

Characterization of BTEX species at Texas Commission on Environmental Quality (TCEQ) Continuous Ambient Monitoring Station (CAMS) sites in Houston, Texas, USA during 2018

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ABSTRACT

Volatile Organic Compounds (VOCs) in the atmosphere negatively impact human and environmental health. Various sources of VOCs include gasoline evaporation, solvent usage, traffic, etc. A dataset 1-year (2018) consisting of BTEX (benzene, toluene, ethylbenzene, and m, p, and o-xyles) concentrations in Houston, Texas, was analyzed to understand the spatial trends and sources of BTEX in the region. This study assesses 24-hour data concentrations from the Continuous Ambient Monitoring Station (CAMS) operated by the TCEQ Texas Commission on Environmental Quality (TCEQ) in Houston. Spatial variations of the BTEX species across the various TCEQ CAMS sites were determined using multiple statistical analyses, including Coefficients of Divergence (COD), Spearman's correlation coefficient, and ANOVA Tukey's test, while the BTEX interspecies ratios were calculated for further inter- and intra-urban exposure characterization. Ozone Forming Potential (OFP) was also calculated to analyze the role of VOCs in the formation of tropospheric ozone and to understand the role of VOCs in OFP in multiple seasons. OFP was higher in colder months than in other seasons of the year. Toluene exhibited greater concentrations with emission sources related to vehicular traffic emissions. The sites near the cluster of refineries were observed to have higher BTEX concentrations than others in Houston, Texas. These findings could help formulate targeted emission reduction strategies, for overall VOC levels in Houston, Texas.

1. Introduction

Volatile organic compounds (VOCs) originate from various sources, including natural and anthropogenic, and can be found in indoor and ambient environments [1,2]. There are hundreds of VOCs present in the air, characterized by their low boiling point and ability to easily transition into the gaseous phase [3,4]. The U.S. Clean Air Act classifies these VOCs as Hazardous Air Pollutants (HAPs), emphasizing their potential environmental and health risks [5,6]. Benzene, toluene, ethylbenzene, and xylenes (BTEX) represent critical subgroups of VOCs with notable environmental implications [3,7]. These aromatic organic solvents play an essential role in the formation of tropospheric ozone, secondary organic aerosols, and various other secondary pollutants [8]. Ground-level ozone, smog, and photochemical oxidants can be formed through the atmospheric photochemical process involving benzene and

other aromatic hydrocarbons present in the atmosphere [9,10,11,12]. Ground-level ozone and photochemical oxidants then increase the development of fine particles and toxic chemicals in the air [1,13]. The photo-oxidation of VOCs can also result in the formation of secondary organic aerosols (SOA) [14,15].

The VOCs in the atmosphere negatively impact both environmental and human health. The primary pathway of exposure for BTEX species in humans is through the inhalation of contaminated air [16]. The health effects caused by exposure to BTEX species are correlated with the duration and concentration of exposure [17]. It has been associated as a causal agent in both noncarcinogenic and carcinogenic effects on humans [17]. Specifically, and according to the International Agency for Research on Cancer, exposure to benzene and ethylbenzene, which belong to Group 1 and Group 2b carcinogens, respectively, are considered highly hazardous for human health [2,18]. BTEX species can

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disrupt the endocrine system, even at exposure levels considered safe by the U.S. Environmental Protection Agency (USEPA) [2,19]. Exposure to concentrations of carcinogenic VOCs below the established threshold can still cause diseases such as asthma and other respiratory and cardiovascular diseases [3,20-22]. Specifically for benzene, both acute and chronic exposures could lead to detrimental health effects. Hence, benzene has no specified safe level [23,3,2,12,24]. Prolonged exposure to benzene has been associated with adverse outcomes such as preterm birth and autism, highlighting the diverse health risks posed by this volatile organic compound [25-27,18,5,28-30].

Increasing rates of urbanization/industrialization result in the growth of emissions and human exposure [12]. While BTEX species have many sources, vehicular exhaust is considered the primary source [31]. Commonly, the highest concentrations of VOCs are identified near petrochemical industries and oil refineries, whereas in urban environments, major sources of VOCs are from vehicle exhaust, gasoline evaporation, solvent usage, and leakage from liquefied petroleum gas and natural gas [32-34,1,35,2,12,36]. Levels of VOCs in ambient air are ubiquitous in urban areas because of high fuel use, traffic, environmental, and road conditions in a typical city [1,5]. With vehicular exhaust being the primary source of BTEX, individuals commuting in metropolitan areas are greatly exposed to traffic-related VOCs, i.e., benzene [37]. Despite the limited commute time in an average person's day, the contribution to their total daily exposure is significant [38,37,39,40].

It is imperative to understand the sources of BTEX in a multi-source urban atmosphere. With a population of 2.3 million [41], Houston is the fourth largest city in the United States. It is home to the largest anthropogenic emission sources of atmospheric pollutants [42]. Most refineries in the state of Texas are located along the major seaports, especially in Houston. There are a total of 10 refineries in Houston City, processing approximately 2.3 million barrels of crude oil per calendar day. This sums up to around 45.4 % of the state's total production and 14.3 % of the nation's production [43]. As crude oil refineries emit sulfur compounds, particulate matter, and other VOC species, it is very paramount to study this specific area [32]. A majority of existing literature exclusively focuses on the Houston Ship Channel area [44-47], leaving a gap in comprehensive citywide assessments. Hence, the primary objective of this study is to study the BTEX species and understand patterns and sources of BTEX throughout the city of Houston.

2. Materials and methods

2.1. Site selection

BTEX (benzene, toluene, ethylbenzene, m & p -xylanes, and o-xylene) concentrations from 10 TCEQ (Texas Commission on Environmental Quality) CAMS (Continuous Ambient Monitoring Station) across the city of Houston in Texas were used in this study. The descriptive statistics for all the 10 CAMS stations, including city details, site, Environmental Protection Agency (EPA) site number, current CAMS station

label, descriptive coordinates, and elevation in meters, are illustrated in Table 1 [48]. The map in Fig. 1 shows the locations of CAMS sites, oil refineries, US EPA's Toxic Release Inventory (TRI) sites for BTEX, major highways, and the Port Houston ship channel, along with buildings identified as residential and industrial in the region. As shown in the figure, most of the TRI sites in the area are along the Port Houston ship channel. There are no oil refineries or TRI sites within a 6.46 km radius of C617. However, C1607 is located 42 km away from the nearest oil refinery, but it has multiple TRI sites in its south-westerly direction. On the other hand, C169, C55, and C167 are closest to multiple oil refineries, as they all share a common set of 4 oil refineries within a 6 km radius.

2.2. Topography and meteorology

Details of elevation above sea level for each CAMS site and the meteorological data are described in Table 1 [48]. Topographic differences between the different regions are significant for climate and meteorological parameters. The area's elevation ranged from 0 to 12.5 m above sea level, averaging 7.8 m. Supplementary Table 1 presents the monthly mean temperature (°C) and relative humidity (%) recorded at the CAMS sites. The temperature trends show that the warmest months are June, July, and August, with temperatures around 28–29°C, while the coolest month is January, with temperatures around 9°C. The relative humidity stays high throughout the year, reaching its peak in February and September when it exceeds 80 %. The Southeast wind patterns prevailing during 2018 are shown in Fig. 2, with wind speeds varying from calm winds to the occasional high-speed winds of 8.80–11.10 m/s.

2.3. Sampling methods

BTEX species concentrations for this study were downloaded from the TCEQ website. 10 TCEQ CAMS sites from Houston during the year 2018 were considered as part of the study [48]. 24-hour averaged ambient concentrations of benzene, toluene, ethylbenzene, m & p -xylanes, and o-xylene were characterized for spatiotemporal relationships and statistical analysis. A minimum of 70 % data completion was considered as a requirement for the statistical analysis and all sites met the criteria. CAMS site meteorological parameters such as resultant wind speed and wind direction were also acquired from these TCEQ CAMS sites.

2.4. Statistical data analysis

The BTEX descriptive statistical analyses for the BTEX species were determined using Microsoft Excel (v.16.06, Microsoft Inc., Redmond, WA, USA). All other plots and calculations, including wind roses, box plots, and spearman correlations, were performed using the Origin Pro (v.2023, Origin Lab Corporation, Northampton, MA, USA). BTEX inter-species ratios were calculated to identify the source origins of individual

Table 1

Characterization and meteorology of TCEQ CAMS sites in Houston.

| Site | EPA Site | CAMS | Latitude | Longitude | Elevation (m) | Temperature (°C) | Relative Humidity (%) |
|-------------------|-----------|-------|------------------|------------------|---------------|------------------|-----------------------|
| Cesar Chavez | 482016000 | C175 | 29° 41' 03.69" N | 95° 15' 12.95" W | 11 | 21.41 ± 7.32 | - |
| Channelview | 482010026 | C15 | 29° 48' 09.74" N | 95° 07' 31.78" W | 11.9 | 21.30 ± 7.42 | 71.03 ± 12.30 |
| Clinton | 482011035 | C55 | 29° 44' 01.46" N | 95° 15' 27.37" W | 12.5 | 21.34 ± 7.39 | 73.51 ± 12.86 |
| Galena Park | 482010057 | C167 | 29° 44' 03.32" N | 95° 14' 18.45" W | 10.3 | 21.67 ± 7.55 | - |
| Deer Park | 482011039 | C350 | 29° 40' 12.21" N | 95° 07' 42.63" W | 6 | 21.32 ± 7.32 | 71.90 ± 12.11 |
| HRM #3 Haden Road | 482010803 | C114 | 29° 45' 53.26" N | 95° 10' 42.13" W | 6 | 21.63 ± 7.39 | - |
| Milby Park | 482010069 | C169 | 29° 42' 22.50" N | 95° 15' 40.06" W | 6 | 21.57 ± 7.27 | - |
| Lynchburg Ferry | 482011015 | C165 | 29° 45' 32.00" N | 95° 04' 45.99" W | 2 | 21.18 ± 7.34 | - |
| Oyster Creek | 480391607 | C1607 | 29° 00' 38.00" N | 95° 18' 47.99" W | 0 | 20.72 ± 7.29 | - |
| Wallisville Road | 482010617 | C617 | 29° 49' 16.99" N | 94° 59' 23.99" W | 12 | 20.95 ± 7.56 | - |

* - indicates data not available

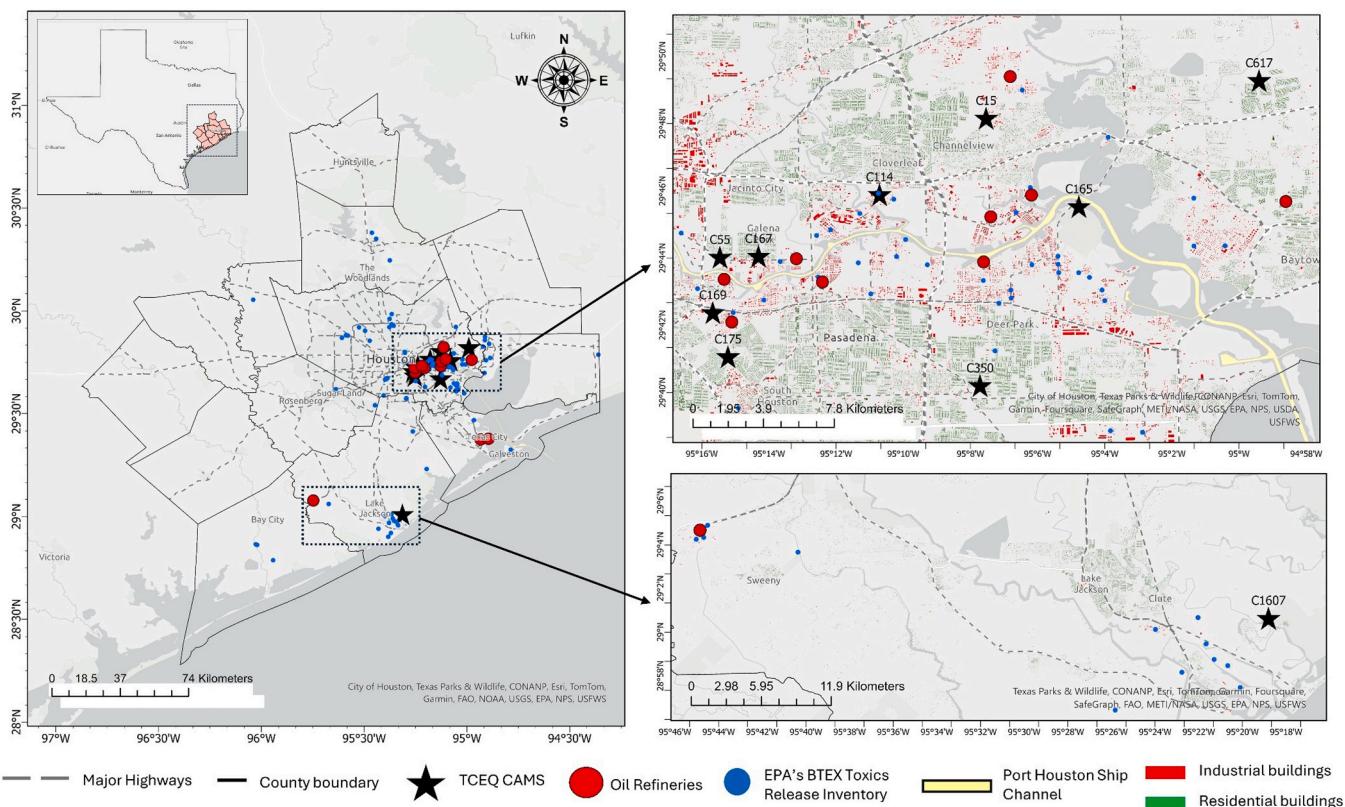


Fig. 1. Location of CAMS in Houston, Texas. Other locations on the map include oil refineries, EPA's BTEX TRI sites, Port Houston Ship Channel, and industrial/residential classification of buildings.

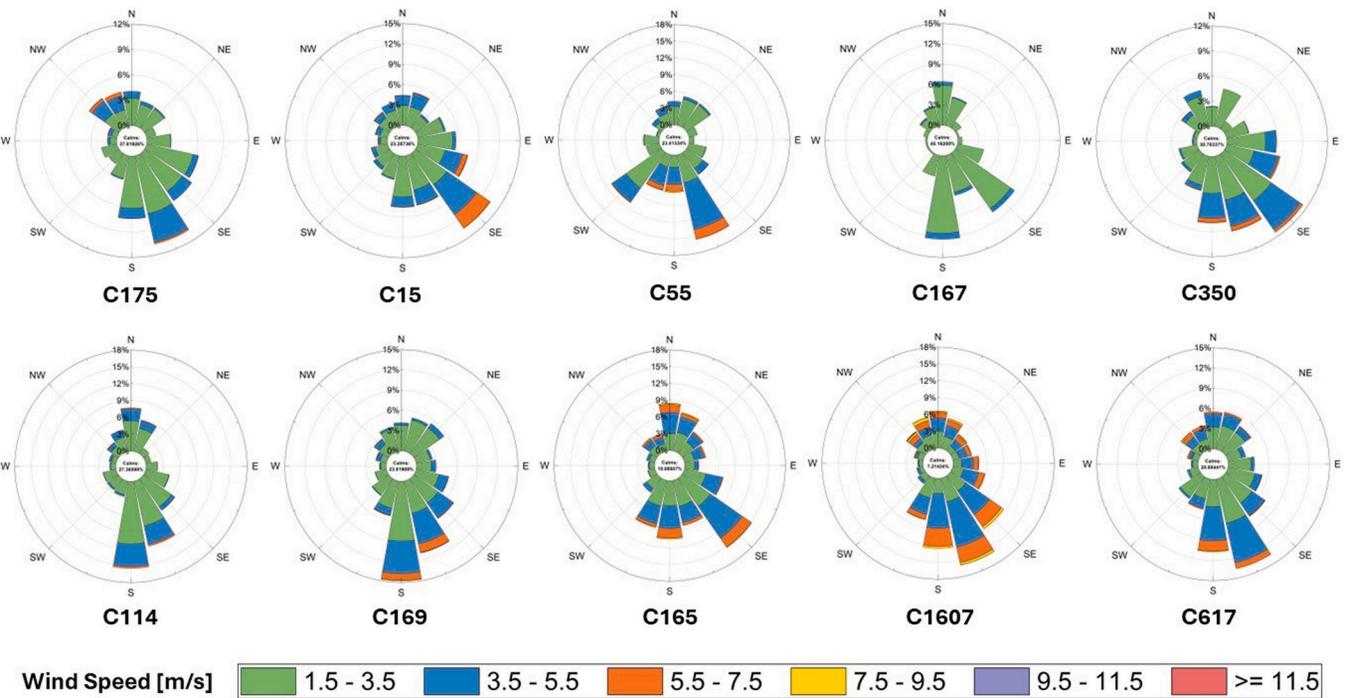


Fig. 2. Wind roses TCEQ CAMS in Houston during 2018.

species. Spatial variations were analyzed using the Coefficients of Divergence (COD) to assess uniformity in the BTEX concentrations at the various studied CAMS sites in the city. Below is the COD formula:

$$COD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left[\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right]^2}$$

inherently identifying x_{ij} as the i^{th} concentration recorded at site j over the sampling duration. The number of observations is p , and the two different sites are represented as j and k [49–51]. COD values less than or equal to 0.2 indicate similar concentrations between the two sites, while a value approaching unity would demonstrate a significant difference in the BTEX pollutant concentrations, indicating a spatial heterogeneity among the studied sites [49–51].

The Analysis of Variance (ANOVA)'s Tukey test was used to assess the impact of location on VOC concentration. This analysis aimed to determine if there were significant differences in VOC concentration among the locations. Tukey's test was then employed to compare multiple groups based on factors that exhibited significant differences. A confidence level of 95 % ($p < 0.05$) was utilized for all tests.

3. Results

3.1. 24-hour BTEX concentration analyses

Descriptive statistics of ambient BTEX species concentrations at the 10 CAMS sites are presented as 24-hour concentrations in Table 2. Additionally, spatial concentrations of the BTEX species across the various CAMS sites are shown as box and whisker plots in Fig. 3 (a–e). The 25th and 75th percentiles determine the box, while the 5th and 95th percentiles determine the whiskers. The square and line inside the box represent the mean and median values, respectively. The y-axis was set at \log_2 , i.e., Base 2 logarithmic scale, to better represent the variations of BTEX compounds at the respective sites.

Benzene and toluene had the highest 24-hour average concentration levels compared to the other species. Of all the study sites, the highest average benzene concentrations were recorded at C167 ($2.37 \pm 2.84 \mu\text{g}/\text{m}^3$). The highest value of toluene ($2.77 \pm 1.75 \mu\text{g}/\text{m}^3$) was also recorded at C167. The highest averaged ethylbenzene concentrations, m & p-xylene, and o-xylene were found at C114 with concentrations of $0.48 \pm 0.88 \mu\text{g}/\text{m}^3$, $2.16 \pm 3.55 \mu\text{g}/\text{m}^3$, and $0.41 \pm 0.67 \mu\text{g}/\text{m}^3$ respectively. Toluene is naturally produced during the production of gasoline and, therefore, is commonly present during heavy vehicular traffic [2,52]. The proximity of C167 to four oil refineries could be the reason for the highest averages of benzene and toluene in the city. All the BTEX compounds at C1607 were very low when compared to the values at others.

Outliers were kept in the boxplots to accurately demonstrate pollutant exposures in a given community. Maximum outliers demonstrated by C165 indicated a benzene level of $38.21 \mu\text{g}/\text{m}^3$ and an ethylbenzene concentration of $12.98 \mu\text{g}/\text{m}^3$ (Fig. 3a and c). Significant outlier concentrations of Toluene were disbursed across the various CAMS sites (Fig. 3 b). C114 exhibited higher outliers in the xylene species group, with o-xylene measuring $10.51 \mu\text{g}/\text{m}^3$ and m & p-xylenes valued at $40.64 \mu\text{g}/\text{m}^3$ (Fig. 3 d–e). The ethylbenzene and o-xylene values were negligible compared to the respective values at other sites.

3.2. Seasonal patterns of BTEX

Understanding the BTEX distribution patterns over time can offer essential insights into seasonal variations. The values are classified into the following seasonal groups: Spring (March, April, May), Summer (June, July, August), Fall (September, October, November), and Winter (December, January, February). The seasonal patterns of BTEX in the region are shown in Fig. 4a, b and c using stack plots and radar charts, respectively. Toluene is the major contributor in each season, ranging from 35 % in summer to 38 % in spring. Followed by Benzene, contributing between 27 % in winter and 31 % in summer. However, when concentration values are observed in each season, concentrations are generally higher in the colder months (Fall and Winter) and lower during the warmer months (Spring and Summer). The mean concentration of Benzene increases gradually from spring ($0.93 \mu\text{g}/\text{m}^3$) to

Table 2

Descriptive statistics of 24-hour averaged BTEX compounds ($\mu\text{g}/\text{m}^3$) at the monitored CAMS in Houston.

| CAMS (Data completion %) | | B | T | E | O | M + P |
|--------------------------|--------|-------|-------|-------|-------|-------|
| C175 (88.75 %) | Mean | 0.72 | 1.66 | 0.25 | 0.26 | 0.79 |
| | SD | 0.50 | 0.94 | 0.18 | 0.17 | 0.56 |
| | Median | 0.57 | 0.45 | 0.04 | 0.04 | 0.17 |
| | Min | 0.15 | 1.39 | 0.22 | 0.22 | 0.61 |
| C15 (76.71 %) | Max | 3.03 | 6.18 | 1.39 | 1.56 | 5.25 |
| | Mean | 1.42 | 1.67 | 0.38 | 0.20 | 0.78 |
| | SD | 1.05 | 1.05 | 0.35 | 0.15 | 0.50 |
| | Median | 1.18 | 0.38 | 0.04 | 0.00 | 0.17 |
| C55 (83.01 %) | Min | 0.35 | 1.43 | 0.30 | 0.17 | 0.65 |
| | Max | 9.39 | 6.97 | 3.17 | 1.09 | 3.43 |
| | Mean | 0.86 | 1.85 | 0.35 | 0.36 | 1.04 |
| | SD | 0.65 | 1.02 | 0.36 | 0.23 | 0.69 |
| C167 (80.00 %) | Median | 0.67 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Min | 0.00 | 1.58 | 0.30 | 0.30 | 0.87 |
| | Max | 3.32 | 6.07 | 4.60 | 2.52 | 7.42 |
| | Mean | 2.37 | 2.77 | 0.45 | 0.38 | 1.23 |
| C350 (73.70 %) | SD | 2.84 | 1.75 | 0.40 | 0.25 | 0.93 |
| | Median | 1.41 | 0.34 | 0.00 | 0.00 | 0.13 |
| | Min | 0.16 | 2.58 | 0.35 | 0.35 | 1.09 |
| | Max | 21.34 | 14.66 | 4.39 | 2.21 | 10.68 |
| C114 (86.85 %) | Mean | 0.91 | 1.22 | 0.17 | 0.16 | 0.58 |
| | SD | 0.85 | 0.79 | 0.16 | 0.13 | 0.39 |
| | Median | 0.70 | 0.30 | 0.00 | 0.00 | 0.09 |
| | Min | 0.06 | 1.06 | 0.13 | 0.13 | 0.48 |
| C169 (93.42 %) | Max | 8.27 | 6.11 | 1.69 | 0.82 | 2.61 |
| | Mean | 1.25 | 1.60 | 0.48 | 0.41 | 2.16 |
| | SD | 0.93 | 1.05 | 0.88 | 0.67 | 3.55 |
| | Median | 1.02 | 0.34 | 0.04 | 0.04 | 0.13 |
| C165 (92.05 %) | Min | 0.19 | 1.32 | 0.30 | 0.30 | 1.30 |
| | Max | 7.35 | 8.18 | 9.94 | 10.51 | 40.64 |
| | Mean | 0.65 | 1.40 | 0.26 | 0.21 | 0.69 |
| | SD | 0.50 | 0.90 | 0.23 | 0.17 | 0.48 |
| C1607 (86.03 %) | Median | 0.51 | 0.26 | 0.00 | 0.00 | 0.13 |
| | Min | 0.06 | 1.17 | 0.22 | 0.17 | 0.56 |
| | Max | 3.26 | 4.82 | 2.47 | 1.00 | 2.82 |
| | Mean | 2.31 | 1.29 | 0.27 | 0.22 | 0.83 |
| C617 (96.44 %) | SD | 3.50 | 1.20 | 0.76 | 0.26 | 0.83 |
| | Median | 1.02 | 0.08 | 0.00 | 0.00 | 0.00 |
| | Min | 0.00 | 0.87 | 0.13 | 0.13 | 0.56 |
| | Max | 38.21 | 9.69 | 12.98 | 1.69 | 5.17 |
| C1607 (86.03 %) | Mean | 0.27 | 0.37 | 0.03 | 0.03 | 0.15 |
| | SD | 0.24 | 0.29 | 0.06 | 0.06 | 0.13 |
| | Median | 0.22 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Min | 0.00 | 0.30 | 0.00 | 0.00 | 0.13 |
| C617 (96.44 %) | Max | 1.31 | 2.11 | 0.69 | 0.65 | 1.09 |
| | Mean | 0.47 | 0.72 | 0.09 | 0.09 | 0.33 |
| | SD | 0.62 | 0.56 | 0.10 | 0.12 | 0.34 |
| | Median | 0.32 | 0.08 | 0.00 | 0.00 | 0.00 |
| C1607 (86.03 %) | Min | 0.00 | 0.57 | 0.09 | 0.09 | 0.26 |
| | Max | 7.86 | 5.99 | 1.26 | 1.78 | 5.04 |

B = Benzene, T = Toluene, E = Ethylbenzene, O = o-Xylene, M + P = m, p-Xylene

winter ($1.17 \mu\text{g}/\text{m}^3$), peaking in the fall ($1.22 \mu\text{g}/\text{m}^3$). Toluene concentrations exhibit a seasonal pattern similar to Benzene, with the lowest levels occurring in Spring ($1.23 \mu\text{g}/\text{m}^3$) and the highest in Winter ($1.64 \mu\text{g}/\text{m}^3$). Ethylbenzene, o-xylene, and m & p -xylenes show a similar trend with a significant increase from spring to winter.

Fig. 4b presents the monthly concentration contributions of the five VOCs from January to December. The concentration of benzene fluctuates throughout the year, with peaks in January ($1.31 \mu\text{g}/\text{m}^3$), May ($1.75 \mu\text{g}/\text{m}^3$), and a moderate-high in August ($1.32 \mu\text{g}/\text{m}^3$). Toluene exhibits a similar pattern to Benzene, with high concentrations in May ($2.46 \mu\text{g}/\text{m}^3$) and January ($1.79 \mu\text{g}/\text{m}^3$). The lowest concentration is observed in June ($0.87 \mu\text{g}/\text{m}^3$). While ethylbenzene concentrations remained consistent throughout the year, o-xylene and m & p -xylene concentrations increased during colder months and decreased in the summer. Multiple studies have observed a similar VOC concentration pattern, with higher values in colder than warmer months [53–56].

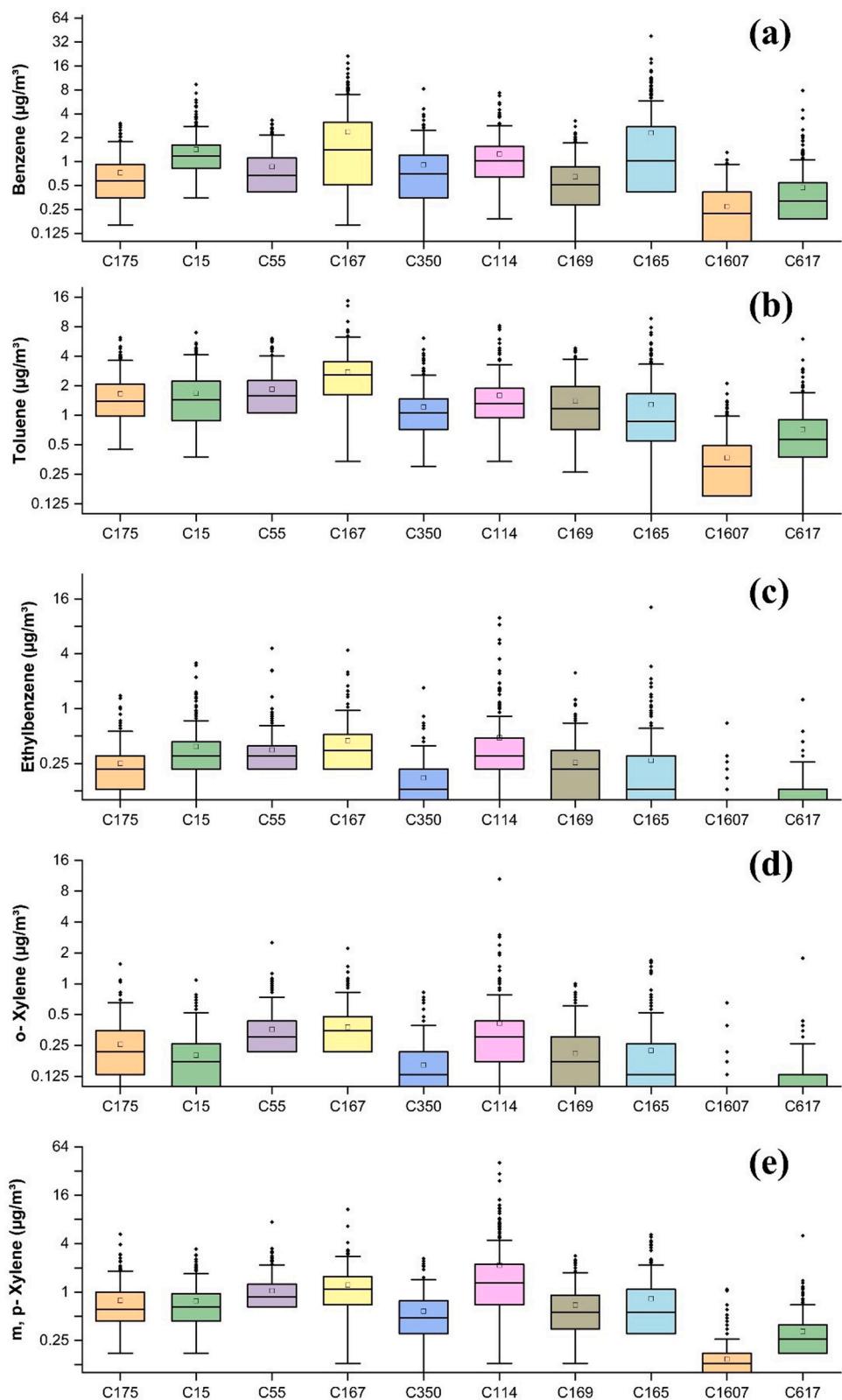


Fig. 3. Boxplots for 24-hour average concentrations of (a) Benzene, (b) Toluene, (c) Ethylbenzene, (d) o - Xylene, (e) m, p - Xylene, in $\mu\text{g}/\text{m}^3$ at studied CAMS sites. (The box plots are in alphabetical order).

Temperature inversion, a common phenomenon in winter months, and low mixing heights can trap pollutants near the ground, worsening air quality [56]. Additional factors for the observed patterns can be lower photochemical reactions [53], stable atmospheric conditions, and low dispersion rates in winter months [54,57].

3.3. Source apportionment using BTEX inter-species ratio

BTEX species concentrations in any urban environment are determined by natural and anthropogenic sources including traffic emissions, types of fuel used, topography and build-up environment,

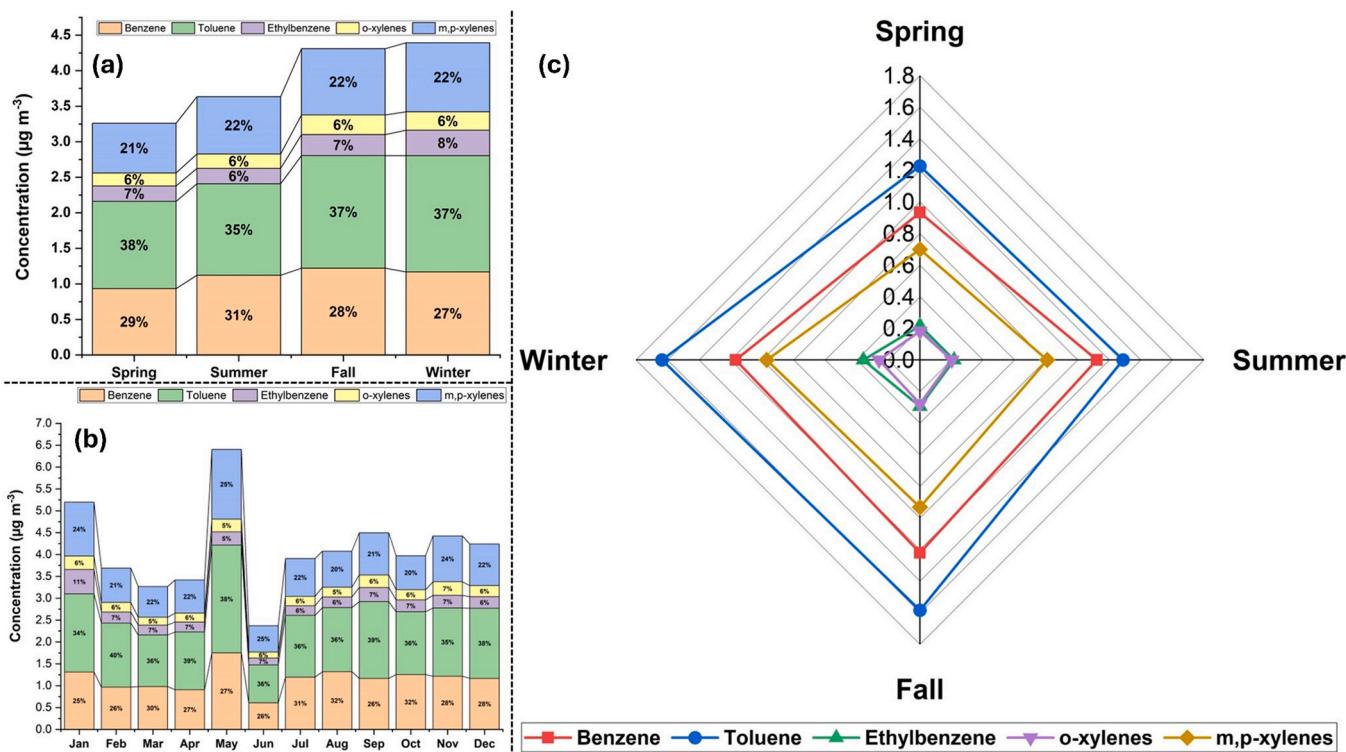


Fig. 4. a) Stacked Box plots of seasonal patterns of BTEX, b) Stacked Box plots of monthly patterns of BTEX, c) Radar chart representing the seasonal patterns of BTEX compounds.

photochemical reactions due to solar radiation, corresponding decay rates of the pollutant species in question, and age of air mass to determine the influences of traffic emissions and photochemical reactions because solar radiation affects varying decay rates in the atmosphere [58,2,12].

Previous studies have utilized multiple methods for apportioning VOC sources [59]. Diagnostic ratios, representing interspecies ratios, characterize traffic emissions, photochemical age, and long-range transport [60,61,11]. The photochemical age is defined as the time-integrated exposure of an air mass to OH radicals [62,63]. Correlation analysis can help identify potential sources of VOCs [64]. Multivariate statistical approaches, such as principal component analysis (PCA), can extract several factors related to the main sources of VOCs [65], while positive matrix factorization (PMF) can be applied to identify VOC sources and quantify their contributions [66,67]. BTEX species concentration ratios were computed in this research work to identify the sources of the studied species in Houston. Because of the different reaction rates of VOCs with hydroxyl radical (OH), these ratios provide information about the varying sources of origin in the environment [68]. Varying BTEX inter-species ratios ($\mu\text{g}/\text{m}^3$) at the ten CAMS sites are shown in Table 3.

The automobile exhaust primarily consists of toluene and benzene [60]. Hence, the toluene to benzene (T/B) ratio represents the distance to vehicular emission sources, with higher ratios suggesting proximity to the polluting sources in question [2,69]. The benzene to toluene (B/T) ratio is reciprocal of the T/B ratio; however, it is a commonly used indicator to determine the photochemical age of air along with predicting long-range transport of pollutants [32]. Toluene has a lifetime of $\sim 2-4$ days compared to benzene ~ 12 days [70], during transport, toluene degrades more easily than benzene [71]. Hence, a higher B/T ratio indicates a longer transport distance for the emissions.

The m & p -xylenes to ethylbenzene (M + P/E) ratios will provide an estimate of the degree of photochemical reaction in the atmosphere [72,2,73]. The emission rate of m & p xylene is 3.6 times higher than

ethylbenzene, but it's removed by chemical reactions about three times faster [11,74]. Additionally, o-xylene to ethylbenzene (O/E) and M+P/E ratios are a good estimator of the hydrocarbon age in the environment, the transport of the air mass, approximation of photochemical ages in the air mass and the probability of transported air mass [1,72]. Xylene to benzene ratio (X/B) can also indicate the photochemical age of air masses [75]. Meanwhile, the ethylbenzene to benzene (E/B) ratio can indicate the emissions from stationary sources [76]. Fig. 5 represents a spatial map visualizing the BTEX compound concentration values and inter-species ratios for each location.

3.3.1. Toluene/ benzene ratios

According to previous studies, T/B ratios were used to determine the influence of traffic emission sources on the studied pollutants [77,64,2]. The 24-hour averaged T/B ratios reached a maximum value of 34.01 and 27.13 at C55 and C167, respectively. These sites' values can be linked to their proximity to major highways. A T/B ratio close to 1 indicates traffic-related emission sources, with the value increasing as the pollution source gets closer [68,69]. [78] and [59] concluded that a T/B ratio below 3 is also a characteristic of vehicular emissions. The mean T/B ratio in the studied sample sites ranges from 1.25 (± 1.23) at C165 to 2.84 (± 2.78) at C55. With all the mean T/B ratios being more than 1 and below 3, it indicates that the main source of benzene and toluene in this region was the vehicular fleet. These T/B ratios are comparable with other results of 2.36 – 3.16 in El Paso, Texas [2] and 2.0 in Bari, Italy [79]. A higher ratio of 4.6 in southern Taiwan [80] and 1.95 – 6.07 in Sakaka City, Saudi Arabia [60] is also recorded in the respective cities. The differences in (T/B) ratios among these cities may be due to variations in their vehicle types, fuel composition, and industrial activities.

3.3.2. Benzene/ toluene ratios

B/T ratios imply the species' transportation and air mass's photochemical age [32,2,81,82]. The mean B/T ratios in the region range from 1.48 (± 0.68) at C165 to 0.44 (± 0.20) at C175. A B/T ratio lower

Table 3

Descriptive statistics of 24-hour averaged BTEX inter-species ratios at the monitored CAMS in Houston.

| CAMS | | T/B | B/T | E/B | MP/B | OX/B | MP/E | OX/E |
|-------|--------|-------|-------|-------|--------|-------|-------|-------|
| C175 | Mean | 2.60 | 0.44 | 0.37 | 1.22 | 0.39 | 3.26 | 1.05 |
| | SD | 0.89 | 0.20 | 0.13 | 0.69 | 0.16 | 1.57 | 0.19 |
| | Median | 2.51 | 0.40 | 0.36 | 1.14 | 0.38 | 3.17 | 1.00 |
| | Min | 0.51 | 0.18 | 0.08 | 0.26 | 0.09 | 1.26 | 0.40 |
| | Max | 5.64 | 1.94 | 1.12 | 10.19 | 1.36 | 30.00 | 2.33 |
| C15 | Mean | 1.31 | 0.97 | 0.30 | 0.61 | 0.15 | 2.47 | 0.61 |
| | SD | 0.63 | 0.57 | 0.24 | 0.29 | 0.08 | 1.03 | 0.27 |
| | Median | 1.24 | 0.81 | 0.25 | 0.57 | 0.14 | 2.67 | 0.63 |
| | Min | 0.18 | 0.22 | 0.04 | 0.08 | 0.00 | 0.11 | 0.00 |
| | Max | 4.50 | 5.66 | 2.67 | 2.08 | 0.43 | 7.86 | 1.20 |
| C55 | Mean | 2.84 | 0.46 | 0.52 | 1.69 | 0.58 | 3.23 | 1.12 |
| | SD | 2.78 | 0.23 | 0.49 | 1.79 | 0.60 | 0.77 | 0.28 |
| | Median | 2.29 | 0.43 | 0.39 | 1.22 | 0.42 | 3.20 | 1.11 |
| | Min | 0.55 | 0.00 | 0.00 | 0.25 | 0.08 | 0.48 | 0.14 |
| | Max | 27.13 | 1.81 | 4.30 | 17.67 | 5.44 | 10.00 | 3.00 |
| C167 | Mean | 2.22 | 0.79 | 0.34 | 1.06 | 0.32 | 2.97 | 0.90 |
| | SD | 2.37 | 0.78 | 0.29 | 0.96 | 0.29 | 0.75 | 0.22 |
| | Median | 1.80 | 0.56 | 0.27 | 0.86 | 0.26 | 3.00 | 0.92 |
| | Min | 0.16 | 0.03 | 0.00 | 0.06 | 0.00 | 0.48 | 0.00 |
| | Max | 34.01 | 6.31 | 1.83 | 6.17 | 1.78 | 7.45 | 1.50 |
| C350 | Mean | 1.83 | 0.74 | 0.23 | 0.84 | 0.22 | 3.67 | 0.97 |
| | SD | 1.04 | 0.43 | 0.14 | 0.48 | 0.15 | 1.15 | 0.30 |
| | Median | 1.62 | 0.62 | 0.20 | 0.71 | 0.19 | 3.50 | 1.00 |
| | Min | 0.38 | 0.15 | 0.00 | 0.20 | 0.00 | 0.49 | 0.00 |
| | Max | 6.82 | 2.62 | 1.00 | 3.40 | 1.02 | 9.00 | 2.00 |
| C114 | Mean | 1.57 | 0.90 | 0.52 | 2.29 | 0.50 | 5.43 | 0.98 |
| | SD | 0.98 | 0.68 | 1.44 | 6.83 | 1.74 | 5.81 | 0.26 |
| | Median | 1.40 | 0.71 | 0.31 | 1.29 | 0.30 | 3.67 | 1.00 |
| | Min | 0.20 | 0.10 | 0.03 | 0.08 | 0.02 | 0.17 | 0.05 |
| | Max | 9.99 | 4.93 | 23.72 | 115.64 | 29.90 | 39.57 | 3.50 |
| C169 | Mean | 2.50 | 0.46 | 0.43 | 1.29 | 0.35 | 3.38 | 0.91 |
| | SD | 0.99 | 0.18 | 0.34 | 0.77 | 0.17 | 1.73 | 0.35 |
| | Median | 2.36 | 0.42 | 0.36 | 1.13 | 0.32 | 3.25 | 1.00 |
| | Min | 0.69 | 0.12 | 0.00 | 0.27 | 0.00 | 0.38 | 0.00 |
| | Max | 8.16 | 1.45 | 3.26 | 9.51 | 0.95 | 18.67 | 2.00 |
| C165 | Mean | 1.25 | 1.48 | 0.22 | 0.86 | 0.21 | 4.49 | 1.09 |
| | SD | 1.23 | 1.28 | 0.39 | 1.24 | 0.31 | 3.87 | 0.80 |
| | Median | 0.86 | 1.16 | 0.13 | 0.47 | 0.12 | 3.75 | 1.00 |
| | Min | 0.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.18 | 0.00 |
| | Max | 8.85 | 14.08 | 5.57 | 13.59 | 3.35 | 50.00 | 11.00 |
| C1607 | Mean | 1.98 | 0.73 | 0.10 | 0.87 | 0.11 | 3.61 | 0.95 |
| | SD | 1.60 | 0.65 | 0.21 | 0.96 | 0.24 | 0.98 | 0.37 |
| | Median | 1.38 | 0.68 | 0.00 | 0.54 | 0.00 | 3.50 | 1.00 |
| | Min | 0.14 | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 | 0.00 |
| | Max | 10.62 | 6.95 | 1.36 | 8.15 | 2.72 | 6.00 | 2.00 |
| C617 | Mean | 2.24 | 0.66 | 0.26 | 1.00 | 0.25 | 3.65 | 1.01 |
| | SD | 1.52 | 0.68 | 0.21 | 0.78 | 0.20 | 1.16 | 0.31 |
| | Median | 1.89 | 0.53 | 0.21 | 0.78 | 0.21 | 3.50 | 1.00 |
| | Min | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.70 | 0.00 |
| | Max | 11.80 | 9.48 | 1.36 | 6.80 | 1.36 | 9.00 | 2.00 |

B/T = Benzene/Toluene, E/B = Ethylbenzene/Benzene, M + P/B = m,p - Xylene/Benzene, O/B = o-Xylene/Benzene, M + P/E = m,p - Xylene/Ethylbenzene, O/E = o-Xylene/Ethylbenzene.

than 0.5 indicates that transport is the area's predominant benzene source [83,84], while a ratio above 0.5 indicates that sources beyond just traffic [53]. The B/T ratios at C175, C55, and C169 are recorded as 0.44 (± 0.20), 0.46 (± 0.23) and 0.46 (± 0.18). This shows that the traffic fleet is the primary source of benzene in these regions. However, the ratios at other sites ranged from 0.66 (± 0.68) at C617 to 1.48 (± 0.68) at C165. This indicates other sources of impact, such as the industries and refineries in the region, other than vehicular activity. These results are comparable to other B/T ratios recorded in regions such as 0.5–0.39 in Delhi, India [77], 0.27 in Ankara, Turkey [85], and 0.56 in Gorakhpur, India [16].

3.3.3. m & p -Xylenes/ ethylbenzene ratios

M+P/E ratios determine the contribution of traffic emissions to the observed BTEX concentrations [2,79] and the extent of photochemical reaction in the atmosphere. With atmospheric lifetimes of 3 hours for m & p -xylenes and 8 hours for ethylbenzene, they react more rapidly than other BTEX compounds [86]. A value higher than two suggests that

traffic emissions are the major source for these two species [11]. The lowest M+P/E ratio was 2.47(± 1.57) in C15, while the highest ratio was 5.43 (± 1.16) in C114. The higher ratio values at C114 may be due to the presence of multiple sites of EPAs BTEX TRI and the influence of wind direction. Even though site C1607 is located away from oil refineries, its proximity to multiple sites of EPAs BTEX TRI can be attributed to a similar M+P/E ratio as the region with clusters of oil refineries.

The reactivity of xylenes with the OH radical is three times that of ethylbenzene. Therefore, high ratios indicate fresh emissions and lower ratio values signify aged air masses due to the more reactive properties of xylene than ethylbenzene [80,1,72]. The M+P/E ratio in the range of 2.3–4.3 has been used in several studies in petroleum refineries in North America, Europe, and Australia [72,87]. With ratios ranging from 2.47 (± 1.57) to 5.43 (± 5.81), it is suggestive that the refineries in the region are potential contributors. However, [11] and [88] mentioned that the M+P/E ratio value decreased as the distance from the source increased. As this trend was not observed in this study, other sources, such as traffic, also had a significant influence.

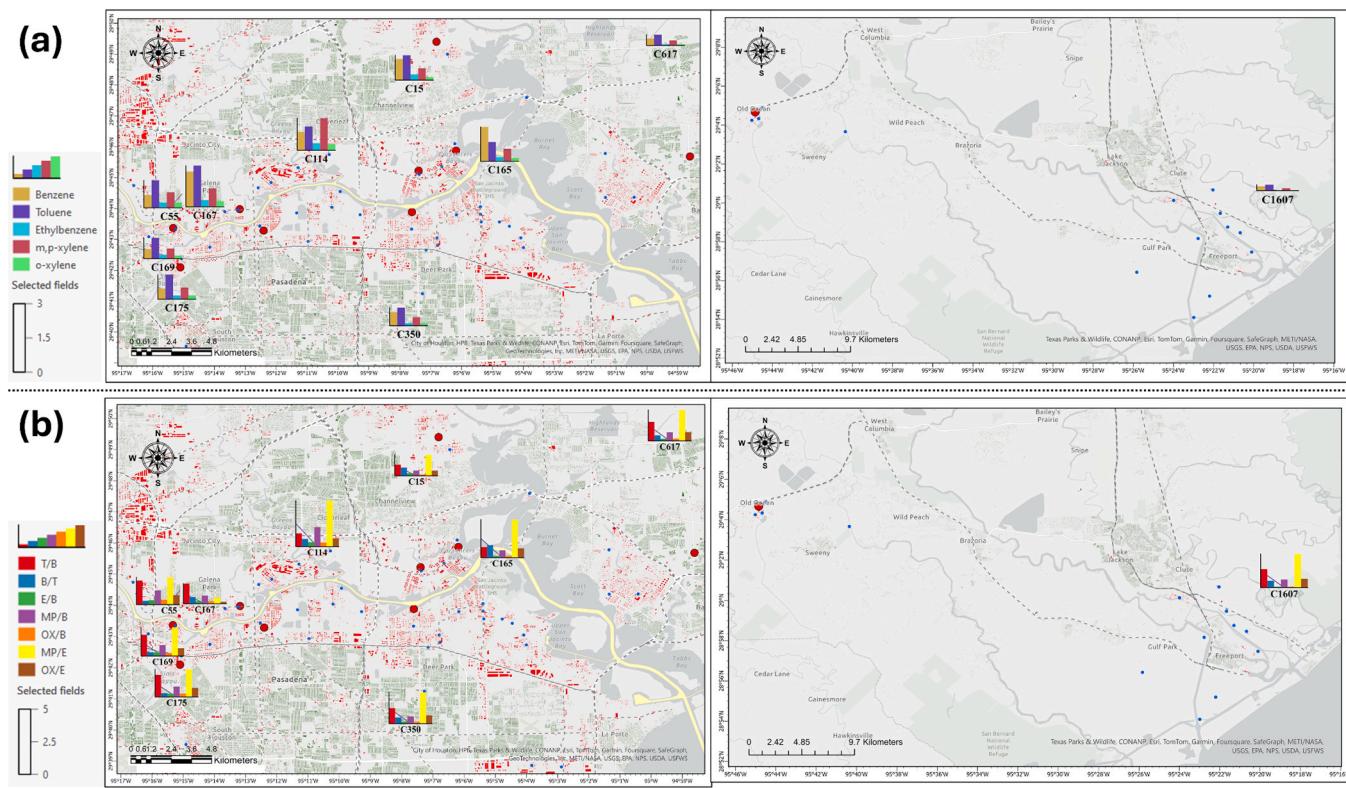


Fig. 5. Spatial map with concentrations of (a) BTEX Concentrations (b) Inter-species ratios across the sites in the region.

3.3.4. Xylenes/ benzene ratios

Comparably, m & p -xylenes to benzene (M+P/B) and o - xylenes to benzene (O/B) ratios indicate the photochemical age of air mass and the distance from emission sources [89,1,2]. M+P/B ratio value ranged from $2.29 (\pm 0.78)$ to $0.61 (\pm 0.69)$ in C15. The highest value is observed at C114, close to sites of EPAs BTEX TRI. The highest M+P/B ratio is followed by C55, C169, C175, and C167, with a range of $1.06 - 1.69$, and this cluster of four sites is very close to four oil refineries. The lowest M+P/B ratio values of 0.61 and 0.84 were observed at C15 and C350, respectively. The higher values indicate the presence of compounds with young photochemical age and fresh emission sources in the study area [74], which suggests that the proximity of oil refineries impacts the local air quality. Additionally, O/B ratios of less than 0.9 indicate vehicular emissions sources [78,1,90]. The highest mean O/B ratio was in C55 with $0.58 (\pm 0.6)$, while the lowest is markedly $0.11 (\pm 1.74)$ in C1607. This indicates that vehicular emissions are the primary source.

3.4. Impact of Refineries on VOC levels

Multiple statistical analyses have been conducted to understand the impact of refineries on VOC levels in the region.

3.4.1. Coefficient of divergence analysis

Coefficient of Divergence (COD) analysis was undertaken to determine the intra-urban heterogeneity in pollutant levels for the BTEX species across the various TCEQ CAMS sites. The COD values are presented in Fig. 6. The color coordination used in Fig. 6 for the COD values is as follows: Green indicates high similarity, and brown indicates low similarity.

According to Fig. 6, CAMS sites in Houston indicate COD values for all BTEX species > 0.45 , representing significant differences in their pollutant concentrations and confirming the spatial non-homogeneity. C1607 was observed to have a COD value of more than 0.60 for all sites and BTEX species. For ethylbenzene and o-xylene, the COD values

jump to 0.85 when C1607 is paired with the other sites. The location of C1607 is far from the other nine CAMS sites and there are no refineries in the site's proximity, explaining the higher band of COD values for all the BTEX compounds. The lowest COD value recorded was for the C169-C175 site pair for benzene. These COD values for benzene, toluene, ethylbenzene, o-xylene, and m & p -xylenes were 0.44 , 0.44 , 0.5 , 0.51 , and 0.45 , respectively, suggesting a lower level of spatial heterogeneity between these two sites. A COD of 0.81 between C167 and C1607 indicates that the two sites are spatially uniform for toluene. All the sites had very high ethylbenzene COD values ≥ 0.88 when paired with each other, suggesting intra-city heterogeneity as well.

3.4.2. Spearman's Correlation Coefficient Analysis

Spearman's correlation coefficient analysis was performed to analyze the temporal relationships between different parameters recorded at the various CAMS sites in Houston. It is a statistical measure of the strength of the monotonic relationship between the variables. The closer the value to $+1$, the stronger the relationship. Fig. 7 shows the inter-site correlation coefficients for the various BTEX species. Color coordination for these correlation coefficient values is as follows: dark green for a stronger positive relationship, light green for a weaker positive relationship, yellow for no relationship, light red for a weak negative relationship, and dark red for a strong negative relationship.

C167 showed a negative correlation, i.e., < 0 with C350, C1607, and C165 in o-Xylene, indicating that the source of o-Xylene at this site differs from the other mentioned sites. C167 is close to four refinery plants, and the other three sites do not have any refineries in their vicinity. The major source of xylenes is petroleum refineries [91]. This highlights the impact of refineries on the concentrations of xylenes in the nearby communities. C1607, despite its distance from oil refineries, exhibited correlations ranging from negative to low positive (precisely, $-0.14 > r > 0.39$) with all sites except for C350, where it displayed a moderate positive correlation of 0.55 . The absence of refineries near C350 can likely explain the observed correlation patterns.

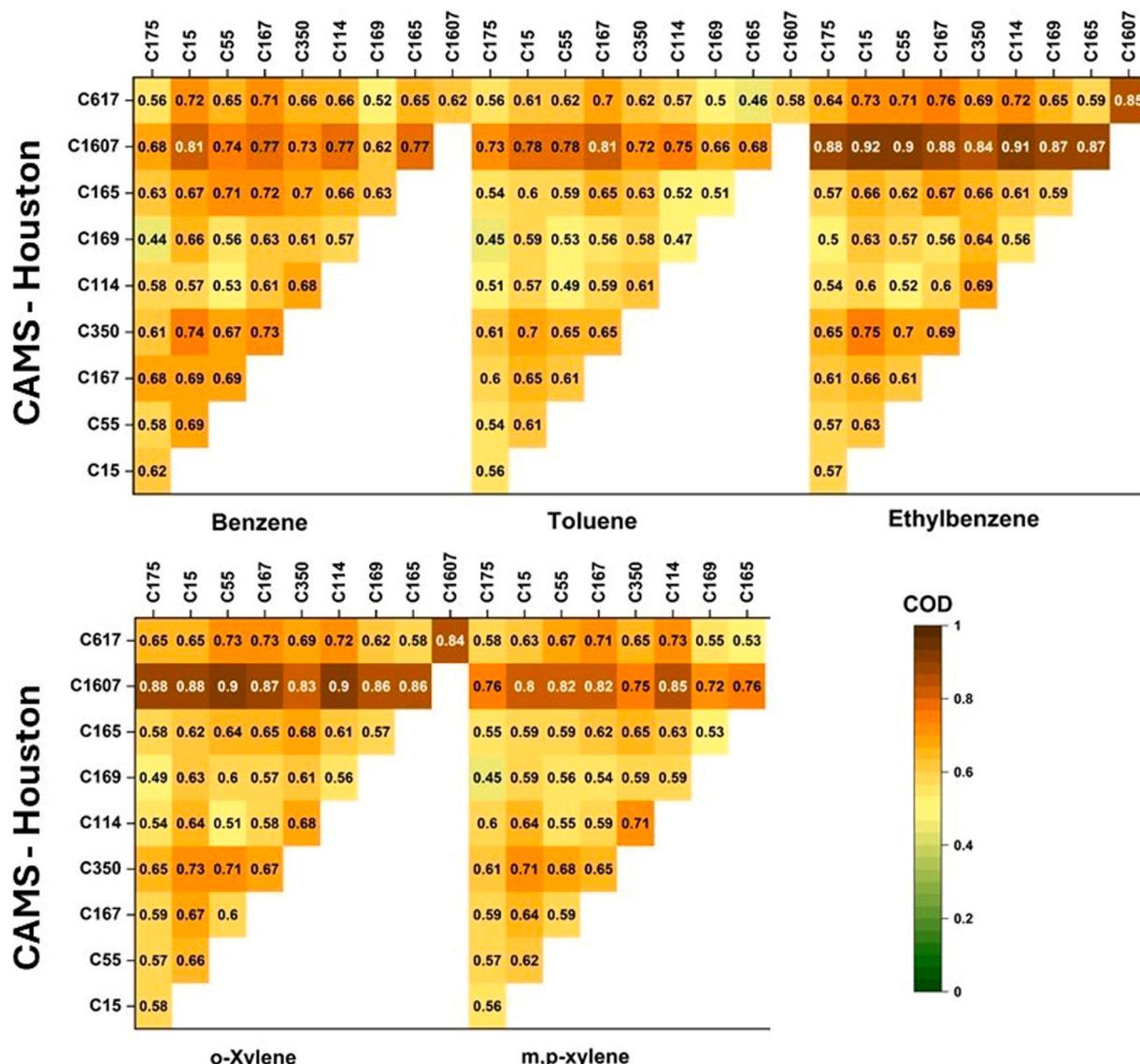


Fig. 6. COD values for 24-hour averaged BTEX concentrations for the studied CAMS sites in Houston.

3.4.3. ANOVA Tukey's test

Supplementary Table 2 includes comparisons of the mean differences in concentrations of various VOCs between different sampling sites, along with the statistical significance (q Value and Alpha) of the differences between the sites. The q Value indicates the statistical significance of the mean difference, with lower values typically suggesting more reliable findings. The alpha value is the threshold level for significance, which is set at 0.05. This will help statistically identify the sites that are significantly different from others for each VOC and the corresponding trends. Fig. 8 shows the mean differences along with the statistical difference being significant or not.

The levels of benzene at C167, C165, and C1607 consistently showed significant differences compared to other sites. The levels at C167 are notably higher than at C175, with a high mean difference of 1.64 and a q-value of 18.35 (significant at the 0.05 alpha level). C167 consistently exhibited higher benzene concentrations than other sites, such as C350 and C15, while C1607 showed lower concentrations than C167, with a mean difference of -2.10 and a q-value of 23.26. C167 also had higher toluene concentrations than C175 (mean difference 1.11, q-value 19.19) and C15 (mean difference 1.09, q-value 18.23). Similar to the trend of benzene levels, C1607 showed significantly lower levels than other sites, especially C167, with a mean difference of -2.40 and a q-value of 41.17.

Ethylbenzene levels appeared significantly higher at C167 than at C175, C15, and C55, with notable mean differences and significant q-values. The most significant difference was found between C167 and C1607, with lower concentrations at C1607 than C167 (mean difference -0.42, q-value 16.49), suggesting a distinct contrast between these sites similar to other VOCs. Xylenes showed a similar trend with higher concentration levels at C167 when compared to other sites and C1607 with lower concentrations.

Altogether, C167 consistently showed the highest concentrations of all VOCs, indicating it is a significant hotspot for VOC emissions. In contrast, C1607 exhibited significantly lower concentrations, especially when compared to C167, suggesting it is a cleaner site with fewer emissions of these compounds. Other sites like C15, C55, and C175 showed intermediate VOC levels, with some significant differences compared to the C167 or C1607, but to a lesser extent. The VOC level differences can be attributed to the oil refineries and vehicular fleet, with C1607 situated away from the refinery cluster at C167.

3.5. Ozone Forming Potential of BTEX Species

When VOCs in ambient air undergo photochemical reactions, they create photochemical smog [92] and tropospheric ozone [93]. As

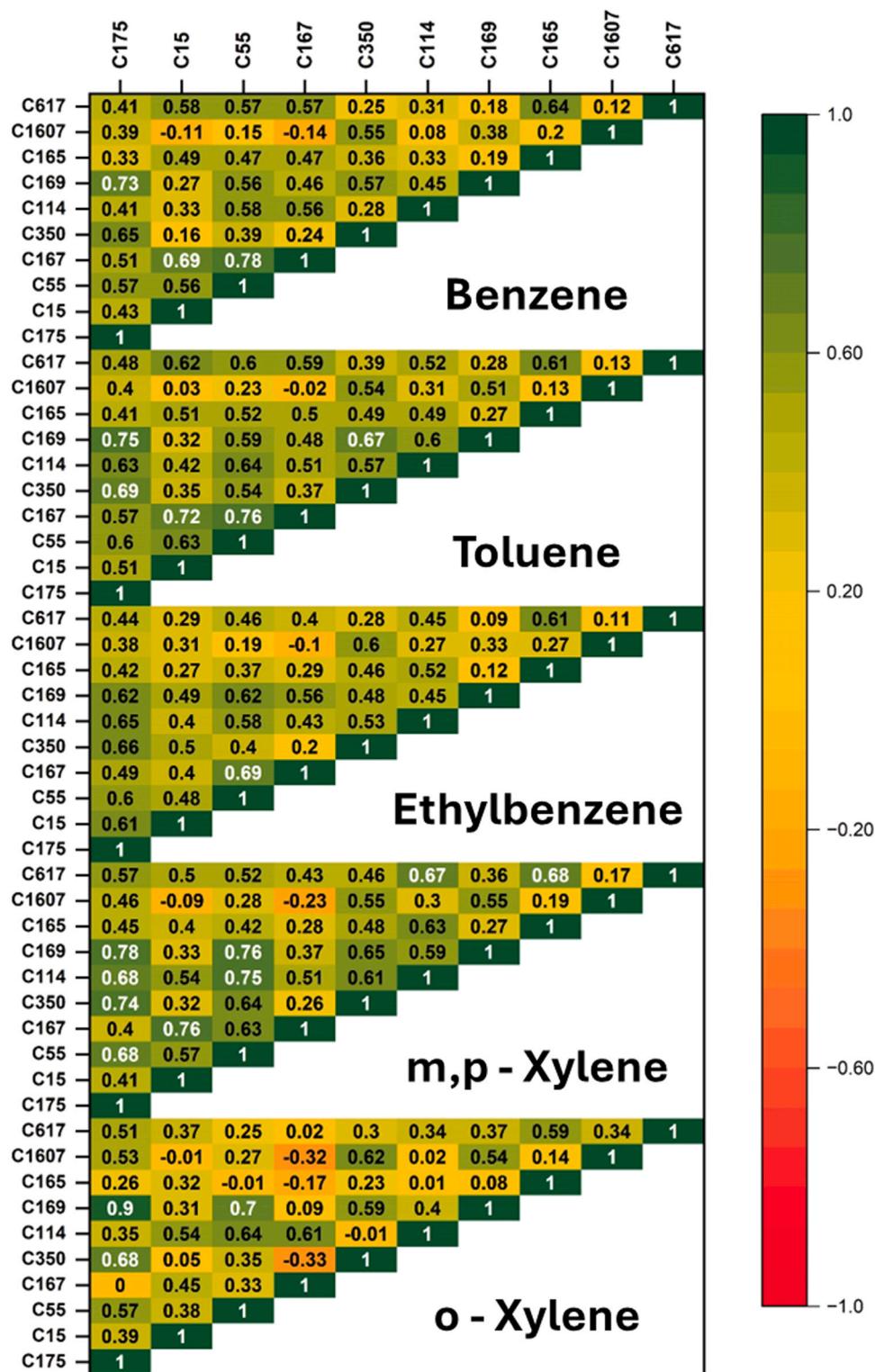


Fig. 7. Spearman correlation coefficient values for 24-hour averaged BTEX compounds across different CAMS in Houston.

highlighted by [94], the ozone-forming potential (OFP) of a VOC in ambient air is determined by its concentration and reactivity, as well as factors such as temperature, sunlight exposure, and atmospheric conditions. The critical indices for non-methane hydrocarbons (NMHC) reactivities in photochemical processes and their impact on ozone formation are the maximum incremental reactivity (MIR) factor and OH radical reactivity [95].

[9] conducted a study to calculate the effects of VOCs on their OFP

under various NO_x variations. The calculations were based on the California Statewide Air Pollution Research Center (SAPRC) box model - SAPRC-90 chemical mechanism. However, subsequent updates were applied to the MIR values, using the SAPRC-99 mechanism in [96], and the SAPRC-07 mechanism in [97]. The three MIR calculation methods were based on the 1988 standard scenario, including meteorological parameters, emission rate, boundary layer height, and VOC composition. The most recent calculations were provided by [98], who examined

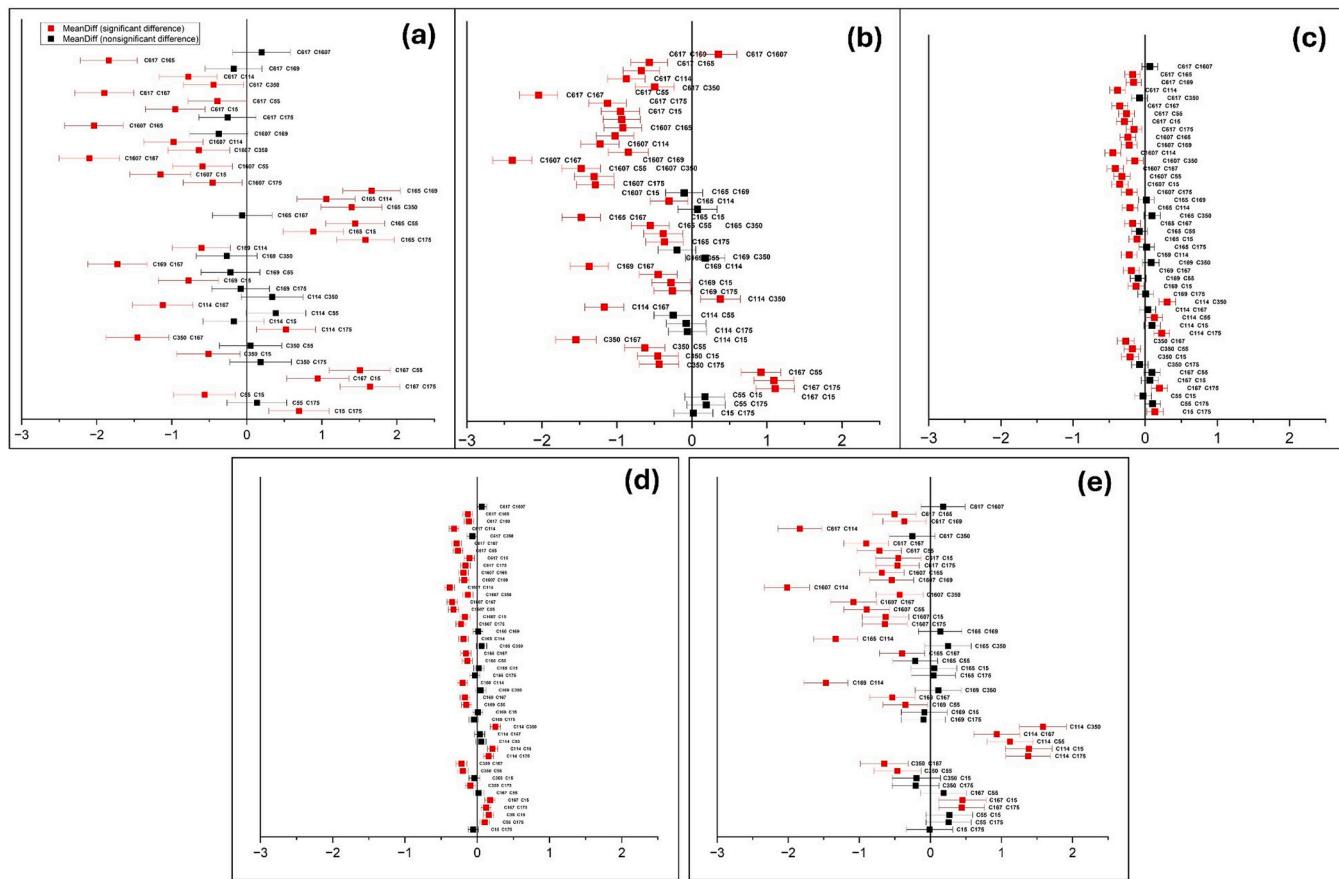


Fig. 8. Mean differences of BTEX compounds (a) Benzene, (b) Toluene, (c) Ethylbenzene, (d) o - Xylene, (e) m, p – Xylene, with a red box indicating significant differences and a black box indicating nonsignificant differences between different sites.

box model scenarios for 39 cities across the United States to calculate the MIR values for 1233 individual compounds and compound mixtures. The main reason for recalculating is to account for reduced ambient ozone concentrations since 1988, using updated meteorology, emission rates, initial conditions, background species concentrations, and VOC profiles. Whereas the previous scales were based on the 1988 scenario, this study replaced it with the 2010 scenario. A decrease of 20.3 % in median MIR values was noticed in the results. Hence the following formula was used for the ozone-forming potential calculations using the updated MIR values:

$$\text{OFP} = C_{\text{BTEX}} \times \text{MIR}$$

where C_{BTEX} is the ambient concentration of the respective BTEX species in $\mu\text{g}/\text{m}^3$, and the MIR coefficient is the maximum incremental reactivity scale [9]. These unitless MIR coefficients are used in high NOx conditions and are essential for ozone control programs [16]. Hydroxyl radicals (OH) reactivity with VOC explains the ability of hydrocarbons to form higher oxidized products such as aldehydes, acids, and organic peroxy radicals [77]. The photochemical reactions of VOC with OH radicals correlate directly with temperature [16]. VOCs combine with NOx in the presence of OH radicals to produce ozone [77].

The OFP of BTEX determined using MIR, along with their reaction with OH for different CAMS stations, is shown in Table 4. The OFP was found to be highest for m & p - xylenes, followed by toluene, o-xylene, ethylbenzene, and benzene. Xylenes with lower concentrations showed higher ozone-forming potential than benzene. This trend was observed in other studies [94,99,92], and the reason for the increased OFP in xylenes is because of the higher MIR coefficients. Despite being the most hazardous, OFP for benzene was observed to be the least among BTEX compounds [77]. The reaction of BTEX with OH radicals, which leads to

the formation of higher oxides, was also found to be highest in m & p - xylenes, and toluene.

Meteorological factors like temperature, solar radiation, and wind speed significantly influence the OFP [54]. Understanding the seasonal variations of OFP and OH reactivity provides insights into their behavior under different atmospheric conditions. Table 5 presents the concentration, OFP, and OH reactivity for all the studied VOCs. VOC concentrations were higher during fall and winter, which can be attributed to reduced atmospheric mixing [54,57]. Similarly, OFP also peaked in fall and winter, particularly for more reactive compounds like xylenes and toluene. Xylenes at lower concentrations in all seasons had higher OFP than benzene and ethylbenzene, which can be attributed to their higher MIR coefficients among BTEX. This trend is similar to studies in other cities like Delhi in India [54,100], Beijing in China [101], and Shenyang in China [102], which found that the OFP is highest in cold months of the year.

4. Conclusions

We have conducted a study showing the 24-hour concentrations of BTEX across 10 CAMS sites in Houston, Texas. The results indicate significant spatial variability of BTEX species, with higher levels observed near industrial and traffic-heavy areas, particularly at C167 and C114. The highest concentrations of benzene and toluene were found at C167, likely due to the proximity of oil refineries, while the highest levels of m & p-xylenes and o-xylene were recorded at C114. B/T ratios below 0.5 at specific sites further support the dominance of traffic-related emissions in those areas. However, elevated B/T ratios at other sites suggest contributions from non-vehicular sources such as refinery emissions. The study also observed lower BTEX concentrations at sites farther from

Table 4

| Hydrocarbon | Benzene | Toluene | Ethylbenzene | m,p-xylene | o-xylene |
|--|---------|---------|--------------|------------|----------|
| MIR Coefficient | 0.79 | 4.02 | 3.11 | 6.99 | 7.17 |
| OH ^a | 1.23 | 5.96 | 7.1 | 23.6 | 13.7 |
| Molecular Weight (g/mole) | 78.1 | 92.14 | 106.17 | 106.18 | 106.18 |
| Outdoor VOC (µg/m ³) | | | | | |
| C175 | 0.72 | 1.66 | 0.25 | 0.79 | 0.26 |
| C15 | 1.42 | 1.67 | 0.38 | 0.78 | 0.2 |
| C55 | 0.86 | 1.85 | 0.35 | 1.04 | 0.36 |
| C167 | 2.37 | 2.77 | 0.45 | 1.23 | 0.38 |
| C350 | 0.91 | 1.22 | 0.17 | 0.58 | 0.16 |
| C114 | 1.25 | 1.6 | 0.48 | 2.16 | 0.41 |
| C169 | 0.65 | 1.4 | 0.26 | 0.69 | 0.21 |
| C165 | 2.31 | 1.29 | 0.27 | 0.83 | 0.22 |
| C1607 | 0.27 | 0.37 | 0.03 | 0.15 | 0.03 |
| C617 | 0.47 | 0.72 | 0.09 | 0.33 | 0.09 |
| Ozone Formation Potential ^b | | | | | |
| C175 | 0.57 | 6.67 | 0.78 | 5.52 | 1.86 |
| C15 | 1.12 | 6.71 | 1.18 | 5.45 | 1.43 |
| C55 | 0.68 | 7.44 | 1.09 | 7.27 | 2.58 |
| C167 | 1.87 | 11.14 | 1.40 | 8.60 | 2.72 |
| C350 | 0.72 | 4.90 | 0.53 | 4.05 | 1.15 |
| C114 | 0.99 | 6.43 | 1.49 | 15.10 | 2.94 |
| C169 | 0.51 | 5.63 | 0.81 | 4.82 | 1.51 |
| C165 | 1.82 | 5.19 | 0.84 | 5.80 | 1.58 |
| C1607 | 0.21 | 1.49 | 0.09 | 1.05 | 0.22 |
| C617 | 0.37 | 2.89 | 0.28 | 2.31 | 0.65 |
| Reaction with OH ^c | | | | | |
| C175 | 0.28 | 2.63 | 0.41 | 4.29 | 0.82 |
| C15 | 0.55 | 2.64 | 0.62 | 4.24 | 0.63 |
| C55 | 0.33 | 2.93 | 0.57 | 5.65 | 1.14 |
| C167 | 0.91 | 4.38 | 0.74 | 6.68 | 1.20 |
| C350 | 0.35 | 1.93 | 0.28 | 3.15 | 0.50 |
| C114 | 0.48 | 2.53 | 0.78 | 11.74 | 1.29 |
| C169 | 0.25 | 2.21 | 0.43 | 3.75 | 0.66 |
| C165 | 0.89 | 2.04 | 0.44 | 4.51 | 0.69 |
| C1607 | 0.10 | 0.59 | 0.05 | 0.82 | 0.09 |
| C617 | 0.18 | 1.14 | 0.15 | 1.79 | 0.28 |

^a Rate Coefficient for compound-OH reaction $\times 10^{12} \text{ cm}^3/\text{molecules}$, ^b C_{BTEX} x MIR Coefficient, ^c VOC in ppb x OH

industrial areas and oil refineries. For instance, CAMS sites situated in suburban and residential regions with less traffic and industrial activity consistently recorded the lowest levels of BTEX species. The seasonal analysis demonstrated that BTEX concentrations were generally higher during the colder months (fall and winter) than in the warmer months (spring and summer). This trend can be attributed to factors such as temperature inversions and lower atmospheric mixing heights during the winter, which trap pollutants closer to the ground, along with reduced photochemical reactions during the colder months.

The study does have some limitations. The data used in the study is collected from just 10 TCEQ CAMS in the region, which might not give an accurate representation of BTEX in the city as a whole. However, based on limited data, this is the best possible assessment of BTEX exposure in the city. The analysis was also for year of 2018. Future studies can focus on more recent years or multi-year analyses to find more insights into the temporal trends of BTEX in the region. Despite the limitations, the findings from this study highlight the urgent need for targeted air quality management and regulatory interventions. By identifying the major sources of BTEX emissions, policymakers can better design and implement strategies to mitigate the exposure of the Houston population to these harmful pollutants. Enhanced regulatory measures and pollution control technologies are recommended to reduce the health risks associated with BTEX exposure, particularly for communities residing near identified hotspots.

Table 5

Ozone formation potential and OH reactivity for BTEX at different TCEQ CAMS in different seasons.

| Hydrocarbon | Benzene | Toluene | Ethylbenzene | m, p-xylene | o-xylene |
|--|---------|---------|--------------|-------------|----------|
| MIR Coefficient | 0.79 | 4.02 | 3.11 | 6.99 | 7.17 |
| OH ^a | 1.23 | 5.96 | 7.1 | 23.6 | 13.7 |
| Molecular Weight (g/mole) | 78.1 | 92.14 | 106.17 | 106.18 | 106.18 |
| Outdoor VOC (µg/m ³) | | | | | |
| Spring | 0.93 | 1.23 | 0.22 | 0.70 | 0.18 |
| Summer | 1.12 | 1.29 | 0.22 | 0.81 | 0.20 |
| Fall | 1.22 | 1.58 | 0.29 | 0.93 | 0.28 |
| Winter | 1.17 | 1.64 | 0.36 | 0.97 | 0.26 |
| Ozone Formation Potential ^b | | | | | |
| Spring | 0.74 | 4.93 | 0.67 | 4.90 | 1.31 |
| Summer | 0.89 | 5.18 | 0.67 | 5.64 | 1.45 |
| Fall | 0.96 | 6.37 | 0.92 | 6.52 | 1.99 |
| Winter | 0.92 | 6.57 | 1.12 | 6.79 | 1.86 |
| Reaction with OH ^c | | | | | |
| Spring | 0.36 | 1.93 | 0.35 | 3.77 | 0.57 |
| Summer | 0.43 | 2.02 | 0.35 | 4.35 | 0.63 |
| Fall | 0.47 | 2.49 | 0.48 | 5.02 | 0.87 |
| Winter | 0.45 | 2.57 | 0.58 | 5.23 | 0.81 |

^a Rate Coefficient for compound-OH reaction $\times 10^{12} \text{ cm}^3/\text{molecules}$, ^b C_{BTEX} x MIR Coefficient, ^c VOC in ppb x OH

Institutional Review Board Statement

Not applicable

Informed Consent Statement

Not applicable

Author Contributions

AUR and GIM conceived and designed the study; AL, SP, and EM analyzed the data; EM and SP wrote the initial draft of the paper and visualized the data; AUR and GIM edited and prepared the final draft. All authors provided valuable comments and ideas when drafting the manuscript. All authors read and approved the final draft of the manuscript.

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CRedit authorship contribution statement

Mendez Esmeralda: Methodology, Formal analysis, Data curation. **Ibarra-Mejia Gabriel:** Writing – review & editing, Conceptualization. **Raysoni Amit U:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Pinakana Sai Deepak:** Writing – original draft, Methodology, Formal analysis, Data curation. **Luna August:** Software, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jscenv.2025.100227](https://doi.org/10.1016/j.jscenv.2025.100227).

Data availability

Data will be made available on request.

References

- [1] M.I. Khoder, Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo, *Atmos. Environ.* 41 (2007) 554–566, <https://doi.org/10.1016/j.atmosenv.2006.08.051>.
- [2] A.U. Raysoni, T.H. Stock, J.A. Sarnat, M.C. Chavez, S.E. Sarnat, T. Montoya, F. Holguin, W.-W. Li, Evaluation of VOC concentrations in indoor and outdoor microenvironments at near-road schools, *Environ. Pollut.* 231 (2017) 681–693, <https://doi.org/10.1016/j.envpol.2017.08.065>.
- [3] H. Amini, M. Yunesian, V. Hosseini, C. Schindler, S.B. Henderson, N. Künzli, A systematic review of land use regression models for volatile organic compounds, *Atmos. Environ.* 171 (2017) 1–16, <https://doi.org/10.1016/j.atmosenv.2017.10.010>.
- [4] P.S. Monks, C. Granier, S. Fuzzi, A. Stohl, M.L. Williams, H. Akimoto, M. Amann, A. Baklanov, U. Baltensperger, I. Bey, et al., Atmospheric composition change – global and regional air quality, *Atmos. Environ.* 43 (2009) 5268–5350, <https://doi.org/10.1016/j.atmosenv.2009.08.021>.
- [5] A. Ramakrishnan, P.J. Lupo, A.J. Agopian, S.H. Linder, T.H. Stock, P.H. Langlois, E. Craft, Evaluating the effects of maternal exposure to benzene, toluene, ethyl benzene, and xylene on oral clefts among offspring in Texas: 1999–2008, *Birth Defects Res A Clin. Mol. Teratol.* 97 (2013) 532–537, <https://doi.org/10.1002/bdra.23139>.
- [6] US EPA, O. (2015, May 6). *Stationary Sources of Air Pollution*. (<http://www.epa.gov/ttn/>).
- [7] J.M. Baldasano, R. Delgado, J. Calbó, Applying Receptor Models to Analyze Urban/Suburban VOCs Air Quality in Martorell (Spain), *Environ. Sci. Technol.* 32 (1998) 405–412, <https://doi.org/10.1021/es970008h>.
- [8] Rosa María Cerón Bretón, et al., Seasonal and Diurnal Variations of BTEX in Ambient Air from a Site Impacted by the Oil Industry in Southeast Mexico, 21 Sept, *Bull. Environ. Contam. Toxicol.* 108 (2) (2021) 212–218, <https://doi.org/10.1007/s00128-021-03379-1>.
- [9] W.P.L. Carter, Development of Ozone Reactivity Scales for Volatile Organic Compounds, *Air Waste* 44 (7) (1994) 881–899, <https://doi.org/10.1080/1073161x.1994.10467290>.
- [10] S.-W. Choi, S.-W. Park, C.-S. Lee, H.-J. Kim, S. Bae, H.I. Inyang, Patterns of VOC and BTEX concentration in ambient air around industrial sources in Daegu, Korea, *J. Environ. Sci. Health, Part A* 44 (2009) 99–107, <https://doi.org/10.1080/10934520802515434>.
- [11] A. Monod, B.C. Sive, P. Avino, T. Chen, D.R. Blake, F. Sherwood Rowland, Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene, *Atmos. Environ.* 35 (2001) 135–149, [https://doi.org/10.1016/S1352-2310\(00\)00274-0](https://doi.org/10.1016/S1352-2310(00)00274-0).
- [12] Lan Tran Dinh, T. Hong, BTEX pollution caused by motorcycles in the megacity of HoChiMinh, *J. Environ. Sci.* 25 (2) (2013) 348–356, [https://doi.org/10.1016/s1001-0742\(12\)60045-x](https://doi.org/10.1016/s1001-0742(12)60045-x).
- [13] B.J. Finlayson-Pitts, J.N. Pitts Jr., Tropospheric air pollution: ozone, airborne toxins, polycyclic aromatic hydrocarbons, and particles, *Science* 276 (1997) 1045–1052, <https://doi.org/10.1126/science.276.5315.1045>.
- [14] M. Majdi, K. Sartelet, G.M. Lanzafame, F. Couvidat, Y. Kim, M. Chrit, S. Turquety, Precursors and formation of secondary organic aerosols from wildfires in the Euro-Mediterranean region, *Atmos. Chem. Phys.* 19 (8) (2019) 5543–5569, <https://doi.org/10.5194/acp-19-5543-2019>.
- [15] L.K. Sahu, R. Yadav, N. Tripathi, Aromatic compounds in a semi-urban site of western India: Seasonal variability and emission ratios, *Atmos. Res.* 246 (2020) 105114, <https://doi.org/10.1016/j.atmosres.2020.105114>.
- [16] Amit Masih, et al., Inhalation Exposure and Related Health Risks of BTEX in Ambient Air at Different Microenvironments of a Terai Zone in North India (Dec), *Atmos. Environ.* 147 (2016) 55–66, <https://doi.org/10.1016/j.jatmosenv.2016.09.067>.
- [17] Zeynab Tabatabaei, et al., Biomonitoring of BTEX in Primary School Children Exposed to Hookah Smoke, 13 May, *Environ. Sci. Pollut. Res.* 29 (45) (2022) 69008–69021, <https://doi.org/10.1007/s11356-022-19882-9>.
- [18] IARC. IARC (International Agency for Research on Cancer) Monographs on the Evaluation of Carcinogenic Risks to Human. Available online: (<https://monographs.iarc.who.int/list-of-classifications/>) (accessed on March 8).
- [19] A.L. Bolden, C.F. Kwiatkowski, T. Colborn, New Look at BTEX: Are Ambient Levels a Problem? *Environ. Sci. Technol.* 49 (2015) 5261–5276, <https://doi.org/10.1021/es505316f>.
- [20] R. Beelen, O. Raaschou-Nielsen, M. Staafoggia, Z.J. Andersen, G. Weinmayr, B. Hoffmann, K. Wolf, E. Samoli, P. Fischer, M. Nieuwenhuijsen, et al., Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project, *Lancet* 383 (2014) 785–795, [https://doi.org/10.1016/S0140-6736\(13\)62158-3](https://doi.org/10.1016/S0140-6736(13)62158-3).
- [21] N. Künzli, M.K. Joss, E. Gintofti, Global standards for global health in a globalized economy!, *Int. J. Public Health* 60 (2015) 757–759, <https://doi.org/10.1007/s00038-015-0729-0>.
- [22] M. Kutlar Joss, M. Eeftens, E. Gintofti, R. Kappeler, N. Künzli, Time to harmonize national ambient air quality standards, *Int. J. Public Health* 62 (2017) 453–462, <https://doi.org/10.1007/s00038-017-0952-y>.
- [23] M. Aksoy, Hematotoxicity and carcinogenicity of benzene, *Environ. Health Perspect.* 82 (1989) 193–197, <https://doi.org/10.1289/ehp.8982193>.
- [24] WHO, W.H.O. Benzene. In: *Air Quality Guidelines for Europe*, second ed. World Health Organization Regional Office for Europe, Copenhagen Available online: (https://www.euro.who.int/_data/assets/pdf_file/0005/74732/E71922.pdf) (accessed on March 8).
- [25] ATSDR. Toxicological Profile for Benzene. Available online: (<https://www.atsdr.cdc.gov/ToxProfiles/tp3.pdf>) (accessed on 2 March 2022a).
- [26] F. Bianchi, D. Cianciulli, A. Pierini, A. Seniori Costantini, Congenital malformations and maternal occupation: a registry-based case-control study, *Occup. Environ. Med* 54 (1997) 223–228, <https://doi.org/10.1136/oem.54.4.223>.
- [27] H. Choi, V. Rauh, R. Garfinkel, Y. Tu, F.P. Perera, Prenatal exposure to airborne polycyclic aromatic hydrocarbons and risk of intrauterine growth restriction, *Environ. Health Perspect.* 116 (2008) 658–665, <https://doi.org/10.1289/ehp.10958>.
- [28] S.R. Reutman, G.K. LeMasters, E.A. Knecht, R. Shukla, J.E. Lockey, G. E. Burroughs, J.S. Kesner, Evidence of reproductive endocrine effects in women with occupational fuel and solvent exposures, *Environ. Health Perspect.* 110 (2002) 805–811, <https://doi.org/10.1289/ehp.02110805>.
- [29] K.W. Whitworth, E. Symanski, A.L. Coker, Childhood Lymphohematopoietic Cancer Incidence and Hazardous Air Pollutants in Southeast Texas, 1995–2004, *Environ. Health Perspect.* 116 (2008) 1576–1580, <https://doi.org/10.1289/ehp.11593>.
- [30] G.C. Windham, L. Zhang, R. Gunier, L.A. Croen, J.K. Grether, Autism spectrum disorders in relation to distribution of hazardous air pollutants in the San Francisco Bay area, *Environ. Health Perspect.* 114 (2006) 1438–1444, <https://doi.org/10.1289/ehp.9120>.
- [31] Prabhat Kashyap, et al., BTEX Concentrations and Associated Health Risks at Urban Vegetative Sites in Delhi, India, 17 July, *Environ. Claims J.* 31 (4) (2019) 349–365, <https://doi.org/10.1080/10406026.2019.1640441>.
- [32] P. Baltrénas, E. Baltrénaitė, V. Serevičienė, P. Pereira, Atmospheric BTEX concentrations in the vicinity of the crude oil refinery of the Baltic region, *Environ. Monit. Assess.* 182 (2011) 115–127, <https://doi.org/10.1007/s10661-010-1862-0>.
- [33] D. Crosby, *Environmental Toxicology and Chemistry*, Oxford University Press, New York, 1998.
- [34] E.M. Fujita, J.G. Watson, J.C. Chow, K.L. Magliano, Receptor model and emissions inventory source apportionments of nonmethane organic gases in California's San Joaquin valley and San Francisco Bay area, *Atmos. Environ.* 29 (1995) 3019–3035, [https://doi.org/10.1016/1352-2310\(95\)00122-F](https://doi.org/10.1016/1352-2310(95)00122-F).
- [35] W.-J. Lee, S.J. Lin Lewis, Y.-Y. Chen, Y.-F. Wang, H.-L. Sheu, C.-C. Su, Y.-C. Fan, Polychlorinated biphenyls in the ambient air of petroleum refinery, urban and rural areas, *Atmos. Environ.* 30 (1996) 2371–2378, [https://doi.org/10.1016/1352-2310\(95\)00353-3](https://doi.org/10.1016/1352-2310(95)00353-3).
- [36] R. Yadav, G. Beig, V. Anand, Ritesh Kalbande, Sujit Maji, Tracer-based characterization of source variations of ambient isoprene mixing ratios in a hilly megacity, India, influenced by the local meteorology, 112465–112465, *Environ. Res.* 205 (2022), <https://doi.org/10.1016/j.envrres.2021.112465>.
- [37] A. Cattaneo, L. Campo, S. Iodice, A. Spinazzè, L. Olgiati, F. Borghi, E. Polledri, L. Angelici, D.M. Cavallo, S. Fustinoni, et al., Environmental and biological monitoring of personal exposure to air pollutants of adult people living in a metropolitan area, *Sci. Total Environ.* 767 (2021) 144916, <https://doi.org/10.1016/j.scitotenv.2020.144916>.
- [38] G. Buonanno, L. Stabile, L. Morawska, Personal exposure to ultrafine particles: The influence of time-activity patterns, *Sci. Total Environ.* 468–469 (2014) 903–907, <https://doi.org/10.1016/j.scitotenv.2013.09.016>.
- [39] S. Kaur, M.J. Nieuwenhuijsen, R.N. Colvile, Fine particulate matter and carbon monoxide exposure concentrations in urban street transport microenvironments, *Atmos. Environ.* 41 (2007) 4781–4810, <https://doi.org/10.1016/j.atmosenv.2007.02.002>.
- [40] A. Spinazzè, A. Cattaneo, G. Garramone, D.M. Cavallo, Temporal variation of size-fractionated particulate matter and carbon monoxide in selected microenvironments of the Milan urban area, *J. Occup. Environ. Hyg.* 10 (2013) 652–662, <https://doi.org/10.1080/15459624.2013.831985>.
- [41] World Population Review. (2022). *Population of Counties in Texas* (2022). <https://worldpopulationreview.com/us-counties/states/tx>.
- [42] S.-K. Song, Y.-N. Choi, Y. Choi, J. Flynn, B. Sadeghi, Characteristics of aerosol chemical components and their impacts on direct radiative forcing at urban and suburban locations in Southeast Texas, *Atmos. Environ.* 246 (2021) 118151, <https://doi.org/10.1016/j.atmosenv.2020.118151>.

- [43] Greater Houston Partnership Research. (2021). GREATER HOUSTON PARTNERSHIP HOUSTON FACTS Your Guide to Data on the Houston Region. (https://www.houston.org/sites/default/files/2021-09/houston%20facts%202020_21_digital_Final.pdf).
- [44] B. Buzcu, M.P. Fraser, Source identification and apportionment of volatile organic compounds in Houston, TX, *Atmos. Environ.* 40 (13) (2006) 2385–2400, <https://doi.org/10.1016/j.atmosenv.2005.12.020>.
- [45] M. Leuchner, B. Rappenglück, VOC source-receptor relationships in Houston during TexAQS-II, *Atmos. Environ.* 44 (33) (2010) 4056–4067, <https://doi.org/10.1016/j.atmosenv.2009.02.029>.
- [46] Port Houston: Overview - Port Houston. (2019). *Overview*. Port Houston. (<https://porthouston.com/about/our-port/about-port-houston/>).
- [47] B. Sadeghi, A. Pouyaei, Y. Choi, B. Rappenglück, Influence of seasonal variability on source characteristics of VOCs at Houston industrial area, *Atmos. Environ.* 277 (2022) 119077, <https://doi.org/10.1016/j.atmosenv.2022.119077>.
- [48] TCEQ. Site List. Available online: (https://www17.tceq.texas.gov/tamis/index.cfm?fuseaction=report.site_list).
- [49] J.P. Pinto, A.S. Lefohn, D.S. Shadwick, Spatial Variability of PM_{2.5} in Urban Areas in the United States, *J. Air Waste Manag. Assoc.* 54 (2004) 440–449, <https://doi.org/10.1080/10473289.2004.10470919>.
- [50] A.U. Raysoni, J.A. Sarnat, S.E. Sarnat, J.H. García, F. Holguin, S.F. Luévano, W.-W. Li, Binational school-based monitoring of traffic-related air pollutants in El Paso, Texas (USA) and Ciudad Juárez, Chihuahua (México), *Environ. Pollut.* 159 (2011) 2476–2486, <https://doi.org/10.1016/j.envpol.2011.06.024>.
- [51] A.U. Raysoni, T.H. Stock, J.A. Sarnat, T. Montoya Sosa, S. Ebelt Sarnat, F. Holguin, R. Greenwald, B. Johnson, W.-W. Li, Characterization of traffic-related air pollutant metrics at four schools in El Paso, Texas, USA: Implications for exposure assessment and siting schools in urban areas, *Atmos. Environ.* 80 (2013) 140–151, <https://doi.org/10.1016/j.atmosenv.2013.07.056>.
- [52] ATSDR. Toxicological Profile for Toluene. Available online: (<https://www.atsdr.cdc.gov/ToxProfiles/tp56.pdf>) (accessed on 2 March 2022b).
- [53] Z. Jiang, B. Grosselin, V. Daële, A. Mellouki, Y. Mu, Seasonal and diurnal variations of BTEX compounds in the semi-urban environment of Orleans, France, *Sci. Total Environ.* 574 (2017) 1659–1664, <https://doi.org/10.1016/j.scitotenv.2016.08.214>.
- [54] P. Kumari, D. Soni, S.G. Aggarwal, K. Singh, Seasonal and diurnal measurement of ambient benzene at a high traffic inflation site in Delhi: Health risk assessment and its possible role in ozone formation pathways, e2023016-e2023016, *Environ. Anal. Health Toxicol.* 38 (3) (2023), <https://doi.org/10.5620/eaht.2023016>.
- [55] C. Popitanu, G. Cioca, L. Copolovici, D. Iosif, F.-D. Munteanu, D. Copolovici, The Seasonality Impact of the BTEX Pollution on the Atmosphere of Arad City, Romania, *Int. J. Environ. Res. Public Health* 18 (9) (2021) 4858, <https://doi.org/10.3390/ijerph18094858>.
- [56] R. Singh, M. Gaur, A. Shukla, Seasonal and Spatial Variation of BTEX in Ambient Air of Delhi, *J. Environ. Prot.* 07 (05) (2016) 670–688, <https://doi.org/10.4236/jep.2016.75060>.
- [57] H.D. Rad, A.A. Babaei, G. Goudarzi, K.A. Angali, Z. Ramezani, M.M. Mohammadi, Levels and sources of BTEX in ambient air of Ahvaz metropolitan city, *Air Qual., Atmosphere Health* 7 (4) (2014) 515–524, <https://doi.org/10.1007/s11869-014-0254-y>.
- [58] P. Iovino, R. Polverino, S. Salvestrini, S. Capasso, Temporal and spatial distribution of BTEX pollutants in the atmosphere of metropolitan areas and neighbouring towns, *Environ. Monit. Assess.* 150 (2009) 437–444, <https://doi.org/10.1007/s10661-008-0242-5>.
- [59] S.-J. Kim, H.-O. Kwon, M.-I. Lee, Y. Seo, S.-D. Choi, Spatial and temporal variations of volatile organic compounds using passive air samplers in the multi-industrial city of Ulsan, Korea, *Environ. Sci. Pollut. Res.* 26 (6) (2019) 5831–5841, <https://doi.org/10.1007/s11356-018-4032-5>.
- [60] M.A. El-Hashemy, H.M. Ali, Characterization of BTEX group of VOCs and inhalation risks in indoor microenvironments at small enterprises, *Sci. Total Environ.* 645 (2018) 974–983, <https://doi.org/10.1016/j.scitotenv.2018.07.157>.
- [61] L. Miller, X. Xu, A. Grgicak-Mannion, J. Brook, A. Wheeler, Multi-season, multi-year concentrations and correlations amongst the BTEX group of VOCs in an urbanized industrial city, *Atmos. Environ.* 61 (2012) 305–315, <https://doi.org/10.1016/j.atmosenv.2012.07.041>.
- [62] L.I. Kleiman, P.H. Daum, Y.-N. Lee, L.J. Nunnermacker, S.R. Springston, J. Weinstein-Lloyd, P. Hyde, P. Doskey, J. Rudolph, J. Fast, C. Berkowitz, Photochemical age determinations in the Phoenix metropolitan area (n/a-n/a), *J. Geophys. Res.: Atmospheres* 108 (D3) (2003), <https://doi.org/10.1029/2002jd002621>.
- [63] L.K. Sahu, N. Tripathi, M. Gupta, V. Singh, R. Yadav, K. Patel, Impact of COVID-19 Pandemic Lockdown in Ambient Concentrations of Aromatic Volatile Organic Compounds in a Metropolitan City of Western India, *J. Geophys. Res.: Atmospheres* 127 (6) (2022), <https://doi.org/10.1029/2022jd036628>.
- [64] L. Miller, L.D. Lemke, X. Xu, S.M. Molaroni, H. You, A.J. Wheeler, J. Booza, A. Grgicak-Mannion, R. Krajenta, P. Graniero, et al., Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada), *Atmos. Environ.* 44 (2010) 1162–1174, <https://doi.org/10.1016/j.atmosenv.2009.12.030>.
- [65] J. An, B. Zhu, H. Wang, Y.-Y. Li, X. Lin, H. Yang, Characteristics and source apportionment of VOCs measured in an industrial area of Nanjing, Yangtze River Delta, China, *Atmos. Environ.* 97 (2014) 206–214, <https://doi.org/10.1016/j.scitotenv.2014.08.021>.
- [66] M.Y. Civan, T. Elbir, R. Seyfioğlu, Ö.O. Kuntasal, A. Bayram, G. Doğan, S. Yurdakul, Ö. Andıç, A. Müezzinoglu, S.C. Sofuoğlu, H. Pekey, B. Pekey, A. Bozlaker, M. Odabasi, G. Tuncel, Spatial and temporal variations in atmospheric VOCs, NO₂, SO₂, and O₃ concentrations at a heavily industrialized region in Western Turkey, and assessment of the carcinogenic risk levels of benzene, *Atmos. Environ.* 103 (2015) 102–113, <https://doi.org/10.1016/j.atmosenv.2014.12.031>.
- [67] Y. Dumanoglu, M. Kara, H. Altıok, M. Odabasi, T. Elbir, A. Bayram, Spatial and seasonal variation and source apportionment of volatile organic compounds (VOCs) in a heavily industrialized region, *Atmos. Environ.* 98 (2014) 168–178, <https://doi.org/10.1016/j.atmosenv.2014.08.048>.
- [68] V. Tiwari, Y. Hanai, S. Masunaga, Ambient levels of volatile organic compounds in the vicinity of petrochemical industrial area of Yokohama, Japan, *Air Qual., Atmosphere Health* 3 (2) (2009) 65–75, <https://doi.org/10.1007/s11869-009-0052-0>.
- [69] A. Gelencsér, K. Siszler, J. Hlavay, Toluene–Benzene Concentration Ratio as a Tool for Characterizing the Distance from Vehicular Emission Sources, *Environ. Sci. Technol.* 31 (1997) 2869–2872, <https://doi.org/10.1021/es970004c>.
- [70] A.I. Skorokhod, E.V. Berezina, K.B. Moiseenko, N.F. Elansky, I.B. Belikov, Benzene and toluene in the surface air of northern Eurasia from TROIKA-12 campaign along the Trans-Siberian Railway, *Atmos. Chem. Phys.* 17 (8) (2017) 5501–5514, <https://doi.org/10.5194/acp-17-5501-2017>.
- [71] R.W. Prinn, D.M. Cunnold, R.A. Rasmussen, P. Simmonds, F.N. Alyea, A. M. Crawford, P.J. Fraser, R.B. Rosen, Atmospheric Trends in Methylchloroform and the Global Average for the Hydroxyl Radical, *Science* 238 (4829) (1987) 945–950, <https://doi.org/10.1126/science.238.4829.945>.
- [72] P.F. Nelson, S.M. Quigley, The m,p-xylesnes:ethylbenzene ratio. A technique for estimating hydrocarbon age in ambient atmospheres, *Atmos. Environ.* (1967) 17 (1983) 659–662, [https://doi.org/10.1016/0004-6981\(83\)90141-5](https://doi.org/10.1016/0004-6981(83)90141-5).
- [73] T. Tunsarsingkarn, T. Prueksasit, D. Morknay, S. Semathong, A. Rungsiyothin, K. Zapapung, Ambient air's volatile organic compounds and potential ozone formation in urban area, Bangkok, Thailand, *J. Environ. Occup. Sci.* 3 (2014) 1, <https://doi.org/10.5455/jeos.20140903015449>.
- [74] M. Miri, M. Rostami Aghdam Shendi, H.R. Ghaffari, H. Ebrahimi Aval, E. Ahmadi, E. Taban, A. Gholizadeh, M. Yazdani Aval, A. Mohammadi, A. Azari, Investigation of outdoor BTEX: Concentration, variations, sources, spatial distribution, and risk assessment, *Chemosphere* 163 (2016) 601–609, <https://doi.org/10.1016/j.chemosphere.2016.07.088>.
- [75] D. Dominick, S.R. Wilson, C. Paton-Walsh, R. Humphries, É. Guérette, M. Keywood, P. Selleck, D. Kubistin, B. Marwick, Particle Formation in a Complex Environment, *Atmosphere* 10 (5) (2019) 275, <https://doi.org/10.3390/atmos10050275>.
- [76] O.O. Emoyan, P.O. Agbaire, E. Ohwo, G.O. Tesi, Priority mono-aromatics measured in anthropogenic impacted soils from Delta, Nigeria: concentrations, origin, and human health risk, *Environ. Forensics* (2021) 1–13, <https://doi.org/10.1080/15275922.2021.1892880>.
- [77] R.R. Hoque, P.S. Khillare, T. Agarwal, V. Shridhar, S. Balachandran, Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India, *Sci. Total Environ.* 392 (2008) 30–40, <https://doi.org/10.1016/j.scitotenv.2007.08.036>.
- [78] Cruz, Santos Daniela Silva Santos, S. Gomes, Santos, Keliane S.P.P. Souza, Exploratory analysis of the atmospheric levels of BTEX, criteria air pollutants and meteorological parameters in a tropical urban area in Northeastern Brazil, *104265–104265, Microchem. J.* 152 (2020), <https://doi.org/10.1016/j.microc.2019.104265>.
- [79] M. Caselli, G. de Gennaro, A. Marzocca, L. Trizio, M. Tutino, Assessment of the impact of the vehicular traffic on BTEX concentration in ring roads in urban areas of Bari (Italy), *Chemosphere* 81 (2010) 306–311, <https://doi.org/10.1016/j.chemosphere.2010.07.033>.
- [80] C.-C. Hsieh, J.-H. Tsai, VOC concentration characteristics in Southern Taiwan, *Chemosphere* 50 (2003) 545–556, [https://doi.org/10.1016/S0045-6535\(02\)00275-8](https://doi.org/10.1016/S0045-6535(02)00275-8).
- [81] A. Srivastava, A.E. Joseph, S. Patil, A. More, R.C. Dixit, M. Prakash, Air toxics in ambient air of Delhi, *Atmos. Environ.* 39 (2005) 59–71, <https://doi.org/10.1016/j.atmosenv.2004.09.053>.
- [82] M. Ting, W. Yue-Si, J. Jie, W. Fang-Kun, W. Mingxing, The vertical distributions of VOCs in the atmosphere of Beijing in autumn, *Sci. Total Environ.* 390 (2008) 97–108, <https://doi.org/10.1016/j.scitotenv.2007.08.035>.
- [83] T. Elbir, B. Cetin, E. Bayram, M. Odabasi, Characterization of Volatile Organic Compounds (VOCs) and Their Sources in the Air of Izmir, Turkey, *Environ. Monit. Assess.* 133 (1–3) (2006) 149–160, <https://doi.org/10.1007/s10661-006-9568-z>.
- [84] J. Zhang, T. Wang, W.L. Chameides, C. Cardelino, D.R. Blake, D.G. Streets, Source characteristics of volatile organic compounds during high ozone episodes in Hong Kong, Southern China, *Atmos. Chem. Phys.* 8 (16) (2008) 4983–4996, <https://doi.org/10.5194/acp-8-4983-2008>.
- [85] S. Yurdakul, M. Civan, G. Tunçel, Volatile organic compounds in suburban Ankara atmosphere, Turkey: Sources and variability, *Atmos. Res.* 120–121 (2013) 298–311, <https://doi.org/10.1016/j.atmosres.2012.09.015>.
- [86] J. Shi, H. Deng, Z. Bai, S. Kong, X. Wang, J. Hao, X. Han, P. Ning, Emission and profile characteristic of volatile organic compounds emitted from coke production, iron smelt, heating station and power plant in Liaoning Province, China, *Sci. Total Environ.* 515–516 (2015) 101–108, <https://doi.org/10.1016/j.scitotenv.2015.02.034>.
- [87] P.D. Kalabokas, J. Hatzianestis, J.G. Bartzis, P. Papagiannopoulos, Atmospheric concentrations of saturated and aromatic hydrocarbons around a Greek oil refinery, *Atmos. Environ.* 35 (14) (2001) 2545–2555, [https://doi.org/10.1016/s1352-2310\(00\)00423-4](https://doi.org/10.1016/s1352-2310(00)00423-4).
- [88] W. Grace, Yung Chen Yao, J. Sheng, Yi. Chyun Hsu, Li. Peng Chang, Ken Hui Chang, Source impacts by volatile organic compounds in an industrial city of

- southern Taiwan, Sci. Total Environ. 398 (1-3) (2008) 154–163, <https://doi.org/10.1016/j.scitotenv.2008.02.053>.
- [89] R.G. Derwent, T.J. Davies, M. Delaney, G.J. Dollard, R.A. Field, P. Dumitresan, P. D. Nason, B.M.R. Jones, S.A. Pepler, Analysis and interpretation of the continuous hourly monitoring data for 26 C2–C8 hydrocarbons at 12 United Kingdom sites during 1996, Atmos. Environ. 34 (2000) 297–312, [https://doi.org/10.1016/S1352-2310\(99\)00203-4](https://doi.org/10.1016/S1352-2310(99)00203-4).
- [90] L. Miller, X. Xu, A. Wheeler, D.O. Atari, A. Grgicak-Mannion, I. Luginaah, Spatial Variability and Application of Ratios between BTEX in Two Canadian Cities, Sci. World J. 11 (2011) 2536–2549, <https://doi.org/10.1100/2011/167973>.
- [91] K. Niaz, H. Bahadar, F. Maqbool, M. Abdollahi, A review of environmental and occupational exposure to xylene and its health concerns, EXCLI J. 14 (2015) 1167–1186, <https://doi.org/10.17179/excli2015-623>.
- [92] S. Kumari, N. Baghel, A. Lakhani, K.M. Kumari, BTEX and formaldehyde levels at a suburban site of Agra: Temporal variation, ozone formation potential and health risk assessment, Urban Clim. 40 (2021) 100997, <https://doi.org/10.1016/j.ulclim.2021.100997>.
- [93] H. Mojarrad, R. Fouladi Fard, M. Rezaali, H. Heidari, H. Izanloo, A. Mohammadbeigi, A. Mohammadi, A. Sorooshian, Spatial trends, health risk assessment and ozone formation potential linked to BTEX, Hum. Ecol. Risk Assess.: Int. J. 26 (10) (2019) 2836–2857, <https://doi.org/10.1080/10807039.2019.1688640>.
- [94] A. Garg, N.C. Gupta, A comprehensive study on spatio-temporal distribution, health risk assessment and ozone formation potential of BTEX emissions in ambient air of Delhi, India, Sci. Total Environ. 659 (2019) 1090–1099, <https://doi.org/10.1016/j.scitotenv.2018.12.426>.
- [95] Y. Zou, E. Charlesworth, N. Wang, R.M. Flores, Q.Q. Liu, F. Li, T. Deng, X.J. Deng, Characterization and ozone formation potential (OFP) of non-methane hydrocarbons under the condition of chemical loss in Guangzhou, China, 118630–118630, Atmos. Environ. 262 (2021), <https://doi.org/10.1016/j.atmosenv.2021.118630>.
- [96] CARB. (2003). *Rulemaking on the adoption of proposed amendments to the tables of maximum incremental reactivity (MIR) values, California air resources board, December 3.* (<https://www.arb.ca.gov/regact/mir2003/mir2003.htm>).
- [97] Carter. (2010). *Development of the SAPRC-07 chemical mechanism and updated ozone reactivity scales, final report to the California air resources board Contract No. 03-318.* January 27. Ucr.edu. (<https://intra.cert.ucr.edu/~carter/SAPRC/>).
- [98] M.A. Venecek, W. Carter, M.J. Kleeman, Updating the SAPRC Maximum Incremental Reactivity (MIR) scale for the United States from 1988 to 2010, J. Air Waste Manag. Assoc. 68 (12) (2018) 1301–1316, <https://doi.org/10.1080/10962247.2018.1498410>.
- [99] H.H.A. Hamid, M.T. Latif, R. Uning, M.S.M. Nadzir, M.F. Khan, G.C. Ta, N. Kannan, Observations of BTEX in the ambient air of Kuala Lumpur by passive sampling, Environ. Monit. Assess. 192 (6) (2020), <https://doi.org/10.1007/s10661-020-08311-4>.
- [100] D. Mehta, Naba Hazarika, A. Srivastava, Diurnal variation of BTEX at road traffic intersection points in Delhi, India: source, ozone formation potential, and health risk assessment, Environ. Sci. Pollut. Res. 27 (10) (2020) 11093–11104, <https://doi.org/10.1007/s11356-019-07495-8>.
- [101] S. Zhao, R. Li, S. Wang, Y. Liu, W. Lu, Y. Zhao, Emission of volatile organic compounds from landfill working surfaces: Formation potential of ozone and secondary organic aerosols, 163954–163954, Sci. Total Environ. 886 (2023), <https://doi.org/10.1016/j.scitotenv.2023.163954>.
- [102] N. Liu, X. Li, W. Ren, L. Li, C.-C. Su, C. Wang, Concentration Characteristics and Photochemical Reactivities of VOCs in Shenyang, China, 1240–1240, Atmosphere 12 (10) (2021), <https://doi.org/10.3390/atmos12101240>.