM₁₀, CO, NO, and NO₂) showed highest concentration values at sampling sites with land-use type 3, decreasing at sites with land-use type 4, and lowest concentrations at sites with land-use type 1. Land-use type 3 included the School of Medicine site, commercial use including some secondary sector activities (See Table 1). This sampling site is located near downtown Leon city, where the footwear industry is commercialized on a large scale, involving intense mobility of people (merchants and buyers) with the associated increase in vehicular traffic in that area.

Bi-variate and multivariate analysis

Pearson correlation coefficient tables for the rainy (Table 3) and cold dry periods (Table 4) are constructed. These tables show bi-variate relations between BTEX concentrations, criteria air pollutants (SO₂, O₃, CO, NO, NO₂, and PM₁₀) and meteorological parameters (relative humidity, temperature, and solar radiation). During the rainy season, benzene, toluene, and ethylbenzene (Table 3) show significant positive correlation with each other indicating that they could originate from common sources. Benzene, toluene, and ethylbenzene showed significant correlations (> 0.80) with CO, indicating that they might possibly originate from common sources (gasoline vehicles and oil and gas service stations). Since 75.47% of CO emissions have been attributed to mobile sources in Guanajuato State (273, 253.34 ton CO/year), CO can be considered as a tracer of vehicular emissions in the study area (SMAOT-Guanajuato 2017) (<https://smaot.guanajuato.gob.mx/sitio/calidad-del-aire/4/Inventario-de-Emissiones-de-Contaminantes-Criterio>). All measured BTEX, NO, and NO₂ showed strong negative correlations with temperature and solar radiation, being most significant for p-xylene (-0.999), indicating that increases in these meteorological variables contribute to the degradation of BTEX by photochemical reactions. p-xylene showed a strong positive correlation with NO, indicating that these compounds probably had their origin in common sources. NO showed a negative strong correlation (-0.96) with ozone (O₃), which was expected as NO is precursor of tropospheric ozone (Parra et al. 2009). NO and NO₂ had a positive significant correlation (0.933), indicating that these air pollutants originated from common sources (high-temperature combustion). Ozone showed significant positive correlation with solar radiation, indicating that there was photochemical production of this pollutant during this

Table 3 Pearson correlation matrix for measured variables during the rainy season

Variables	B	T	Ebz	X	SO ₂	O ₃	PM ₁₀	CO	NO	NO ₂	RH	Temp	SR
B	1												
T	0.98*	1											
Ebz	0.99*	0.97	1										
X	0.59	0.74	0.57	1									
SO ₂	0.79	0.65	0.80	- 0.03	1								
O ₃	0.95	0.99	0.95	0.81	- 0.28	1							
PM ₁₀	- 0.08	0.12	- 0.11	0.76	- 0.68	- 0.51	1						
CO	0.94*	0.86*	0.95*	0.29	0.95	- 0.58	- 0.41	1					
NO	0.62	0.77	0.60	0.99*	0.007	- 0.96*	0.73	0.33	1				
NO ₂	0.29	0.48	0.27	0.95	- 0.35	- 0.80	0.93	- 0.03	0.93*	1			
RH	- 0.93	- 0.98	- 0.92	- 0.85	- 0.51	0.97	- 0.29	- 0.76	- 0.87	- 0.63	1		
Temp	- 0.55	- 0.71	- 0.53	- 0.99*	0.07	0.94	- 0.79	- 0.25	- 0.99	- 0.96	0.82	1	
SR	- 0.59	- 0.74	- 0.57	- 0.99*	0.03	0.95*	- 0.76	- 0.30	- 0.99*	- 0.5	0.85	0.99*	1

* Values are different from 0 at a significant level of $\alpha = 0.05$

B benzene; T toluene; Ebz ethylbenzene; X p-xylene; SO₂ sulfur dioxide; O₃ ozone; PM₁₀ particulate matter with aerodynamic radio $\leq 10 \mu\text{m}$; CO carbon monoxide; NO nitric oxide; NO₂ nitrogen dioxide; RH relative humidity; Temp temperature; SR solar radiation

period. All measured air pollutants showed negative correlations with relative humidity, being most significant for ozone, indicating that high concentrations of water vapor could partially remove pollutants from the atmosphere (by chemical reaction or condensation).

During the cold dry season (Table 4) benzene, toluene and p-xylene are positively and significantly correlated with each other, indicating that these compounds probably came from the same sources. There was a lack of correlation between temperature and BTEX during this sampling period, except

for ethylbenzene, which also did not correlate with the rest of BTEX, probably due to an origin in a different source. Benzene, toluene, and p-xylene had a strong positive correlation with SO₂, indicating that these air pollutants could originate from combustion sources using high-sulfur fuels (gasoline and diesel). Benzene and toluene had strong positive correlations with CO, NO, and NO₂, indicating that these aromatic hydrocarbons could originate from vehicular emissions and high-temperature combustion sources. Benzene, toluene, p-xylene, CO (- 0.88), NO (- 0.94), and NO₂ (- 0.94) showed

Table 4 Pearson correlation matrix for measured variables during the cold dry season

Variables	B	T	Ebz	X	SO ₂	O ₃	PM ₁₀	CO	NO	NO ₂	RH	Temp	SR
B	1												
T	0.97*	1											
Ebz	0.29	0.05	1										
X	0.97*	0.99*	0.06	1									
SO ₂	0.95*	0.99*	0.03	0.99*	1								
O ₃	- 0.95	- 0.99*	- 0.02	- 0.99	- 0.90*	1							
PM ₁₀	- 0.15	0.09	0.99*	0.08	0.17	- 0.16	1						
CO	0.96*	0.85*	0.49	0.84*	0.88*	- 0.88*	0.60	1					
NO	0.99*	0.96*	0.33	0.96*	0.94	- 0.94*	- 0.19	0.97*	1				
NO ₂	0.99*	0.95*	0.33	0.96*	0.94	- 0.94*	- 0.19	0.97*	0.99*	1			
RH	0.78	0.91	0.38	0.90	0.93	- 0.93	0.49	0.99	0.76	0.76	1		
Temp	- 0.15	0.09	0.99*	0.08	0.17	- 0.16	0.90*	0.61	- 0.19	- 0.19	0.50	1	
SR	- 0.98*	- 0.97*	0.29	- 0.97*	- 0.95*	0.95*	0.16	- 0.69	- 0.99*	- 0.99*	- 0.78	0.16	1

* Values are different from 0 at a significance level of $\alpha = 0.05$

B benzene; T toluene; Ebz ethylbenzene; X p-xylene; SO₂ sulfur dioxide; O₃ ozone; PM₁₀ particulate matter with aerodynamic radio $\leq 10 \mu\text{m}$; CO carbon monoxide; NO nitric oxide; NO₂ nitrogen dioxide; RH relative humidity; Temp temperature; SR solar radiation

negative correlation with ozone, suggesting that they may act as ozone precursors at the study sites during this period. Solar radiation correlated negatively with most BTEX species, suggesting a photochemical degradation process (mainly involving the hydroxyl radical). Relative humidity affected BTEX concentrations to a lesser extent than found during the rainy season. PM₁₀ and ethylbenzene showed a significant positive correlation with each other and positive significant correlations with temperature, indicating that this aromatic compound could contribute to secondary organic aerosol formation (SOA). Photochemical production of tropospheric ozone was evident by a strong positive correlation of ethylbenzene with solar radiation (0.95). SO₂ and O₃ showed a significant negative correlation (− 0.90), indicating that SO₂ probably suffered photochemical degradation in order to produce ozone (Wilson et al. 1972). SO₂ influences the production of oxidants as O₃ during episodes of photochemical smog in urban areas. This behavior already was reported by Ceron and collaborators (2019) in a previous study in the metropolitan area of Leon.

A principal component analysis was carried out in order to explore the relations among all measured variables. Table 5 shows the factor loadings for the rainy and the cold dry sampling seasons. During the rainy season (Table 5), two principal components (PC1 and PC2) are necessary to explain 97% of the total data variance. PC1 exhibited 69.22% of the data variance and included air pollutants that were influenced by

photochemical activity and relative humidity (with large absolute loadings in benzene, toluene, ethylbenzene, p-xylene, ozone, NO, NO₂, relative humidity, temperature, and solar radiation). This was expected as BTEX, NO, and NO₂ are precursors of tropospheric ozone and suffer photochemical degradation during the hours of strong solar radiation. On the other hand, PC2 contains 27.278% of the data variance (Table 5) and included only SO₂, CO, and PM₁₀, air pollutants probably originating from vehicular sources. During the cold dry season (Table 5), both principal components (PC1 and PC2) together explained 94.003% of the data variance. The first component, PC1, contained 71.38% of the data variance. This component grouped the pollutants with a higher influence of vehicular emissions, high-temperature combustions processes, and solar radiation (benzene, toluene, p-xylene, O₃, SO₂, CO, NO, NO₂). These compounds could thus originate from gasoline and diesel combustion sources. PC2 contributed 22.622% of the total variance and included the more temperature-dependent compounds (ethylbenzene and PM₁₀) (Table 5).

Inter-species ratios of BTEX

BTEX concentration ratios (toluene/benzene: T/B and xylene/ethylbenzene: X/Ebz) were calculated in order to further identify the probable origin of these compounds during the study period. These ratios indicate whether emissions may come from mobile or area sources and provide a means to estimate the photochemical age of air masses (fresh or aged). The T/B ratio has been commonly used as an indicator of vehicular traffic emissions since benzene and toluene are common constituents of gasoline and are released into the atmosphere from motor vehicle exhaust. Toluene content in gasoline has been reported as 3 to 4 times higher than benzene content (Pekey and Yilma 2011). Values of this ratio less than 2–3 are characteristic of vehicular emissions and have been reported in this range for many urban areas around the world (Elbir et al., 2005; Baghani et al. 2019). High values of this ratio may indicate that BTEX levels are associated with other sources such as industrial facilities and area sources including evaporative emissions, automotive paint shops, emissions from food cooking processes, and dry cleaners. The T/B ratios found during both sampling periods for each sampling site are shown in Fig. 5a. The highest value for this ratio was registered in site B (CICEG site with land-use type 4), and the lowest value for this ratio was found in site H (Lomas Blancas site with land-use type 3). Site B is located in an area classified as an industrial zone of medium intensity (IMPLAN 2017), located on Adolfo Lopez Mateos Boulevard, one of the city's busiest avenues, near to the Leon-Silao and Silao-San Felipe roads, and surrounded by industries of medium intensity. The mean T/B ratios for each land-use type classification showed the following behavior during the rainy season: type 4

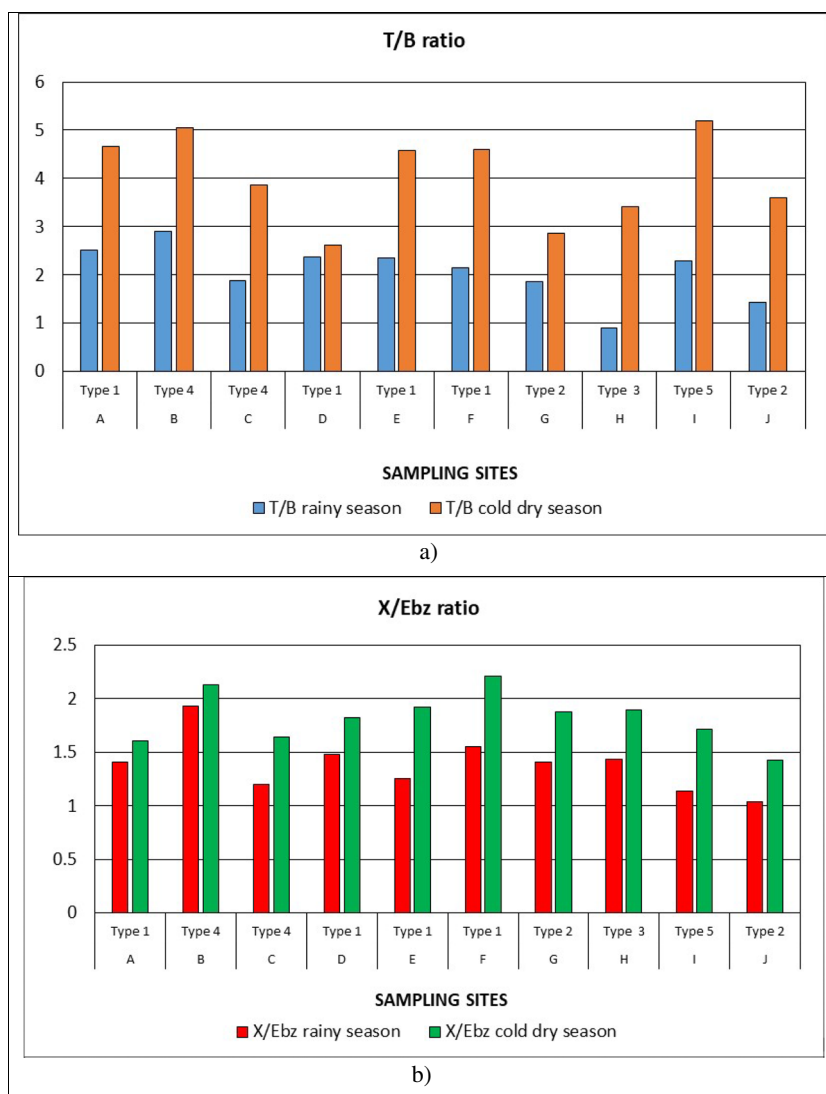
Table 5 Factor loadings of the measured variables for the two principal components during the rainy (a) and the cold dry (b) seasons

Variables	a) Rainy season		b) Cold dry season	
	PC1	PC2	PC1	PC2
B	0.70*	0.30	0.93*	0.07
T	0.86*	0.14	0.99*	0.01
Ebz	0.68*	0.33	0.001	0.99*
X	0.88*	0.12	0.99*	0.01
SO ₂	0.10	0.90*	0.99*	0.04
O ₃	0.99*	0.001	0.99*	0.003
PM ₁₀	0.23	0.77*	0.01	0.99*
CO	0.37	0.63*	0.73*	0.27
NO	0.90*	0.09	0.91*	0.09
NO ₂	0.60*	0.40	0.91*	0.09
RH	− 0.96*	0.04	0.84*	0.16
Temp	0.85*	0.15	0.01	0.99*
SR	0.88*	0.12	0.93*	0.07

* Values are different from 0 at a significance level of $\alpha = 0.05$

B benzene; T toluene; Ebz ethylbenzene; X p-xylene; SO₂ sulfur dioxide; O₃ ozone; CO carbon monoxide; NO nitric oxide; NO₂ nitrogen dioxide; PM₁₀ particulate matter with aerodynamic radius $\leq 10 \mu\text{m}$; RH relative humidity; Temp temperature; SR solar radiation

Fig. 5 BTEX ratios for both sampling periods at each sampling site. (a) T/B ratio, (b) X/Ebz ratio



(2.39) > type 1 (2.34) > type 5 (2.28) > type 2 (1.64) > type 3 (0.89), indicating that zones with high housing density and industrial medium intensity had the highest levels of benzene and toluene. During the cold dry season, T/B ratios had the following behavior: type 5 (5.2) > type 4 (4.46) > type 1 (4.11) > type 3 (3.42) > type 2 (3.23). Sampling sites with land-use type 4 are surrounded by thermoplastic industries, adhesive manufacturing, tanneries, textile, resin and paint, and resin manufacturing, among others. The sampling sites with type 1 land-use classification are located in areas with high population density, which implies greater mobility throughout the city, with greater traffic of both private and public vehicles. Sampling site type 5 is located in an urban consolidation zone near some major roads (León-Silao and Silao-San Felipe).

A seasonal variation of T/B ratio is observed, with higher values during the cold dry sampling season (Fig. 5b). T/B ratios ranged from 0.90 to 2.91, with an average value of

2.15 during the rainy season. During the dry cold season, the highest T/B ratio value was found at site I (Technological Institute of Leon, with land-use type 5), and the lowest value was found at site D (Colinas de Jade site, with land-use type 1). During this period, T/B ratios were higher than those found during the rainy season, ranging from 2.61 to 5.20 with an average value of 4.07, indicating that BTEX sources were likely a combination of vehicular, industrial-type emissions and area sources. The seasonal variation of T/B ratio is consistent with the higher BTEX concentrations observed during the cold dry period, probably due to lower rates of dispersion and degradation, the occurrence of thermal inversions with lower mixing heights, and lower temperatures during this period. On the other hand, the rainy sampling period coincides with the summer season in Mexico, with higher temperatures, solar radiation values, and rain occurrence, leading to increased degradation by photochemical activity and dispersion of air pollutants. In addition, from the PCA analysis carried

Table 6 Estimated values of life time cancer risk due to benzene exposure levels (LTCR)

Sampling sites	LTCR benzene rainy season				LTCR benzene cold dry season			
	Adults determined at LLIUR	Adults determined at ULIUR	Child determined at LLIUR	Child determined at ULIUR	Adults determined at LLIUR	Adults determined at ULIUR	Child determined at LLIUR	Child determined at ULIUR
A Municipal Institute for Women	5.37×10^{-7}	1.89×10^{-6}	1.34×10^{-7}	4.75×10^{-7}	2.43×10^{-7}	8.61×10^{-7}	6.07×10^{-8}	2.15×10^{-7}
B CICEG	9.52×10^{-7}	3.37×10^{-6}	2.38×10^{-7}	8.45×10^{-7}	6.09×10^{-7}	2.16×10^{-6}	1.52×10^{-7}	5.39×10^{-7}
C Technological Institute of Leon	4.34×10^{-7}	1.54×10^{-6}	1.09×10^{-7}	3.86×10^{-7}	2.52×10^{-7}	8.93×10^{-7}	6.30×10^{-7}	2.23×10^{-7}
D IMSS-T21	5.46×10^{-7}	1.93×10^{-6}	1.37×10^{-7}	4.84×10^{-7}	4.24×10^{-7}	1.50×10^{-6}	1.06×10^{-7}	3.80×10^{-7}
E Lomas Blancas Neighborhood	4.25×10^{-7}	1.51×10^{-6}	1.06×10^{-7}	3.77×10^{-7}	5.62×10^{-7}	1.99×10^{-6}	1.40×10^{-7}	4.98×10^{-7}
F CECYT	6.22×10^{-7}	2.21×10^{-6}	1.55×10^{-7}	5.51×10^{-7}	4.80×10^{-7}	1.70×10^{-6}	1.20×10^{-7}	4.30×10^{-7}
G University of Guanajuato	5.10×10^{-7}	1.89×10^{-6}	1.27×10^{-7}	4.51×10^{-7}	4.68×10^{-7}	1.66×10^{-6}	1.17×10^{-7}	4.15×10^{-7}
H School of Medicine	5.30×10^{-7}	1.88×10^{-6}	1.32×10^{-7}	4.69×10^{-7}	5.61×10^{-7}	1.99×10^{-6}	1.40×10^{-7}	4.98×10^{-7}
I Zoo	4.35×10^{-7}	1.54×10^{-6}	1.08×10^{-7}	3.85×10^{-7}	3.68×10^{-7}	1.31×10^{-6}	9.21×10^{-8}	3.26×10^{-7}
J Colinas de Jade	3.80×10^{-7}	1.34×10^{-6}	9.50×10^{-7}	3.37×10^{-7}	2.32×10^{-7}	8.24×10^{-7}	5.81×10^{-8}	2.06×10^{-7}
Mean value LTCR	5.37×10^{-7}	1.90×10^{-6}	1.34×10^{-7}	4.76×10^{-7}	4.20×10^{-7}	1.49×10^{-6}	1.05×10^{-7}	3.72×10^{-7}

LLIUR: Lower level of the inhalation unit risk for benzene, $2.2 \times 10^{-6} (\mu\text{g}/\text{m}^3)^{-1}$

ULIUR: Upper level of the inhalation unit risk for benzene, $7.8 \times 10^{-6} (\mu\text{g}/\text{m}^3)^{-1}$

Values in bold exceeded this reference value: 1×10^{-6} , Recommended reference value of LTCR (US-EPA 2002)

out in this study, a stronger influence of vehicular emissions on BTEX concentrations was found during the cold dry season, which coincides with the winter period in Mexico. Higher T/B ratios have been reported in other urban areas

Table 7 Estimated hazard quotient (HQ) values due to exposure to BTEX levels

Sampling sites	Benzene		Toluene		Ethylbenzene		p-Xylene	
	Rainy season	Cold dry season	Rainy season	Cold dry season	Rainy season	Cold dry season	Rainy season	Cold dry season
A Municipal Institute for Women	0.0008	0.0004	0.0001	0.0001	0.00015	0.00011	0.002	0.0018
B CICEG	0.014	0.0090	0.0002	0.0003	0.00022	0.00016	0.004	0.0034
C Technological Institute of Leon	0.0060	0.0030	7.41×10^{-5}	8.81×10^{-5}	0.00014	0.00011	0.0010	0.0019
D IMSS-T21	0.0080	0.0060	0.0001	0.0001	0.00016	0.00012	0.0020	0.0023
E Lomas Blancas Neighborhood	0.0060	0.0080	9.12×10^{-5}	0.0002	0.00014	0.00014	0.0010	0.0027
F CECYT	0.0090	0.0070	0.0001	0.0002	0.00017	0.00016	0.0030	0.0037
G University of Guanajuato	0.0080	0.0070	8.6×10^{-5}	0.0001	0.00016	0.00013	0.0020	0.0025
H School of Medicine	0.0080	0.0090	4.3×10^{-5}	0.0001	0.00016	0.00014	0.0020	0.0026
I Zoo	0.0060	0.0060	9×10^{-5}	0.0002	0.00013	0.00012	0.0010	0.0021
J Colinas de Jade	0.0050	0.0040	4.9×10^{-5}	7.58×10^{-5}	0.00013	0.00011	0.0010	0.0014
Mean Value of HQ	0.0080	0.0060	0.0001	0.00015	0.00016	0.00014	0.0020	0.0025
IHQ* value for rainy season	0.0919							
IHQ* value for cold dry season	0.0864							
Recommended reference value (US EPA 2002)	1							

* Integrated Hazard Quotient

during the cold months (Hoque et al. 2008; Singh et al. 2016) due to an increase in emissions of aromatic compounds associated with cold start of gasoline-powered vehicles. These conditions, together with the seasonal characteristics of the prevailing meteorology in the study area, variations in source strength, and the differences in the removal process of atmospheric BTEX, could explain differences in the T/B ratios between the two sampling periods.

The X/Ebz ratio values are characteristic of urban areas and are in agreement with those reported by many authors in different urban areas around the world (Dehghani et al. 2018; Hazrati et al. 2016). The X/Ebz ratio is commonly used as an indicator of the photochemical age of air masses at a given site and for characterizing the distance emission sources. A ratio of 3.6:1 has been established as a typical value in urban areas (Keymeulen et al. 2001). Values of this ratio higher than 3.8 indicate aged air masses, while lower values indicate that the air masses are fresh (recent emissions) (Kuntasal et al. 2005). The X/Ebz ratios found during both sampling periods for each sampling site are shown in Fig. 5b. The average X/Ebz ratio during the rainy and cold dry seasons was 1.39 and 1.86, respectively, indicating that during both sampling periods the air masses containing BTEX came from recent emissions (fresh air masses) as a result of the combustion of liquid fuels in motor vehicle combustion engines. The highest X/Ebz ratios were found at sites B (CICEG, land-use type 4) and F (IMSS-T21, land-use type 1) during the rainy and the cold dry seasons, respectively. The lowest values were registered in site J (Zoo, land-use type 2) during both sampling periods. Even though these ratios were higher for the cold dry season compared to the rainy season, the Mann–Whitney test revealed that the differences were not significant. The X/Ebz ratios suggest local sources for atmospheric BTEX concentrations in the study area, and that long range transport is not a significant contributor.

Health risk assessment results

Life time cancer risk due to benzene exposure (LTCR) and hazard quotient values (non-cancer risk: HQ) for all measured BTEX species were estimated according to the US EPA methodology (1989, 2011), considering both child and adult populations. The LTCR values found in the present study season ranged from 1.05×10^{-7} to 1.90×10^{-6} , with an average value of 6.79×10^{-7} . For the adult population during the rainy season, LTCR values ranged from 5.37×10^{-7} to 1.90×10^{-6} . For the child population, the rainy season LTCR values ranged from 1.34×10^{-7} to 4.76×10^{-7} (see Table 6). The LTCR values found during the cold dry season ranged from 4.20×10^{-7} to 1.49×10^{-6} for adults and from 1.05×10^{-7} to 3.72×10^{-7} for children. Taking into account the upper level of the inhalation unit risk for benzene (ULIUR), these values represent a possible cancer risk for adult population at the studied

sites according to the classification proposed by Sexton and collaborators (Sexton et al. 2007) (LTCR values between 1×10^{-5} and 1×10^{-6}). According to these results, inhabitants of the study area in the city of Leon are at risk of developing cancer in their lifetime by inhalation of the measured benzene concentrations reported here. The estimated LTCR values for the infant population, at all the sampling sites during the two sampling seasons, were lower than the reference value proposed by US-EPA (2002) (1×10^{-6}). These results indicate that adult population is more vulnerable due to an increased exposure associated with a greater mobility related to their work activities. In Table 6, it can be observed that the highest LTCR values for both children and adults are found at site B: CICEG, which is located in an area classified as an industrial zone of medium intensity (IMPLAN 2017), located on an avenue with high traffic flow (Adolfo Lopez Mateos Boulevard). On the other hand, the lowest LTCR values were observed at site J: Colinas de Jade neighborhood, located in a habitable zone with low-density residential and mixed land use, characterized by urban potential that still is in development, and therefore, the mobility of the population in that area is less.

The estimated HQ values for each BTEX species during both sampling seasons are shown in Table 7. The average HQ values were 0.0080, 0.0060, 0.0001, and 0.00015 for benzene, toluene, ethylbenzene, and p-xylene, respectively, during the rainy season. During the cold dry season, the corresponding values were 0.00016, 0.00014, 0.0020, and 0.0025. All HQ values based on the measured BTEX concentrations were lower than the reference value of 1.00 established by the World Health Organization (Miri et al. 2016; Zhang et al. 2012). It can thus be concluded that the population in the study area is not at risk of suffering from diseases other than cancer (respiratory and cardiovascular diseases) due to the inhalation of the pollutants evaluated.

Regarding the integrated hazard quotient (IHQ), Leon, Guanajuato (present study) reports values similar (IHQ: 0.0919 and 0.0864 for rainy and cold dry sampling seasons, respectively) to those reported in studies carried out in Tehran, Iran (IHQ: 0.000123–0.0358) (Golghorshidi et al. 2019) and the east coast of China (0.0600–0.1400) (Zhang et al. 2015). The Leon results are higher than those reported by Dehghani and collaborators (Dehghani et al. 2019) in Iran (0.0186), but lower than those reported in Delhi, India (IHQ: 0.2576) (Kumar et al. 2018), and Kuala Lumpur, Malaysia (IHQ: 0.6221) (Latif et al. 2019). The results of the life time cancer risk due to benzene exposure (LTCR) found in this study (5.37×10^{-7} – 1.90×10^{-6} and 1.34×10^{-7} – 4.76×10^{-7} for adult and child populations, respectively, during the rainy season, and 4.20×10^{-7} – 1.49×10^{-6} and 1.05×10^{-7} – 3.72×10^{-7} for adult and child, respectively, during the cold dry season) are similar to that reported in Tehran, Iran (3.97×10^{-7}) (Miri et al. 2016), Düzce, Turkey (9×10^{-6} for a rural

area) (Bozkurt et al. 2018) and Aliaga, Turkey (12.9×10^{-6}) (Civan et al. 2015), and lower than those found in Kuala Lumpur, Malaysia (1.59×10^{-5} – 5.75×10^{-6}) (Latif et al. 2019), Delhi, India (6.1×10^{-5}) (Kumar et al. 2018), Düzce, Turkey (2×10^{-5} for an industrial area) (Bozkurt et al. 2018), Tehran, Iran (2×10^{-5}) (Nabizadeh et al. 2020a, b) and the east coast of China (1.66×10^{-5} – 3.73×10^{-5}) (Zhang et al. 2015).

Conclusions

Benzene, toluene, ethylbenzene, and p-xylene concentrations were measured for the first time in Leon city using passive samplers during two sampling seasons: rainy 2019 and cold dry 2020. BTEX concentrations showed lower levels during the rainy season, probably due to a combination of summertime photochemical degradation of BTEX and wet deposition processes. The spatial variation revealed that sites with land use characterized as industrial medium intensity and urban high-density habitable zones (mainly located at the south of the study area where multiple industries, commercial zones, and avenues with dense vehicular traffic are located) showed higher levels of BTEX concentrations. This demonstrates the need to improve the management of land use in the study area through more efficient strategies of urban planning and industrialization control. A meteorological analysis showed that transport from long distances was unlikely to be an important contributor and that the measured BTEX originated from local sources located to the southeast of the study area. This was confirmed by the BTEX ratios results (T/B and X/Ebz) which were typical of those reported in urban areas where local (fresh) vehicular emissions are the dominant source of BTEX. The statistical bi-variate analysis and the principal component analysis (PCA) showed that BTEX had strong correlations with solar radiation and temperature during both sampling periods, confirming their contribution to tropospheric ozone formation, especially during the (warmer) rainy season. During the cold dry season, PCA showed that BTEX were strongly associated with SO_2 , suggesting a contribution from combustion sources using high-sulfur fuels. BTEX levels in Leon city were similar to those reported in Tri-City, Poland, and Düzce, Turkey, but were lower than those reported in Delhi, India.

The hazard quotient (HQ) results obtained during this research indicate that the population within the study area does not face a risk of suffering from diseases other than cancer (cardiovascular or respiratory diseases). However, according to the lifetime cancer risk assessment, the population of Leon may be at risk of developing cancer sometime in their life, especially the adult population, since LTCR values exceeded the reference value established by US EPA. It is important to note that these results are an estimate of the probable risk to

public health, and the development of cancer associated with benzene inhalation will depend on other factors including the time of exposure, specific health conditions, and vulnerability of the individual, as well as synergy with other pollutants. The results of this study demonstrate the need for continuous monitoring of these pollutants. Given their health implications and potential to cause cancer in humans, these results also demonstrate the need to establish a standard that regulates the maximum permissible levels of benzene in ambient air in Mexico. This study also reveals the need to implement BTEX emission reduction policies in the study area, improve the emission control strategies of vehicular sources, introduce more sustainable transportation, and improve the quality of fuels.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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