Determination of the risk level from BTEX inhalation at a gas station in Ciudad del Carmen, Campeche

Determinación del nivel de riesgo por inhalación de BTEX en una estación de gasolina en Ciudad del Carmen, Campeche

Pérez-Vera, Joselin Itzell*[a], Cerón-Bretón, Rosa María[b], Cerón-Bretón, Julia Griselda[c] and Lara-Severino, Reyna del Carmen[d]

[a] ROR Autonomous University of Carmen • KMX-2663-2024 • 0009-0001-1273-6651 • 1307518
[b] ROR Autonomous University of Carmen • LFV-4405-2024 • 0000-0001-8647-022X • 30106
[c] ROR Autonomous University of Carmen • AGP-0379-2022 • 0000-0003-1551-7988 • 122903
[d] ROR Autonomous University of Carmen • AIB-1448-2022 • 0000-0001-6173-0187 • 357254

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The main contribution of this work is to know the current levels of BTEX in ambient air near a gas station and to determine the possible health risk associated to this exposure. Results obtained in this study deserve to be disseminated not only at a local level but also at regional and global level. Results obtained can be compared with those reported in other regions of the world. This will allow a diagnosis of the level of risk that this type of gas station in Mexico represent within a global context. The cancer risk index for benzene exposure exceeded the reference value proposed by the US EPA (LTCR $1x10^{-6}$), suggesting a significant risk, and being even higher for the child population. The overall potential for no carcinogenic effects due to BTEX exposure was determined as an HQ risk quotient. In all cases, a value of HQ<1 was obtained, indicating that the population is not exposed to a significant risk of contracting diseases other than cancer (respiratory and cardiovascular diseases) due to the daily exposure to the BTEX levels found in the study area. It is necessary to carry out more studies around the city including other climatic seasons and a greater number of sampling sites (service stations) to obtain more precise conclusions regarding the risk associated to this type of emissions.

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* ✉ [101168@mail.unacar.mx]

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Abstract

Health risks associated with inhalation of BTEX were determined near a service station in Ciudad del Carmen, Campeche. BTEX levels and meteorological parameters were measured in the ambient air of an urban site during the dry season. Samples were analyzed by GC with FID detection. The BTEX showed high concentrations during sampling B1. The X/E and B/T ratios indicate that the emissions were recent, of local origin and from vehicle and service station emissions. The cancer risk index for benzene exposure exceeded the guideline value proposed by the US EPA, suggesting significant risk. The overall potential for non-carcinogenic effects was determined as a hazard ratio (HQ). The value of HQ<1 indicates that the population is not exposed to a significant risk of contracting diseases other than cancer.

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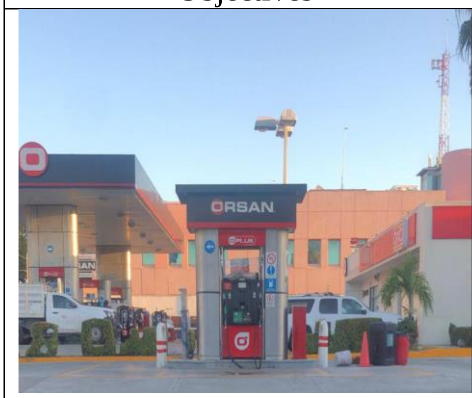
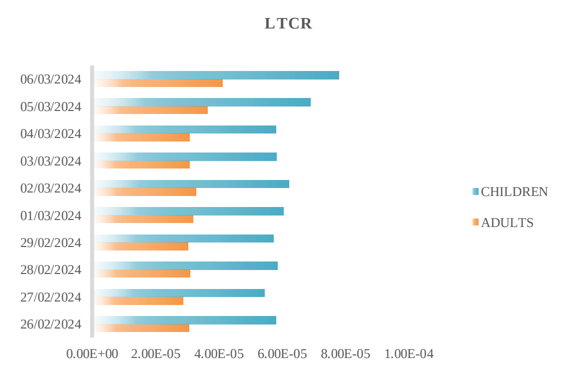
Objectives	Methodology	Contribution
 	 	

BTEX, Health risk, Gas station

Resumen

Se determinaron riesgos para la salud asociados con la inhalación de BTEX cerca de una estación de servicio en Ciudad del Carmen, Campeche. Se midieron niveles de BTEX y parámetros meteorológicos en el aire ambiente de un sitio urbano durante la estación seca. Las muestras se analizaron por CG con detección FID. Los BTEX mostraron altas concentraciones durante el muestreo B1. Las relaciones X/E y B/T indican que las emisiones fueron recientes, de origen local y proveniente de emisiones de vehículos y de la estación de servicio. El índice de riesgo de cáncer por exposición al benceno excedió el valor de referencia propuesto por EPA de EE. UU. lo que sugiere riesgo significativo. El potencial general de efectos no cancerígenos fue determinado como índice de riesgo (HQ). El valor de HQ<1, indica que la población no está expuesta a un riesgo significativo de contraer enfermedades distintas al cáncer.

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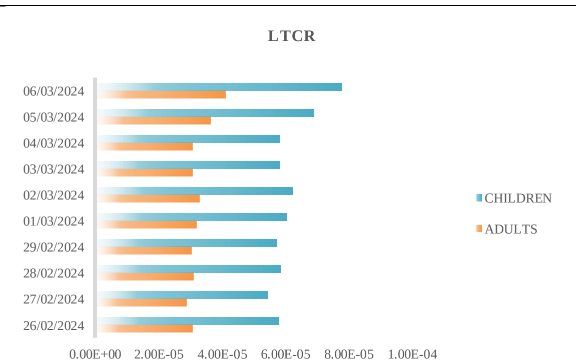
 	 	

BTEX, Riesgo a la salud, Estación de gas

Introduction

The World Health Organization (WHO) reports that 99% of the global population breathes air that exceeds the recommended limits for health protection due to high levels of contaminants. This exposure is particularly high in low- and middle-income countries, including Mexico (WHO, 2023). The WHO's global burden of disease report identifies exposure to air pollutants as the main environmental risk leading to premature mortality. In 2019, there were 48,331 deaths attributable to air pollution in Mexico (IHME, 2019; ONU, 2021; SEMARNAT, 2024), making air pollution the primary environmental risk to health, causing around 7 million premature deaths annually.

A recent World Bank publication revealed that air pollution cost the world approximately $8.1 trillion in 2019, equivalent to 6.1% of global GDP. Over 95% of air pollution-related deaths occur in developing countries, with the economic burden of premature mortality and morbidity equivalent to 5-14% of GDP in these nations. Furthermore, the impact of air pollution on health surpasses that of other well-known risk factors like chronic diseases such as high blood pressure, diabetes, tobacco use, obesity, high cholesterol, and malnutrition (State of Global Air, 2019).

Volatile organic compounds (VOCs) are a group of chemical compounds emitted from highly volatile liquids at room temperature and from industrial processes (FAO & UNEP, 2022). These compounds and their reaction products pose an unacceptable risk to public and occupational health and biological and physical environments (Bloemen & Burn, 1993). Studies worldwide have reported that BTEX (benzene, toluene, ethylbenzene, and the three isomers of xylene) are potentially dangerous for the environment and human health (Campos-Candel, Llobat-Estelles & Mauri-Aucejo, 2007). While these compounds can be released from natural sources like forest fires, the majority are emitted by human-related activities such as oil and natural gas extraction and combustion, petrochemical activities, and various industrial processes. Due to their volatile nature, humans are primarily exposed to VOCs through inhalation. Both chronic and acute exposure can have serious health consequences, including neurological diseases, cancer, and teratogenic effects (ATSDR, 2004; Ma et al, 2024; Chaiklieng et al, 2024; Baghani et al, 2024; Hosseinpour et al, 2024). The World Health Organization (WHO) estimates that exposure to 1 mg/m^3 of benzene puts 4 in 1 million people at risk of developing leukemia during their lifetime (PAHO & WHO, 2012).

Background

The presence of BTEX compounds in the atmosphere is concerning because there are no established maximum limits for these pollutants. As a result, there is a lack of continuous or systematic measurements of these contaminants in Mexico. To address this, we need to establish a theoretical framework by reviewing the available regulatory standards and examining results from other national and international studies. Criterion pollutants have well-established limits and extensive information on their sources and health impacts. In contrast, non-criterion pollutants, like BTEX compounds, are not as well studied and lack sufficient information for regulatory frameworks. Therefore, it is necessary to conduct a health risk assessment to determine if the levels of BTEX in a specific area are acceptable or pose a risk to public health and well-being (Comisión Federal para la Protección contra Riesgos Sanitarios, 2017).

Regulations for non-criterion pollutants

The current regulations in our country only address criterion pollutants. However, no Mexican regulation sets the Maximum Permissible Limit (MPL) for BTEX pollutants released into the air. There are official Mexican standards that focus on recognizing, evaluating, and controlling chemical agents in the workplace and for occupationally exposed personnel (POE). Since no standard indicates maximum exposure values, international organisms such as the World Health Organization (WHO), the National Institute for Occupational Safety and Health (NIOSH), and some foreign government agencies are frequently consulted. WHO (2005) developed the Global Air Quality Guidelines (GCA) for the entire world. These guidelines were created to minimize the health effects of air pollution and contain recommendations for indicative levels of air quality and targets for the six major air pollutants.

Table 1 shows the reference values established by NIOSH for the concentrations of non-criterion contaminants, specifically BTEX compounds.

Box 1

Table 1

Maximum Permissible Limits for exposition to BTEX

Pollutant	Maximum Permissible Limits	Source
Benzene	1 ppm, 3.25 mg/m^3 , 24 h	NIOSH, 1976
Toluene	100 ppm, 375 mg/m^3, 10 h	NIOSH, 1973
Ethylbenzene	100 ppm, 435 mg/m^3, 10 h	OSHA, 2021
O-Xylene	100 ppm, 435 mg/m^3, 10 h	NIOSH, 2014
m-Xylene	100 ppm, 435 mg/m^3, 10 h	NIOSH, 2014
p-Xylene	100 ppm, 435 mg/m^3, 10 h	NIOSH, 2014

Source: Own elaboration

National Background

In previous studies, García et al. (2014) conducted research on the emission of BTEX at gas stations in Ensenada, Baja California, Mexico. The selected sites were in areas with high population density and vehicular traffic, and a total of 37 service stations were studied. The study measured the annual BTEX concentrations (tons per year) in Ensenada, Baja California, Mexico in 2014, and the results are summarized in Table 2.

Box 2

Table 2

Annual concentrations of BTEX (Tons per year) Ensenada, Baja California, Mexico (2014)

Year	**Benzene**	**Toluene**	**Ethylbenzene**	**mp-Xylene**	**o-Xylene**
2010	18.17	54.99	0.078	3.35	1.40
2011	17.70	53.57	0.075	3.26	1.36
2012	14.40	43.58	0.061	2.65	1.11

García et al. (2014) concluded that human exposure to volatile organic compounds, such as benzene, toluene, and xylene (BTEX), has various effects on the short and long-term health of men, women, and children. These compounds can interact with the genome and epigenome during cell division in somatic and germ cells. The presence of gas stations in urban areas leads to BTEX emissions, which are associated with a higher risk to the population's health (García et al. 2014). The study used a Geographic Information System (GIS) methodology, employing ARC/INFO for digitization and ArcView for visualization and attribute creation. The resulting maps indicated a higher presence of BTEX in areas closest to the service stations. García et al. (2014) suggested that the high BTEX emissions at Ensenada gas stations may be due to the absence of a vapor removal and recovery system in the gasoline delivery pumps at the service stations, rather than in the fuel transfer from the pipes to the storage tanks.

On the other hand, Cerón et al, (2018) conducted a study in the city of Tijuana, Baja California, Mexico, to characterize and determine the sources of aromatic hydrocarbons (BTEX). Samples were collected over four sampling periods, resulting in a total of 24 samples during January 2017 (See Table 3).

Box 3

Table 3

Mean Concentrations of BTEX (μg/m^3) in Tijuana, Baja California, Mexico (January 2017)

Site	**Benzene**	**Toluene**	**Ethylbenzene**	**p-Xylene**
Tijuana, Baja California México (μg/m^3)	32.40	13.28	7.02	17.16

The levels of BTEX compounds at the study site followed a daily pattern, with the highest concentrations occurring during the morning and afternoon sampling periods. Benzene was found to be the most abundant aromatic compound, followed by p-Xylene, toluene, and ethylbenzene. Analysis showed that vehicular traffic was the main source of benzene, toluene, and p-xylene during the sampling period, and that toluene and p-xylene could contribute to tropospheric ozone. Meteorological analysis revealed that BTEX levels were influenced by local and fresh emissions, particularly from vehicle traffic (Cerón et al., 2018).

Cerón et al. (2020) assessed the health risk associated with BTEX levels in the ambient air at the CICEG monitoring station, in an industrial area with the highest population density in the state of Guanajuato, Mexico. BTEX samples were collected three times a day for a week during both summer and autumn, resulting in a total of 48 samples (refer to Table 4).

Box 4

Table 4

Mean Concentration of BTEX (μg/m^3) in Leon, Guanajuato (2020)

Season	Benzene	Toluene	Ethylbenzene	Xylene
Summer and Autumn (μg/m^3)	1.73	11.85	11.86	3.31
Summer (μg/m^3)	2.633	15.78	15.28	3.46

The Mann-Whitney test showed significant differences in BTEX concentration between summer and autumn. The test also revealed significant differences in wind speed, direction, and temperature between the two seasons, suggesting that air masses from different directions could contribute to BTEX levels, influenced more by local and regional sources such as industrial emissions and vehicular traffic rather than by photochemical activity. BTEX levels were higher in summer due to higher wind speeds. The estimated cancer risk (LTCR values) for adults and children ranged from 5.26×10^{-6} to 4.33×10^{-5}, exceeding the limit values set by the US EPA (1×10^{-6}) and the World Health Organization (WHO) (1×10^{-5}) (Cerón, et al., 2020).

In another study by Estéves et al. (2015) in Orizaba, Veracruz, BTEX levels in ambient air and the carcinogenic risk levels of benzene in an urban site were determined during the autumn season, with a total of 36 samples collected (See Table 5).

Box 5

Table 5

Mean Concenration of BTEX (μg/m^3) in Orizaba, Veracruz (2015)

Site	Benzene	Toluene	Ethylbenzene	Xylene
Orizaba, Veracruz, Mexico (μg/m^3)	74.51	5.33	2.26	3.35

The authors found that BTEX levels were significantly affected by winds from the south and south-southeast, primarily due to emissions from the Veracruz-Mexico highway, indicating that these compounds mainly came from vehicular sources. The PCA analysis revealed that Benzene was strongly influenced by vehicle emissions. The results for Benzene exceeded the maximum permissible limits set in Europe and the United States. The average daily exposure at the study site was 22.83 x10^{-3} mg/kg per day.

The lifetime benzene cancer risk (LTCR) was 68 x 10^{-5}, surpassing the acceptable LTCR value of 1 x 10^{-6} for adults, as per the US EPA. The authors emphasized that the potential for cancer risk due to environmental benzene exposure through inhalation should be a concern for health authorities in the region of Orizaba, Veracruz, Mexico. In terms of non-cancer risk, HQ values ranged from 2.483 to 3.038, exceeding the limit set by the US EPA, which suggests that contaminants may pose a risk of producing cardiovascular and respiratory effects, among others, if the HQ value exceeds 1.

Justification

The rapid population growth, expansion of urban areas, and increased utilization of natural resources, energy, and transportation lead to the release of pollutants into the air of many cities worldwide (Lan & Minh, 2013). Air pollution disrupts ecosystems and results in economic and social costs, as well as significant health risks to humans at local and regional levels globally. In 2019, according to the World Health Organization (WHO), outdoor air pollution, in both urban and rural areas was estimated to cause 4.2 million premature deaths annually worldwide. This mortality is attributed to exposure to fine particles, which contribute to cardiovascular and respiratory diseases, as well as various types of cancer (WHO, 2022).

In 2019, the World Health Organization (WHO) estimated that outdoor air pollution contributed to 37% of premature deaths from ischemic heart disease and stroke, 18% from chronic obstructive pulmonary disease, 23% from acute lower respiratory tract infections, and 11% from respiratory tract cancer. This highlights the importance of monitoring ambient air quality. Volatile organic compounds (VOCs) are some of the most dangerous air pollutants (Bloemen & Burn, 1993; FAO & UNEP, 2022). Evaluating VOCs is crucial in understanding atmospheric pollution due to their high volatility, fat solubility, toxicity, and flammability. They are highly reactive and contribute to ozone formation and, consequently, to climate change (Finlayson & Pitts, 1993). Benzene, toluene, ethylbenzene, and o-, p-, and m-xylene (BTEX) are among the VOCs emitted into the atmosphere from both anthropogenic and biogenic sources and can also be formed photochemically (FAO & UNEP, 2022). Studies have shown that in densely populated and industrialized cities, BTEX can significantly contribute to the total VOCs in the atmosphere (Yalcin et al., 2020).

The monoaromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes can cause various health issues such as asthma, dizziness, fatigue, and irritation of the eyes, nose, and throat. Nausea and other non-specific symptoms have also been linked to BTEX exposure (US EPA 1987, 1991). Humans are exposed to BTEX through the respiratory system or skin contact (Li et al., 2014). In developing countries like ours, it's common to employ attendants to pump fuel at service stations. These attendants come into direct contact with vehicles using multi-octane unleaded fuels, lead substitute gasoline, and diesel, putting them at risk of inhaling volatile organic compounds (VOCs) released by these fuels. The released contaminants include benzene, toluene, ethylbenzene, and xylenes (BTEX), which are highly toxic. As a result, service station personnel experience long-term exposure, leading to adverse health effects and potential environmental impact. As a result, this study aims to analyze the daily variation of BTEX levels in the ambient air of a service station (gas station) during the dry season using active samplers.

Methodology

Study Site

The study site is located in the State of Campeche, in the southeastern region of Mexico. It shares borders with the State of Yucatan to the North, the state of Quintana Roo and Belize to the East, the Republic of Guatemala to the South, and the state of Tabasco and the Gulf of Mexico to the West. The state covers an area of 57,507 km^2 and has a total population of 928,363 inhabitants, which represents 0.7% of the country's total population (INEGI, 2020). The predominant climate in the state is warm subhumid in approximately 92% of its territory, while 7.75% has a warm humid climate, mainly in the Eastern and Northern parts. A small percentage of 0.05% has a semi-dry climate. The average annual temperature ranges from 26 to 27°C, with the highest temperature frequently exceeding 30°C and the minimum at 18°C. Rainfall is abundant, varying between 1200 and 2000 mm annually, except in the Northern region with a semi-dry climate, where it is around 800 mm per year (INEGI, 2020).

Ciudad del Carmen is the main city in the municipality of Carmen, in the state of Campeche. It is situated in the Southwestern part of the Yucatan peninsula, on the Western side of the Island of Carmen, between the Gulf of Mexico and the Terminos Lagoon. The primary economic activity in the city is the production and extraction of oil. Ciudad del Carmen is also recognized as the leading port in the country for transporting personnel and materials to the oil platforms of the Campeche Sound. Currently, it has 20 service stations supplying gasoline and diesel, benefiting the population, and over 100 companies operating in the area, which, in turn, have environmental effects due to the consumption of these fuels.

In this study, we will assess the levels of BTEX in the ambient air of an area affected by urban and oil activities in the municipality of Carmen, Campeche. The sampling site was chosen at a service station (gas station) that is frequently visited by motorists and other means of transportation. The sampling site's location is presented in Figure 1.

Box 6

Figure 1
Location of the sampling site

Sampling

Active sampling of ambient air was conducted using the "Determination of aromatic hydrocarbons (benzene, toluene, ethylbenzene, p-xylene, 1, 2, 4-trimethylbenzene) in air - Activated carbon adsorption method/Gas chromatography" method, which is approved by the National Institute of Safety and Hygiene at Work (INSHT) (MTA/MA-030/A92) (INSHT, 1995). A total of 30 samples of ambient air were gathered in glass tubes containing activated carbon brand 226-01 Anasorb CSC from SKC. These tubes are 7 cm in length, with an external diameter of 6 mm and an internal diameter of 4 mm. Each tube contains two sections of activated carbon separated by a 2 mm portion of polyurethane foam (see Figure 2). It is important to note that the tubes should have well-fitting polyethylene caps to prevent leaks and contamination during the transport and storage of the samples.

Box 7

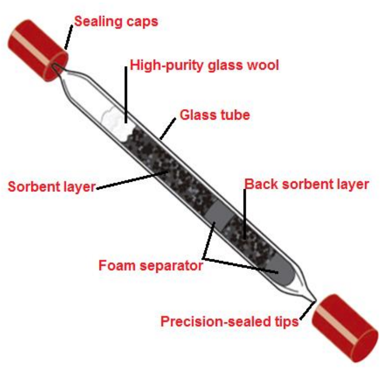


Figure 2
Characteristics of the active sampling tubes

Ambient air was drawn through a GAST-type vacuum pump at a controlled flow rate of 200 ml/min through horizontally placed tubes. The ends of both sections were broken, and section 2 (containing 50 mg of activated carbon) was securely positioned on a rubber or plastic tube holder of suitable length and diameter. The tube was covered with aluminum foil to prevent photochemical reactions and interference when reading the samples. The process of obtaining ambient air samples was conducted during three time periods based on diurnal variation: morning B1 (7:00 a.m. to 8:00 a.m.), midday B2 (12:00 p.m. to 1:00 p.m.), and afternoon B3 (5:00 p.m. to 6:00 p.m.), each lasting 1 hour. A total of 30 samples were collected over 10 sampling days in the 2024 dry season. After each sampling, the tubes were covered, labeled, and stored in special bags to prevent direct sunlight exposure and potential photochemical reactions. Subsequently, they were refrigerated to preserve them for no more than 20 days until analysis at the Environmental Protection laboratory of the Autonomous University of Carmen (UNACAR).

Chemical Analysis

The chemical analysis was conducted at the Environmental Protection Laboratory of the Autonomous University of Carmen following the method established by the National Institute of Safety and Hygiene of Spain MTA/MA-030/A92 (INSHT, 1995). Calibration curves were prepared using reagent-grade solutions of 99.98% purity from the Sigma-Aldrich brand. After this, chemical desorption was carried out, by using 2 ml amber vials with lids and septa. These vials were labeled and subjected to pre-treatment by rinsing with distilled water and then dried. A small amount of HPLC-grade carbon disulfide was added as an adsorbent reagent, allowing it to dry to avoid contamination of the samples with impurities. After pre-treatment, desorption was carried out by carefully breaking the end of section 1 of the tube to remove the glass wool using a metal clamp. The material was then emptied into the vial, and 2 ml of CS_2 was added. The vial was closed, and the steps were repeated for section 2 and for each sample. After closing the vials, they were shaken vigorously for 5 minutes and refrigerated for a maximum of 24 hours before analysis by gas chromatography.

Statistical Analysis

Statistical analysis on the BTEX concentration data and meteorological data was conducted by using the Excel statistical package XLSTAT version 2019. Several statistical tools were using, including:

1. Pearson correlation to identify relationships between BTEX, criterion pollutants, and meteorological variables.
2. Principal component analysis (PCA) to explain the variance and discover the structure of the data set. PCA results help identify whether a contaminant is secondary or primary, or to identify the specific source of the contaminants.
3. Friedman non-parametric tests ($\alpha = 0.05$) to evaluate the differences between the sampling periods of the concentrations of atmospheric pollutants measured. This helps determine whether the data studied come from the same population and if there is significant diurnal variation.
4. Box plot to display the descriptive statistics of the results obtained, including the concentrations, means, maximum, and average of each of the aromatic hydrocarbons. This allows for easy identification of the contaminant with the highest average concentrations and any diurnal pattern or trend during sampling.

Meteorological Analysis

Wind analysis was performed to determine the places where the BTEX emissions probably came from. Windrose program and Google Earth were used to create wind roses and to identify potential emission sources based on wind direction over ten sampling days. Then, Excel was used to estimate the average wind direction during morning, afternoon, and night for the sampling period. Additionally, the HYSPLIT trajectory model from the National Oceanic and Atmospheric Administration (NOAA) was applied to estimate air mass trajectories and to identify regional influences. Finally, Radar Chart were obtained to visually represent the possible origin of BTEX concentrations (NOAA, 2024).

Health Risk Analysis

The carcinogenic potential of benzene is well known (Moolla et al., 2015). The European Union recommends an annual limit of 5 µg m^{-3} for benzene in ambient air, while the USEPA establishes a value of 4.0 ppbV for this contaminant (US EPA, 2012). To determine the daily exposure (E), the cancer risk potential (LTCR), and the non-cancer risk potential (HQ), we used the methodology proposed by Zhang et al. (2012). The daily exposure (mg/kg per day) of an individual by inhalation can be calculated as follows:

$$E = \frac{C*Ira*Da}{Bwa} \quad (1)$$

Where:
C (mg/m^3), is the mean concentration of benzene
Ira, is the inhalation rate for an adult person (0.83 m^3/hr) (US EPA, 1998)
Da, is the exposure duration for an adult (24 hr/día)
Bwa, is the mean weight for an adult -- 65 kg -- (US EPA, 1998)

In addition, the lifetime cancer risk (LTCR) is calculated as follows:

$$LTCR = E * SF \quad (2)$$

Where:
E, is the daily exposure for a person by inhalation
SF, is the slope factor for benzene toxic inhalation risk when considering the linear carcinogenic effect due to exposure. The proposed SF value for benzene (0.029 kg/mg per day) was based on US EPA 2012.
Finally, the non carcinogenic risk of BTEX was estimated as a risk quotient (HQ):

$$HQ = \frac{C}{Rfc} \quad (3)$$

Where:
C, is the daily mean concentration (µg/m^3)
Rfc, is the reference concentration of inhalation, proposed by U.S. EPA for benzene (0.03 µg/m^3), toluene (5 µg/ m^3), ethylbenzene (1 µg/m^3) and xylene (0.1 µg/m^3) (USEPA, 2012).

Results

Descriptive Statistic

In the case of Benzene, the average concentration in schedule B1 was 3.88 µg/m^3, with maximum and minimum values of 6.51 and 3.10 µg/m^3, respectively, and a standard deviation of 0.96 µg/m^3. For schedule B2, the average concentration was 3.34 µg/m^3, with maximum and minimum values of 3.95 and 3.07 µg/m^3, respectively, and a standard deviation of 0.29 µg/m^3. Lastly, for schedule B3, the average concentration was 3.45 µg/m^3, with maximum and minimum values of 4.43 and 3.18 µg/m^3, respectively, and a standard deviation of 0.37 µg/m^3. Figure 3 (a) illustrates the descriptive statistics for benzene concentrations during the 3 sampling times at the study site. It is evident that benzene concentrations were significantly higher during sampling period B1, which corresponds to the time from 07:00 to 08:00 hrs.

Box 8

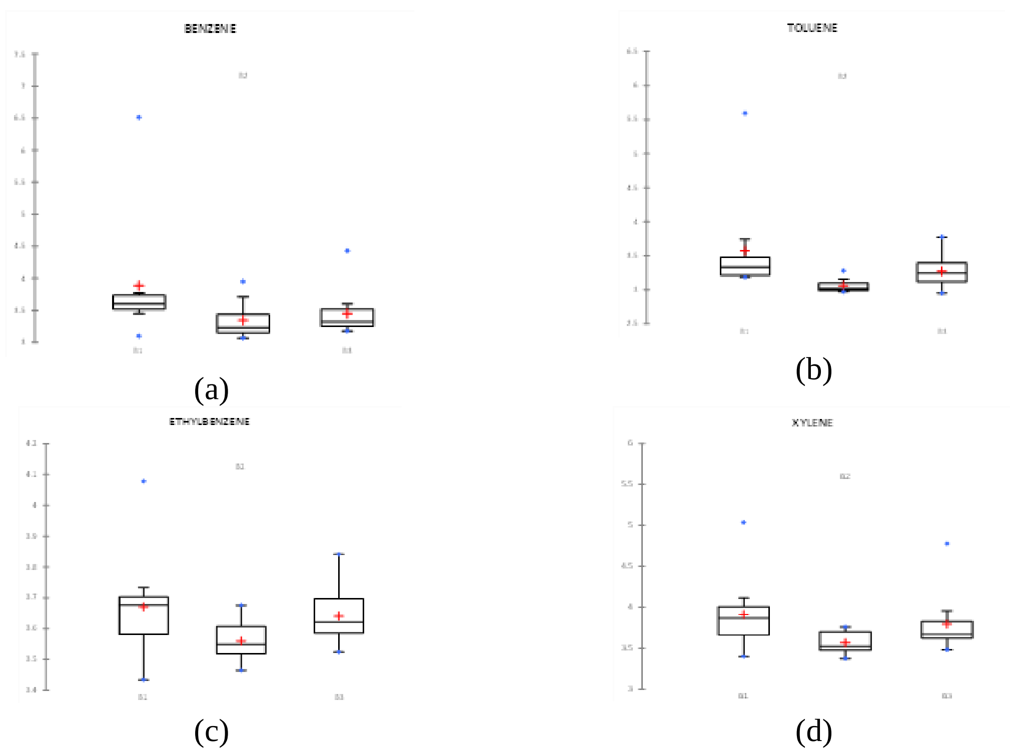


Figure 3

Descriptive Statistic for (a) Benzene, (b) Toluene, (c) Ethylbenzene and (d) Xylene

To assess the significance of these differences, a hypothesis test was conducted. Normality testing of the benzene concentration data obtained at three different sampling times indicated that they follow a normal distribution. Therefore, Levene's inferential statistical test was used to determine the significance of the observed differences in benzene concentration at different sampling times.

The null hypothesis Ho states that the variances are identical, while the alternative hypothesis suggests that at least one of the variances is different from the other. In this case, the calculated p-value exceeded the significance level alpha=0.05. Therefore, the null hypothesis should be accepted, and the alternative hypothesis rejected. In other words, it can be inferred that no significant differences were found between benzene concentrations at different sampling times.

For Toluene, the average concentration in schedule B1 was 3.57 µg/m^3, with maximum and minimum values of 5.59 and 3.18 respectively, and a standard deviation of 0.73 µg/m^3. In schedule B2, the average concentration was 3.06 µg/m^3, with maximum and minimum values of 3.28 and 2.97 respectively, and a standard deviation of 0.10 µg/m^3. Lastly, for schedule B3, the average concentration was 3.27 µg/m^3, with maximum and minimum values of 3.78 and 2.95 respectively, and a standard deviation of 0.24 µg/m^3.

Figure 3 (b) shows the descriptive statistics for toluene concentrations at the study site during the 3 sampling times. Similar to benzene, the concentrations of toluene were notably higher during sampling period B1, which corresponds to the time from 07:00 to 08:00 hrs.

In order to determine if the differences in the concentration of toluene at different sampling times are statistically significant, a hypothesis test was conducted. The normality test of the concentration data for toluene during the 3 sampling times indicated that they do not follow a normal distribution. Therefore, the Friedman non-parametric test was used to determine the significance of the observed differences in the toluene concentration at different sampling times.

Based on the established null hypothesis Ho (the samples come from the same population) and the alternative hypothesis (the samples do not come from the same population), in this case, the calculated p-value was less than the significance level alpha=0.05. As a result, the alternative hypothesis should be accepted, and the null hypothesis rejected. Therefore, it can be concluded that the differences found between toluene concentrations at the different sampling times were significant.

For Ethylbenzene in schedule B1, the average concentration was 3.67 µg/m3, with maximum and minimum values of 4.08 and 3.44 µg/m3, respectively, and a standard deviation of 0.17 µg/m3. For schedule B2, the average concentration was 3.56 µg/m3, with maximum and minimum values of 3.68 and 3.47 µg/m3, respectively, and a standard deviation of 0.06 µg/m3. Finally, for schedule B3, the average concentration was 3.64 µg/m3, with maximum and minimum values of 3.84 and 3.52 µg/m3, respectively, and a standard deviation of 0.10 µg/m3.

The descriptive statistics in Figure 3 (c) show the concentrations of ethylbenzene during the 3 sampling times at the study site. Similar to benzene and toluene, the concentrations of ethylbenzene were notably higher during sampling period B1, which is from 07:00 to 08:00 hrs. To determine if these differences are statistically significant, a hypothesis test was conducted. The concentration data for ethylbenzene during the 3 sampling times were found to follow a normal distribution, and Levene's inferential statistical test was used to ascertain if the differences in ethylbenzene concentration at different sampling times are significant.

In this study, we set the null hypothesis Ho: the variances are identical, and the alternative hypothesis Ha: At least one of the variances is different from the other. After analyzing the data, the calculated p-value was greater than the significance level alpha=0.05. Therefore, we should accept the null hypothesis and reject the alternative hypothesis. This means that no significant differences were found between the concentrations of ethylbenzene at the different sampling times.

For Xylene in schedule B1, the average concentration was 3.91 µg/m^3, with maximum and minimum values of 5.03 and 3.40, respectively, and a standard deviation of 0.46 µg/m^3. In schedule B2, the average concentration was 3.57 µg/m^3, with maximum and minimum values of 3.76 and 3.37, respectively, and a standard deviation of 0.14 µg/m^3. Lastly, in schedule B3, the average concentration was 3.79 µg/m^3, with maximum and minimum values of 4.78 and 3.48, respectively, and a standard deviation of 0.37 µg/m^3. Figure 3 (d) provides the descriptive statistics for xylene concentrations during the 3 sampling times at the study site. Similar to benzene, toluene, and ethylbenzene, the concentrations of xylene were significantly higher during the sampling period B1, which corresponds to the time from 07:00 to 08:00 hr.

In order to determine if the differences in xylene concentration at different sampling times are statistically significant, a hypothesis test was conducted. The normality test of the concentration data for xylene during the 3 sampling times showed that they follow a normal distribution. Subsequently, Levene's inferential statistical test was applied to assess the significance of the observed differences in xylene concentration at different sampling times.

In this study, the null hypothesis (Ho) was that the variances are identical, while the alternative hypothesis (Ha) suggested that at least one of the variances was different from the other. After analyzing the data, it was found that the calculated p-value was greater than the significance level (alpha=0.05). Therefore, we accept the null hypothesis and reject the alternative hypothesis. In other words, we can conclude that there were no significant differences found between the xylene concentrations at the different sampling times.

Meteorological Analysis

From Figure 4, it can be observed that the prevailing wind direction was from SE.

Box 9

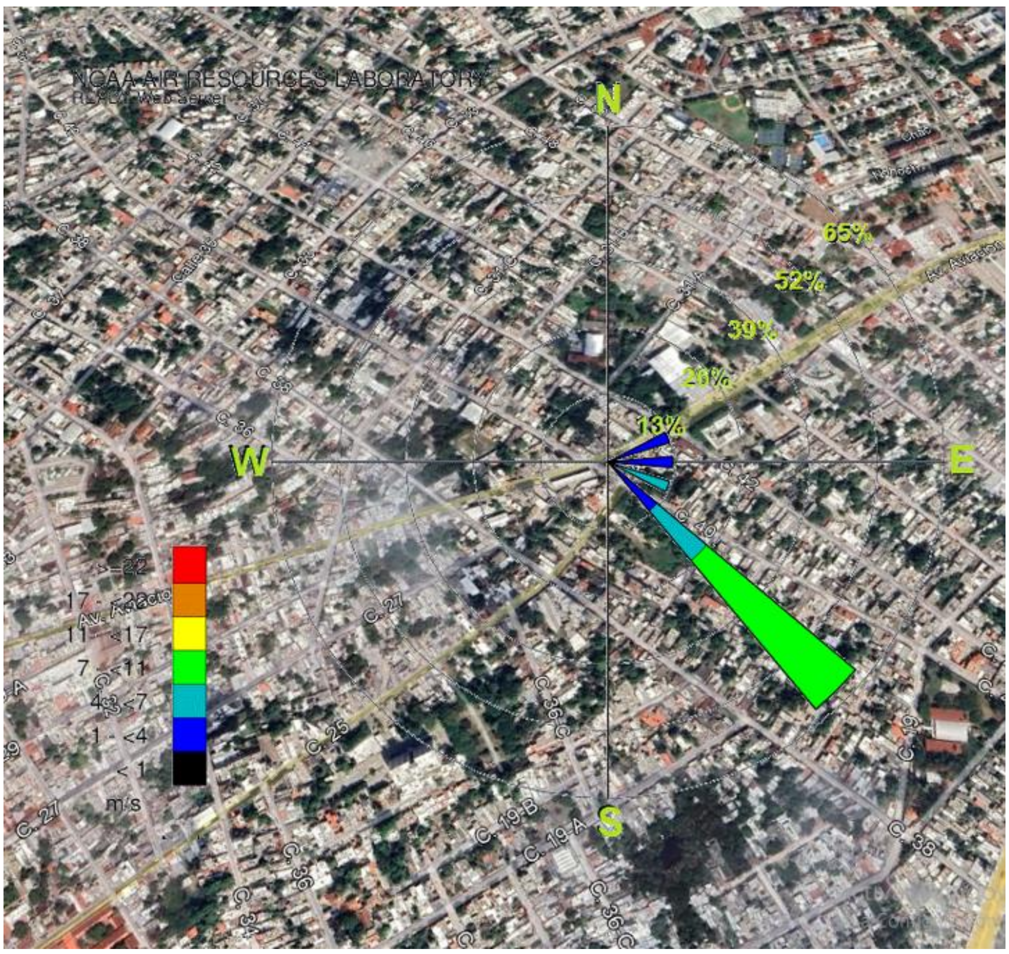


Figure 4

Prevailing wind direction in the sampling site

In Figure 5, the wind roses are plotted against the concentration for each of the BTEX compounds. Figures 5 (a-d) indicate that the concentrations of all BTEX compounds were higher when the wind blew from the southeast to the northwest.

Box 10

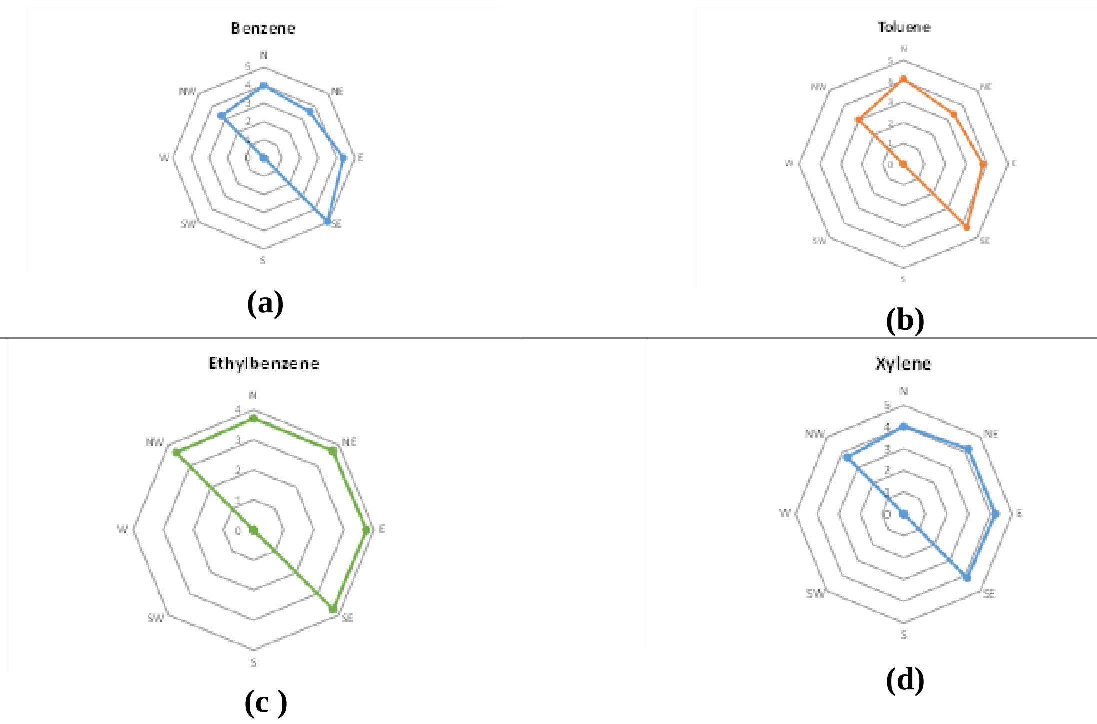


Figure 5

Wind roses vs concentration in the sampling site for (a) benzene, (b) toluene, (c) ethylbenzene and (d) xylene

Bivariate Analysis and Principal Components Analysis

To identify significant correlations between the BTEX compounds and the meteorological variables, we conducted a bivariate analysis using Pearson correlation (see Table 6).

From Table 6, we observed the following significant correlations: toluene-benzene (0.972), benzene-ethylbenzene (0.825), toluene-ethylbenzene (0.934), benzene-xylene (0.868), toluene-xylene (0.960), and xylene-ethylbenzene (0.997). It's important to note that the correlation between BTEX compounds in ambient air can vary based on factors such as emission sources, atmospheric conditions, and geographic location. These volatile organic compounds (VOCs) are commonly found in the air due to industrial, automotive, and other human-made sources.

BTEX compounds can be released into the air during processes such as incomplete combustion of fossil fuels, vehicle emissions, and various industrial activities. The correlation between these compounds may differ depending on the emission source. For instance, in urban areas with heavy traffic, the correlation is likely to be higher due to vehicle emissions. However, in industrial areas where toluene-containing solvents are used, the correlation may be different. It's crucial to note that although BTEX compounds may be correlated in certain situations, they may also have independent emission sources and different atmospheric behaviors. Additionally, each compound has different effects on human health.

Correlations between temperature-pressure (0.454), humidity-benzene (0.789), humidity-toluene (0.910), humidity-ethylbenzene (0.998), and humidity-xylene (0.990) were observed. Studies have shown that humidity can influence the volatility and transfer rate of BTEX compounds between air and other environmental matrices, such as soil and water. Furthermore, humidity can impact the atmospheric oxidation processes of these compounds, which can affect their concentrations in the air. However, the relationship between atmospheric humidity and BTEX concentration may not be direct and can be influenced by other factors such as temperature, human activity, local emission sources, and meteorological conditions. Therefore, while there may be a significant correlation in certain contexts or conditions, it's important to consider all these factors before generalizing this relationship. The ambient temperature had significant inverse correlations with benzene (-0.982), toluene (-0.999), ethylbenzene (-0.917), and xylene (-0.946). This means that as the temperature increases, the concentration of volatile organic compounds (VOCs) such as BTEX (benzene, toluene, ethylbenzene, and xylenes) in the ambient air decreases. This inverse relationship is due to several factors:

1. *Volatility:* BTEX compounds are highly volatile, so they evaporate more easily at higher temperatures. This leads to a greater release of BTEX from natural and human-made sources into the air.
2. *Atmospheric Stability:* Weather conditions, including temperature, can affect atmospheric stability. Higher temperatures can lead to thermal inversions, trapping contaminants near the ground and increasing their concentrations.
3. *Chemical Reactions:* Higher temperatures can trigger chemical reactions in the atmosphere that either produce or degrade BTEX, thus influencing their concentrations in the air.

It's important to consider that the relationship between ambient temperature and BTEX concentration can be influenced by various factors, such as season, geographic location, local emission sources, and specific meteorological conditions. While we generally expect an inverse correlation between temperature and BTEX concentration in ambient air, this relationship can vary in different contexts.

Additionally, there were correlations found between pressure and benzene (-0.277), pressure and toluene (-0.493), pressure and ethylbenzene (-0.772), pressure and xylene (-0.717), humidity and temperature (-0.891), and humidity and pressure (-0.809). The correlation between atmospheric pressure and the concentration of BTEX compounds in ambient air may be inverse in certain cases, but it's important to note that this relationship can be more complex due to the influence of multiple factors. For example, atmospheric stability, influenced by atmospheric pressure, can also affect the concentration of BTEX in the air. Under high-pressure conditions, thermal inversions are more likely to form, trapping contaminants near the ground and increasing their concentrations. The inverse correlation between pressure and humidity indicates that high-pressure systems are associated with low humidity, while low pressures are accompanied by high humidity, which is a characteristic phenomenon of the atmosphere.

Box 11

Table 6

Pearson correlation matrix between BTEX concentrations and meteorological variables in the sampling site

Variables	Benzene	Toluene	Ethylbenzene	Xylene	Temperature	Pressure (Hpa)	Humidity
Benzene	1	0.972	0.825	0.868	-0.982	-0.277	0.789
Toluene	0.972	1	0.934	0.960	-0.999	-0.493	0.910
Ethylbenzene	0.825	0.934	1	0.997	-0.917	-0.772	0.998
Xylene	0.868	0.960	0.997	1	-0.946	-0.717	0.990
Temperature	-0.982	-0.999	-0.917	-0.946	1	0.454	-0.891
Pressure (Hpa)	-0.277	-0.493	-0.772	-0.717	0.454	1	-0.809
Humidity	0.789	0.910	0.998	0.990	-0.891	-0.809	1

Principal component analysis (PCA) on the BTEX concentration data collected at the sampling site was carried out. The analysis revealed that 2 factors were sufficient to explain the variability of the data. Factor F1 contributed the greatest proportion (86.77%) to the total observed variability. In Factor 1, benzene, toluene, ethylbenzene, xylene, temperature, and humidity were grouped together, while atmospheric pressure was grouped in Factor 2 (Table 7).

Box 12

Table 7

Results of the Principal Components Analysis (PCA) for the sampling site

	F1	**F2**
Own value	6.074	0.926
Variability (%)	86.774	13.226
% accumulated	86.774	100.000

Figure 6 displays the biplot of the PCA analysis. There is noticeable clustering between BTEX compounds and humidity, as well as a significant inverse correlation between BTEX compounds and temperature. Additionally, there is a significant inverse correlation between atmospheric pressure and xylene, ethylbenzene, and humidity.

Box 13

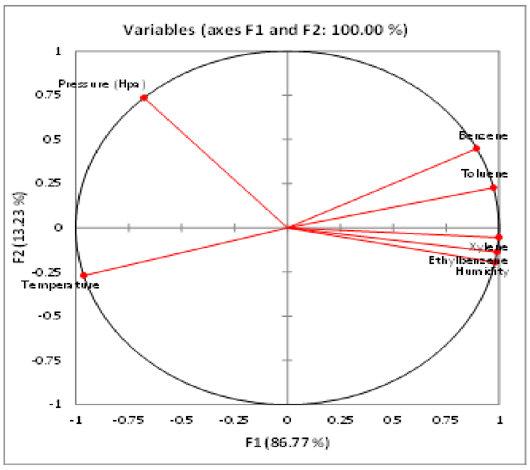


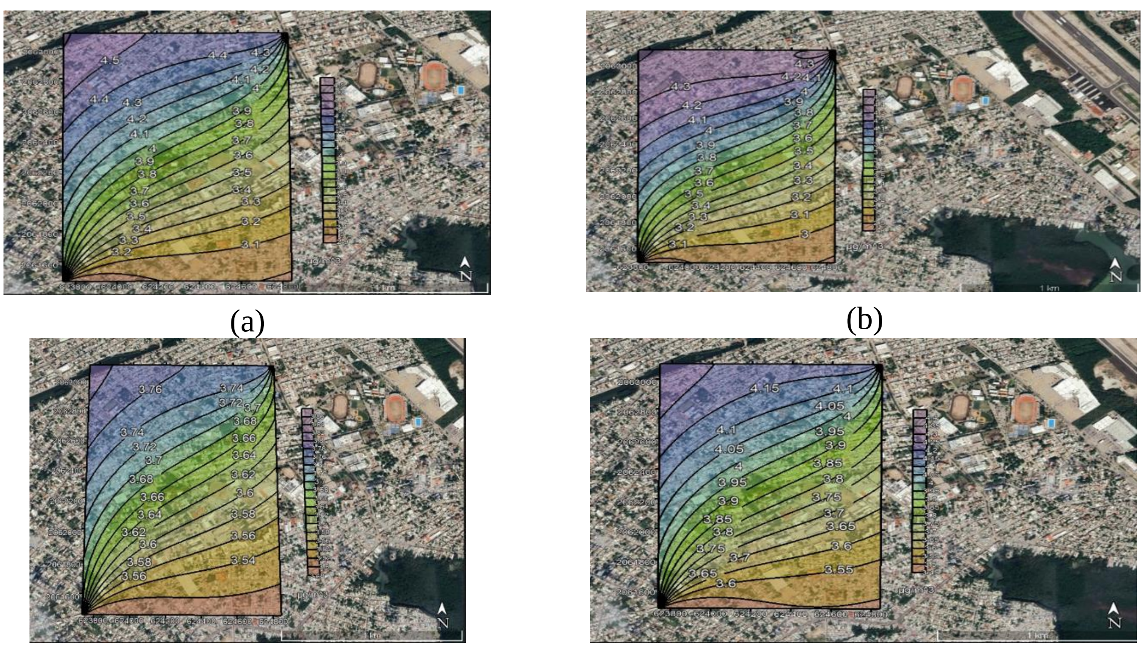
Figure 6

Biplot graph of PCA applied to BTEX concentrations and meteorological variables in the sampling site

Mapping

The BTEX concentrations were determined using the Kriging method to create a new set of estimated data. These estimates were then used to create concentration isolines in Surfer. The isolines were georeferenced to produce maps showing the spatial distribution of each BTEX compound.

Box 14



(a) (b)

(c) (d)

Figure 7

Map of isolines for (a) Benzene, (b) Toluene, (c) Ethylbenzene and (d) Xylene concentrations in the study area

The spatial distribution of benzene is depicted in Figure 7 (a), indicating higher concentrations towards the northwest of the sampling area, specifically near the fishing port, North Beach, and a section of the city center. This area also encompasses the Atasta sour gas recompression station and the offshore platform region. Similarly, Figure 7 (b) displays the spatial distribution of Toluene, revealing a similar pattern.

Figure 7 (c) illustrates the spatial distribution of ethylbenzene, indicating that ethylbenzene concentrations were higher toward the northwest of the sampling area, specifically near the North Beach, Fishing Port, and City Center area. Conversely, Figure 7 (d) demonstrates the spatial distribution of xylene, displaying a similar spatial pattern to the other BTEX compounds.

B/T and X/E ratios

The B/T and X/E ratios can help determine the likely origin of BTEX at a specific site. A toluene/benzene ratio (B/T) of less than 2-3 indicates a high influence of vehicular emissions, suggesting that BTEX comes from motor vehicle emissions, as both toluene and benzene are present in gasoline (Elbir et al., 2007). On the other hand, in the case of the xylene/ethylbenzene (X/E) ratio, this ratio is used to estimate the age of air masses and to infer whether the emissions are local and come from fresh emissions, or if they come from aged air masses, that is, of regional nature and with a certain history of photochemical processing. This way, values below 4.4 in this ratio indicate that the air masses are recent and carry fresh emissions, so their origin can be considered local (Keymeulen et al., 2001).

The B/T ratios for the 3 sampling times (B1, B2, and B3) from Table 8 were equal to or greater than 1, indicating a high influence of vehicular emissions at the sampling sites. This suggests that BTEX emissions likely originated from vehicular sources, possibly even from the same service station where the sampling was conducted.

Box 15

Table 8

Results of the Principal Components Analysis (PCA) for the sampling site

B/T		
B1	**B2**	**B3**
1.0162	1.0417	1.0209
0.9499	1.0250	1.0218
1.0765	1.0576	1.0383
1.0895	1.0510	1.0230
1.1019	1.0677	0.9286
1.1065	1.1298	1.0239
1.0953	1.0758	1.1047
1.1298	1.0669	1.0639
1.0823	1.2516	1.1733
1.1644	1.1543	1.1448
1.0812	**1.0921**	**1.0543**

B/T ratios obtained in the sampling site

In Table 9, it is evident that the X/E ratios for the 3 sampling times (B1, B2, and B3) were close to 1. This suggests that these are recent air masses carrying fresh emissions, indicating that the BTEX compounds measured can be considered to have a local origin.

Box 16

Table 9

X/E ratios obtained in the sampling site Results of the Principal Components Analysis (PCA) for the sampling site

X/E		
B1	**B2**	**B3**
0.9894	0.9732	0.9934
0.9869	0.9827	1.0101
1.0152	1.0142	1.0340
1.0762	0.9863	0.9882
1.1099	0.9887	1.0462
1.0736	1.0395	1.0050
1.0595	1.0132	1.2433
1.0401	0.9864	1.0041
1.0411	1.0289	1.0662
1.2343	0.9988	1.0114
1.0626	**1.0012**	**1.0402**

B/T ratios obtained in the sampling site

The B/T ratios are used to determine the relative abundance between vehicular and non-vehicular sources. In this case, the B/T ratios for the sampling site were less than 3, ranging from 0.998 to 1.168 with an average value of 1.076. This indicates that BTEX emissions come from vehicular sources, as this range has been reported in various urban areas worldwide (see Figure 8).

Box 17

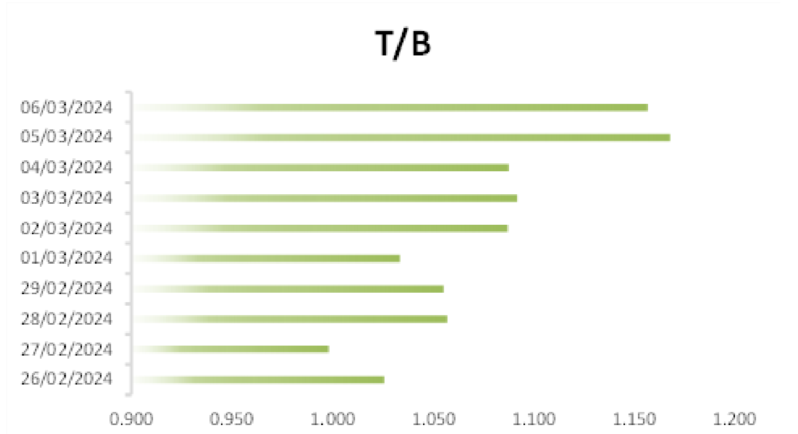


Figure 8

B/T ratios in the sampling site

The X/E ratios are used as an indicator of the photochemical age of the air masses at the sampling site. This is because xylene is more reactive compared to ethylbenzene, leading to photochemical reactions. In this study, the X/E ratios indicate that the air masses are fresh (see Figure 9).

Box 18

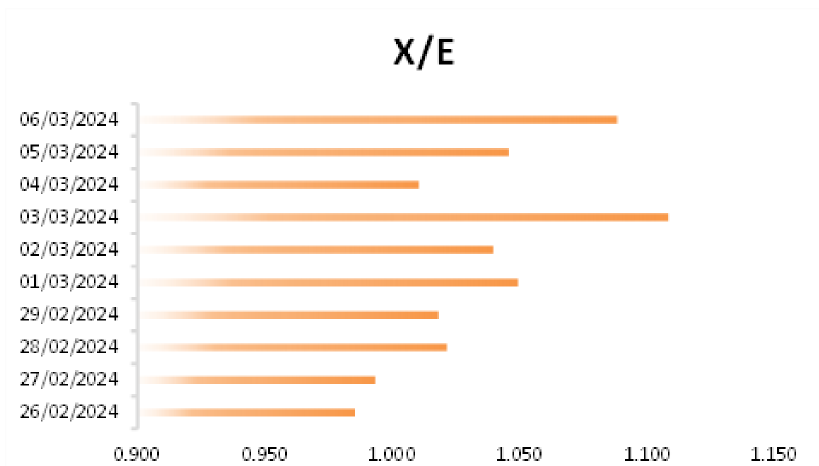


Figure 9

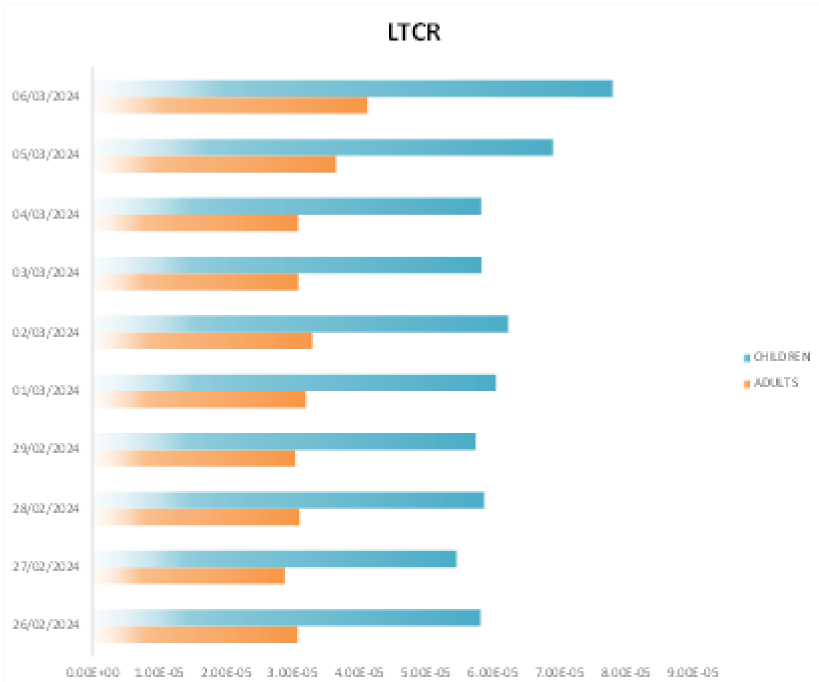
X/E ratios in the sampling site

Therefore, from B/T and X/E ratios, it can be concluded that BTEX levels found in the sampling site had a local origin, specifically in fresh emissions from vehicular sources at NW of the sampling sites, probably, in the surroundings of the fishing port, the downtown of the city, and North Beach.

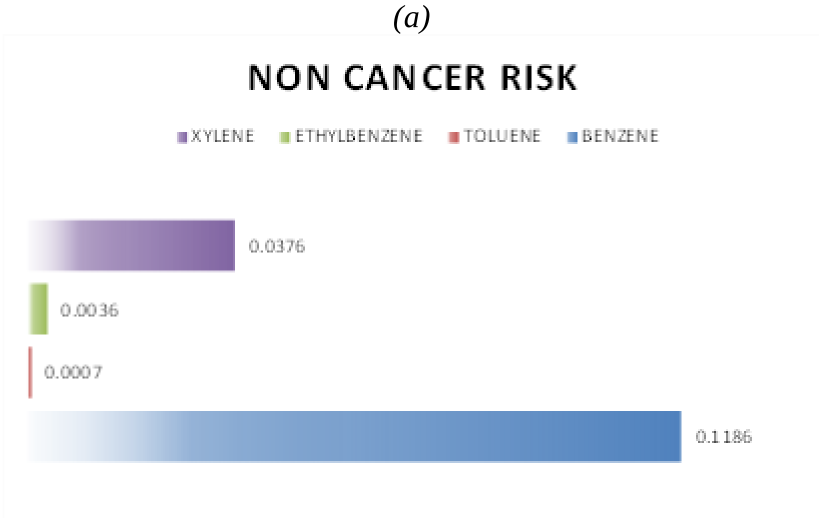
Health Risk Assessing

The cancer risk index due to exposure to benzene at the sampling site was calculated for both, adult and child populations (Figure 10 a). Lifetime cancer risk (LTCR) values for the sampling site were from 2.88×10^{-5} to 4.12×10^{-5}, with a mean value of 3.25×10^{-5} for adults; and 5.45×10^{-5} to 7.8×10^{-5} with a mean value of 6.15×10^{-5} for children. The averages in both cases can be seen to exceed the reference value proposed by the US EPA (LTCR 1×10^{-6}); being the risk significantly higher for the child population.

Box 19



(a)



(b)

Figure 10

(a) Cancer risk (LTCR) due to benzene exposure, (b) Non-cancer risk quotient (HQ) due to exposure to BTEX

Non-carcinogenic risk quotients were estimated for the BTEX compounds. The overall potential for non-carcinogenic effects due to exposure to more than one chemical was determined as an HQ risk quotient, where a value of HQ <1 indicates that the population is not exposed to a significant risk of contracting diseases other than cancer (respiratory and cardiovascular diseases) as a consequence of daily exposure to this type of compounds. From Figure 10 (b) the HQ values were in all cases less than unity, which suggests that the population near the study area does not present a risk of suffering respiratory and cardiovascular diseases.

Comparison with other works

Table 10 compares the results obtained in the present study with those reported by other authors in other regions of the world. In the case of Benzene, it can be observed that the levels obtained in the study site were considerably lower than those reported by Baimatova et al. (2016) in Kazakhstan; Chaiklieng (2021) in Thailand, Cerón et al. (2018) in Tijuana, Estéves et al. (2015) in Orizaba, and by Cerón et al. (2017) in Mérida. However, they were higher than those found by Mainka and Kozielska (2016) in a kindergarten in Poland, by Tecer et al. (2018) in Turkey, by Moolla et al. (2015) in South Africa, and by Cerón et al. (2020) in Leon.

The Toluene levels found were lower than those reported in other studies and considerably lower than those reported by Kerchich and Kerbachi (2012) in Algeria, and by Chaiklieng (2021) in Thailand. On the other hand, the levels of Ethylbenzene obtained were comparable to those found by Molla et al. (2015) in South Africa and lower than those reported by other authors. Finally, in the case of xylene, the concentrations found were lower than those reported by other authors, and significantly lower than those found by Chaiklieng (2021) in Thailand and by Cerón et al. (2018) in Ensenada.

Box 20

Table 10

Comparison with results obtained in other regions of the world

Location	**B**	**T**	**E**	**X**	**Reference**
:indergarten in Gliwice, oland (µg/m³)	1.24	0.78	0.22	0.46	Mainka and Kozielska (2016)
Almaty, Kazajistán (µg/m³)	53	57	11	14	Baimatova et al. (2016)
Algiers, Alger (µg/m³)	16.7	40.5	6.8	10.74	Kerchich and Kerbachi (2012)
Yalova, Turkey (µg/m³)	2.6	11	1.32	3.8	Tecer et al. (2018)
Johannesburg, South Africa (µg/m³)	1.41	3.22	0.67	4.1	Moolla et al. (2015)
Khon Kaen, Thailand (µg/m³)	33.1	142.7	14.4	41.3	Chaiklieng (2021)
Ensenada, Baja California (µg/m³)	16.8	50.7	0.1	3.1	García et al. (2014)
Tijuana, Baja California, (µg/m³)	32.4	13.28	7.02	17.16	Cerón et al. (2018)
Leon, Guanajuato (µg/m³)	1.73	11.85	11.86	3.31	Cerón et al. (2020)
Orizaba, Veracruz (µg/m³)	74.51	5.33	2.26	3.35	Estéves et al. (2015)
Merida, Yucatan (µg/m³)	40.91	6.87	6.23	13.87	Cerón, et al. (2017)
Merida, Yucatan (µg/m³)	32.86	3.29	4.48	8.29	Cerón, et al. (2017)
This study (µg/m³)	3.56	3.30	3.62	3.76	Cerón et al. (2024)

Conclusions

Temporal variability in BTEX levels was evaluated at a site adjacent to a gas station in Ciudad del Carmen, Campeche, during the dry season of 2024. The concentrations of all BTEX were highest during the B1 sampling period, which corresponds to the time from 07:00 to 08:00 hrs; However, when applying hypothesis tests, it was found that these differences were only significant for toluene. The BTEX concentrations in the present study were generally lower than those reported by other authors in other world regions.

From plots of wind vs concentration, it was assessed the influence of surface meteorology on the measured BTEX levels, regarding this, it was found that the trend was the same for all BTEX compounds, with the highest concentrations when the wind had a SE component, that is, when the wind blew from the SE to the NW.

Applying geo-statistical tools, the spatial variability of BTEX compounds in the study area was evaluated, finding in all cases that the levels of BTEX tend to be higher towards the NW of the sampling area, that is, towards the zone of North Beach, the downtown of the city and the Fishing Port. This area includes avenues and roads that connect the East edge of the island with the West edge; so, at certain times of the day, these roads stay congested and have high vehicle traffic.

In this regard, to determine whether vehicular sources had a significant impact on the emission of BTEX compounds, the B/T and X/E ratios were estimated. The B/T ratios for the 3 sampling times (B1, B2, and B3) were close to 1, which can be considered characteristic of sites with a high influence of vehicle emissions. Therefore, we conclude that BTEX emissions had their origin in vehicular emissions and, also from the service station where the sampling was done.

On the other hand, since the X/E ratios are used as an indicator of the photochemical age of the air masses at the sampling site, in this study, all cases, in a range of 0.998 to 1.168 with an average value of 1.076, which indicates that the emissions were recent and of local origin, indicating that they are fresh air masses. The sour gas recompression station and the offshore platform area are also located in the NW direction; However, according to what was found from the B/T and X/E ratios, it is concluded that the influence of regional sources was not significant.

Finally, the cancer risk index for benzene exposure exceeded the reference value proposed by the US EPA (LTCR $1x10^{-6}$), suggesting a significant risk, and being even higher for the child population. The overall potential for no carcinogenic effects due to BTEX exposure was determined as an HQ risk quotient. In all cases, a value of HQ<1 was obtained, indicating that the population is not exposed to a significant risk of contracting diseases other than cancer (respiratory and cardiovascular diseases) due to the daily exposure to the BTEX levels found in the study area. However, it is necessary to carry out more studies around the city including other climatic seasons and a greater number of sampling sites (service stations) to obtain more precise conclusions regarding the risk associated to this type of emissions.

Annexes

Tables and adequate sources.

Declarations

Conflict of interest

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence in this chapter.

Author contribution

Cerón-Bretón, Rosa María: Contributed to the project idea, research method, technique, financial support, result analysis and paper redaction.

Cerón-Bretón, Julia Griselda: Contributed to the project idea, research method, technique, financial support, result analysis and paper redaction.

Pérez-Vera, Joselyn Itzell: Contributed to the sampling and chemical analysis.
Reyna del Carmen Lara Severino: Contributed to research method and technique, statistical analysis.

Availability of data and materials

The Data is available if required.

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Abbreviations

ATSDR	Agency for Toxic Substances and Disease Registry
UNACAR	Autonomous University of Carmen
BTEX	Benzene, Toluene, Ethylbenzene, and the three isomers of Xylene
FAO	Food and Agriculture Organization of the United Nations
UNEP	UN Environment Programme
GIS	Geographic Information System
GCA	Global Air Quality Guidelines
INEGI	National Institute of Statistic and Geography
LTCR	Lifetime cancer risk
MPL	Maximum Permissible Limit
NIOSH	National Institute for Occupational Safety and Health
INSHT	National Institute of Safety and Hygiene at Work)
NOAA	National Oceanic and Atmospheric Administration

HQ	Non-cancer risk potential
POE	Occupationally exposed personnel
PAHO	Pan American Health Organization
PCA	Principal component analysis
LTCR	The lifetime benzene cancer risk
US EPA	EPA de EE. UU.)
VOCs	Volatile organic compounds
WHO	World Health Organization

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