CASE STUDY

Spatiotemporal variations, photochemical characteristics, health risk assessment and mid pandemic changes of ambient BTEX in a west Asian metropolis

Sam Dehhaghi[1] · Hossein Hasankhani[2] · Ahmad Taheri[2]

Abstract

This study examined the concentration of BTEX in Tehran from 2018 to 2020 in five monitoring stations with different backgrounds, which has been accomplished using the combination of passive sampling and GC-FID method. The total concentration of BTEX was estimated to be 65.39 ($\mu g/m^3$), with a higher average concentration in 2019–2020 (77.79 $\mu g/m^3$) compared to 2018–2019 (53.48 $\mu g/m^3$) due to the leaping concentration of Toluene in the pandemic era. Despite a Benzene concentration decline in recent years, the average annual concentration of Benzene (5.66 $\mu g/m^3$) at five stations remained higher than the EU commission and India standards (5 $\mu g/m^3$) as well as Japan and Iraq thresholds (3 $\mu g/m^3$). Toluene dominated other species in terms of concentrations, mass distribution ($\sim 0.6\%$), followed by m,p–Xylene ($\sim 0.2\%$), Benzene (~ 0.05–0.1) and Ethylbenzene (< 0.05). The evidence regarding seasonal changes of BTEX in 2019 shows the maximum concentration of these compounds in autumn, which is probably due to heavier traffic compared to other seasons. In contrast, in the first half of 2020 (which encompasses the start of the pandemic period and urban lockdown), point sources seem to play a prominent role in concentration fluctuations, as confirmed by changes in inter-species relationships and lower traffic congestion. The highest mean concentrations were observed in high-traffic, residential and suburban sites, respectively. The study reveals that m,p-Xylene possess the highest Ozone formation potential (~ 109.46), followed by Toluene (~ 85.34), o-Xylene (~ 46.87), Ethylbenzene (~ 13.52) and Benzene (~ 2.61). Health risk assessment results indicated the high carcinogenic risk of Benzene (mean = 3.6×10^{-6}) and the acceptable non-carcinogenic risk of BTEX (hazard index $\sim 0.03 <$ specified limit of 1). Finally, the estimated weighted exposures of BTEX emphasized that residents near the high-traffic districts are more exposed to BTEX.

Keywords Air pollution · Tehran · Volatile organic compounds · BTEX · Ozone formation potential · Health risk assessment

1 Introduction

Ambient air pollution is one of the most prominent threats to public health in different countries, especially in industrial and developing societies, causing more than 7 million deaths per year (Lelieveld et al. 2019; Vohra et al. 2021). Moreover, residents of most of low and middle-income countries are deprived of clean air inhalation (Carvalho 2016). As the capital of Iran, Tehran is no exception, being saturated with a population that breathes polluted air for more than a third of the year (Hassani and Hosseini. 2016). This environmental crisis has occurred due to the supermassive consumption of fossil fuels, which does not seem far from expectation despite the average daily commuting of more than two million motor vehicles in the city, while poor maintenance of automobiles may also be an influential cause (Atash 2007; Naddafi et al. 2012).

Among air contaminants, volatile organic compounds (VOCs) are a group of pollutants that emit from various sources, and non-point sources are claimed to be the main origins of the emission of these compounds (Buczynska

✉ Sam Dehhaghi
dehhaghis@gmail.com

1 Environmental Sciences Research Institute, Shahid Beheshti University, Tehran, Iran

2 Tehran Air Quality Control Company, Tehran Municipality, Tehran, Iran

et al. 2009; Kanjanasiranont et al. 2017). The share of mobile sources in the production and dissemination of VOCs is estimated at 86% in Tehran (Shahbazi et al. 2016). The effects of these compounds on human health consist of cardiovascular and pulmonary diseases as well as mutagenic and carcinogenic effects (Allouch et al. 2013; Bolden et al. 2015). In addition, the environmental effects of these pollutants include the greenhouse effect and their role in producing tropospheric Ozone and Peroxyacetil Nitrate (DeMore et al. 1997; Pappas et al. 2000; Soni et al. 2018).

BTEX stands for Benzene, Toluene, Ethyl-Benzene, p, m, o-Xylene. In describing the importance of these aromatic compounds, many studies have illustrated their short and long-term effects on human health, which range from symptoms such as nausea and dysfunction of various body organs to pregnancy issues (Wilbur and Bosch 2004). Furthermore, BTEX has also been mentioned as the indicator of the presence of VOCs in urban areas, as the study of interspecies relationships represents clues regarding their distributional patterns and their possible sources (Na and Kim 2001; Zalel and Broday 2008; Kerchich and Kerbachi 2012). Furthermore, since atmospheric phenomena such as temperature inversion cause pollution stability in winter, the study of seasonal variations of these species helps identify climatic interactions which are partially responsible for the leap of BTEX pollution.

In addition, photochemical smog is one of the most pervasive pollution events which frequently occur in high-density metropolitan cities. Ozone (which is a criteria air pollutant) is known as a gaseous product of this event. Ozone has also been accused of raising the global mortality rate to 0.7 million deaths per year and adversely affecting vegetation and ecosystems (Zarandi et al. 2015). It is also known that its tropospheric entity is dependent on photochemical reactions (Anenberg et al. 2010). In this process, BTEX has been shown to play a direct role in Ozone production and an indirect role in secondary aerosols formation due to reaction with hydroxyl radicals (OH°) and decomposition of VOCs (Brocco et al. 1997; Odum et al. 1997).

In recent years, many studies have been conducted on air pollution in Tehran (Shahbazi et al. 2016; Taheri et al. 2019). According to studies, mobile sources emit approximately 85% of air pollutants in Tehran (Shahbazi et al. 2016). Nevertheless, the worldwide pandemic seems to have affected the air quality and recent studies achieved novel findings in this regard (Berman and Ebisu 2020; Venter et al. 2020; Wu et al. 2020; Travaglio et al 2021).

Recent local research on BTEX presented valuable information regarding some of the point and non-point sources causing the heightened levels of these pollutants (Dehghani et al. 2017; Golkhorshidi et al. 2019; Ghaderpoury et al. 2021), while questions still remain unanswered

about their significance. Hence the long-term temporal study of ambient BTEX pollution, especially during the pandemic period may provide worthy clues as it unveils possible sources involved in the dispersion of these contaminants during the temporary absence of heavy traffic congestion with respect to the traffic restriction laws enacted during this epoch. In addition, the participation of each compound in Ozone formation and the quantification of their reactivity with OH° helps prioritize these compounds to monitor their sources as the causal origins of ambient Ozone pollution.

The purpose of this study includes the examination of BTEX spatiotemporal variations, the conjecture of their possible sources after the beginning of the Covid-19 outbreak, the analysis of interspecies relationships, the ranking of pollutants based on their Ozone formation potential and reactivity with OH°, and the assessment of possible health risks associated with current levels of public exposure to these contaminants.

2 Materials and methodology

2.1 Site description and study interval

Tehran, the capital of Iran, has an area of more than 600 km^2, which is divided into 22 municipal districts. In terms of geographical coordinates, it is located at 41.35° North and 51.25° East and is surrounded by Alborz and Varamin plains in the north and south, respectively. The average annual daily temperature is estimated to be 19 °C, and the average temperature varies from 5 to 40 °C, while January and July are the coldest and warmest months, respectively (Tayyebi et al. 2018). In recent years, the cumulative rainfall in Tehran has been approximately 300 mm (Tayyebi et al. 2018). It is estimated that the Tehran population, which is more than 12 million people, has made it the most populous city in Iran (Esteghamati et al. 2009).

Figure 1 shows the five BTEX sampling stations in the study area. For further demonstration, monitoring site characteristics are provided in Table S1.

District 22 station (RES 1) is located in a residential area, being far away from traffic congestion and surrounded by some fixed sources (Shahbazi et al. 2016). Tehran-Karaj and Azadegan highways are the nearest main roads lying at a distance of about 0.5 to 1 km from this station to the south and east.

Aqdasiyeh station (RES 2) is the other residential area with lower traffic of private motor vehicles compared to other monitoring stations. The establishment of the BRT bus line has also been effective in controlling urban traffic in this area. The nearest suspected sources of pollution are known to be traffic intersections such as Sadr, Imam Ali,
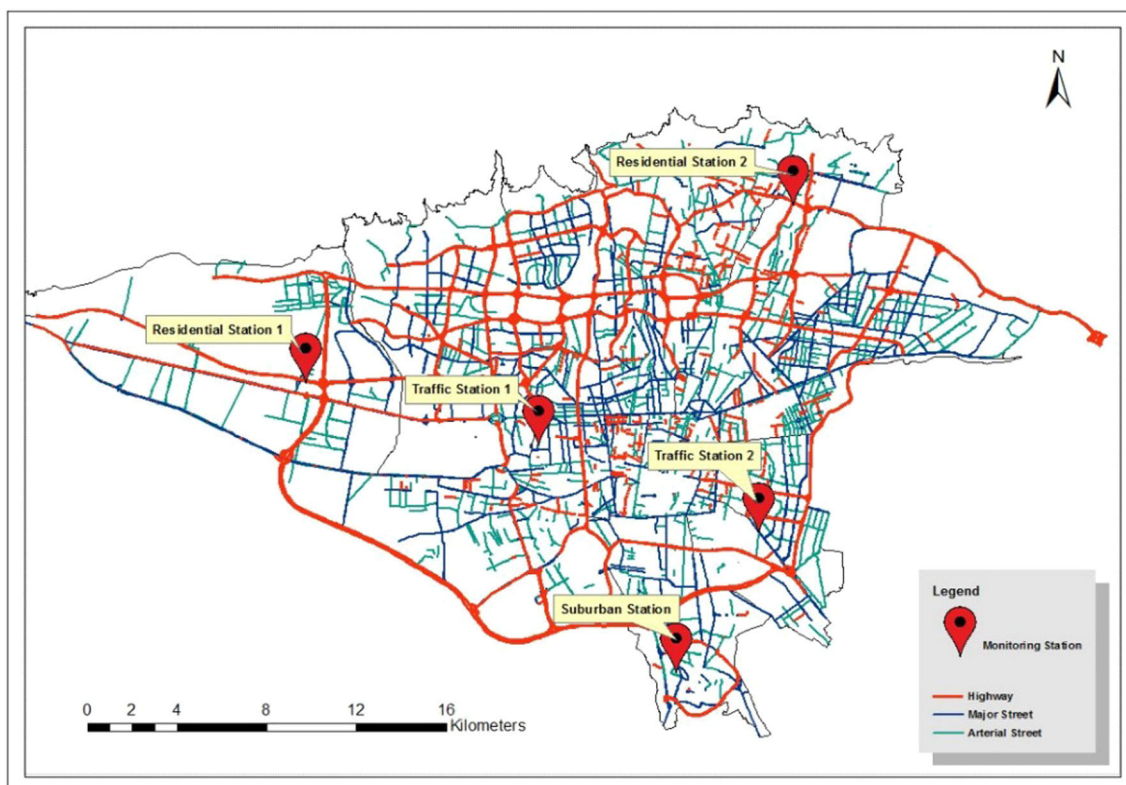
Figure1 Map of sampling points located in Tehran, Iran along with indication of main streets, highways and arterial streets

and Sayad Shirazi highways, which are well accessible from this area. In addition, according to the latest Tehran emissions inventory, some gas stations are considered as important immobile emission sources in this site (Shahbazi et al. 2016).

District 10 station (TRS 1) is located in Tehran's downtown and is considered a high-traffic area with a distance of less than 1.5 km away from the public transportation terminal of Azadi Square and some of the most important and crowded passages. For example, the distance from this station to Niayesh Highway, Azadi Street, and Saeedi Highway is about 1.5 km, less than 1 km, and about 0.5 km, respectively.

The Mahallati station (TRS 2) is known as a high-traffic station. The evidence that confirms this fact, is its 0.5 km distance from Imam Ali Highway, being overwhelmed by massive vehicle commuting.

Shahr Rey station (SUS), located in the southern suburbs of Tehran, is one of the most polluted areas. Its proximity to the crowded Azadegan and Basij highways, various industrial settlements such as the Tehran oil refinery, and the vast cemetery of Behesht Zahra are important factors that intensify air pollution in this area. The detailed map of the surrounding environment of each monitoring station is provided in Figure S1 for further demonstration.

A sum of 52 samples were gathered from September 2018 to September 2020 in bi-weekly periods. 26 bi-weekly sampling operations were conducted in each year, including 6 operations each season (2 sampling sessions per month). Sampling duration was 24 h for each sampling session. The study of seasonal changes was conducted according to the climatic pattern of Iran (based on solar calendar).

2.2 Sampling protocols and quality assurance/ quality control (QA/QC) program

Samples were taken using passive samplers made by Passam corporation (Passam Co. 2016). Sampling operations were performed according to the instructions defined at EN 14662–5. The diffusive samplers were installed at a height of 350 cm above the ground. Before using passive samplers, the accuracy and correctness of their results were validated with the active sampling method. The sampler installation was considered in suitable conditions in terms of altitude, environmental changes, and weather conditions such as wind, rain, and sunshine. The samplers and their installed appearance are shown in Figure S2. The samplers consist of a double-ended glass tube containing charcoal and coated with cellulose acetate. Shelters are designed for pipes to minimize the effects of meteorological events such

as rain and storms (Passam ag. 2019a, 2019b). The collection tube is opened by removing one of the porous buffer layers, and after adding activated charcoal to the duct, 1.5 ml of carbon disulfide is added. The duct is then closed and gently shaken. After 60 min, the solvent is transferred to the autosampler vial and tightly closed. Due to air diffusion into the tube, BTEX is absorbed by activated carbon. By removing the plastic cover of the absorbent tube and the sponge located in its front part, the active carbon present in the front part of the tube is poured into a glass vial, and one milliliter of carbon disulfide was added to it. Then the plastic lid of the glass vial was sealed with parafilm. The same procedure was done for the rear part of the active carbon tube. The vials containing the front part and the back part were placed inside the vibrator for five minutes and prepared for BTEX measurement. Finally, these materials were analyzed using gas chromatography—flame ionization detection (GC-FID) (HP 5890).

The BTEX concentrations were calculated using Eq. (1):

$$C_{BTEX} = (Q \times 10^6)/(SR \times t) \qquad (1)$$

where C_{BTEX} (μg/m^3) is the BTEX concentration, Q (μg) is the mass of BTEX, t (min) is the exposure duration, and SR (ml/min) is the sampling rate. The sampling accuracy was monitored and evaluated in 5% of the sampling operations using duplicate and blank samples (laboratory blank: 50% and field blank: 50%). The sampling rate of Benzene, Toluene, Ethylbenzene, p-Xylene, m-Xylene, and o-Xylene was 6.44, 5.72, 5.2, 5.03, 5.03, and 5.45 ml/min, respectively. The lower limit of detection and limit of quantification was equal to 0.4 (μg/m^3) and 1.33 (μg/m^3) for BTEX (considered for 14 days of sampling).

2.3 Ozone formation potential and OH° reactivity

Since tropospheric Ozone enters the atmosphere due to photochemical reactions between VOC_S and NO_X, MIR (maximum incremental reactivity) coefficients are used to quantify the effect of each compound on the process of photochemical smog and tropospheric Ozone formation (Carter 1994). Furthermore, the importance of the contribution of volatile organic compounds in this process is slightly clarified. As subsets of volatile organic compounds, BTEX species also play a role in this process, but the importance of each is different. Therefore, their prioritization in the Ozone formation cycle plays a vital role in controlling air pollution. The Ozone formation potential (OFP) of BTEX is calculated according to Eq. (2):

$$OFP = C_{BTEX}(\mu g/m^3) \times MIR(gO_3/gVOC_S) \qquad (2)$$

The reactivity of BTEX with OH °, which is a measure of the ability of these compounds to form more oxidized hydrocarbons (Hoque et al. 2008), is determined using Eq. (3):

$$BTEX - OH^0 = C_{BTEX}(ppb) \times RC_{BTEX-OH^0} \qquad (3)$$

where $RC_{BTEX\text{-}OH°}$ is the constant rate of BTEX reaction with hydroxyl radical (10^{-12} cm^3/molecule/s) multiplied by 10^{12}. In this study, the reaction rate constants are derived from the studies conducted by Atkinson (1997) and Carter (1994, 2010).

2.4 Health risk assessment

Regarding the effects of VOCs on human health, many studies indicate the carcinogenic and non-carcinogenic effects of these compounds, such as cancer risk of Benzene and potential cancer risk of Ethylbenzene which is inferenced by the International Agency for Research on Cancer. Furthermore, Toluene and Xylene possess chronic effects (IARC 2012). Therefore, health risk assessment is the most effective way to estimate the effects of these substances on human health (Edokpolo et al. 2014).

This study used the US Environmental Protection Agency (US EPA) method, which was modified in 2009 (US EPA 2009). Therefore, the first step in estimating the associated health risks of BTEX is to calculate the exposure concentration of these pollutants, which is defined by Eq. (4):

$$EC = (C \times ET \times EF \times ED)/AT \qquad (4)$$

where EC is the exposure concentration (μg/m^3), C is the concentration of pollutants in the ambient air (μg/m^3), ET is the exposure time (8 h/day), EF is the exposure frequency (175 days/year), ED is the Exposure duration (30 years) and AT is the average lifetime (70 years = 613,200 h). These values were in conformity with US-EPA defaults and had been used in similar studies (Masih et al. 2016; Garg et al. 2019; Borhani and Noorpoor 2017).

The chronic risk of BTEX is calculated using the Hazard quotient (HQ), which is presented by Eq. (5):

$$HQ = EC/RfC \qquad (5)$$

where RfC is the reference concentration (μg/m^3), the hazard index (HI) is also used to indicate the overall risk of chronic effects, which is equal to the sum of total hazard quotients of BTEX. The cancer risk (CR) of carcinogens is calculated via Eq. (6):

$$CR = EC \times IUR \qquad (6)$$

where IUR is the inhalation unit risk (m^3/μg), equal to 7.8×10^{-6} for Benzene and 2.5×10^{-6} for Ethylbenzene based on EPA-IRIS (US EPA 1998) and OEHHA

instructions. According to the EPA recommendations, the permissible cancer risk limit is equal to 1×10^{-6}. Therefore, a hazard index of more than 1 indicates unhealthy conditions in terms of non-cancer risk of BTEX in ambient air (Dehghani et al. 2018). To eliminate the uncertainties of the model (which is the result of the variation of model parameters), Oracle Crystal Ball 11.1.2.3 was used to calculate the potential non-carcinogenic risk of BTEX and the potential cancer risk of Benzene with a probabilistic approach. ET and EF are considered as the risk assessment and sensitivity analysis parameters which are defined as the hours (8 ± 2 h/day) and days (175 ± 50 days/year) that citizens spend in the outdoor environment on average, and their presumed distribution was normal.

Since the health risk levels associated with BTEX vary from site to site, the weighted exposure for each site is calculated based on the mean BTEX concentration and the neighboring population of the stations using Thiessen polygon.

The BTEX weighed exposure in each monitoring station is calculated by Eq. (7) (Nyhan et al. 2016):

$$W_E = \sum_{i}^{j} C_{ij} P_{ij} \tag{7}$$

where W_E represents the weighted exposure, C_{ij} is the estimated concentration of a certain pollutant at the location (i) and time (j), and P_{ij} is the proportion of total population at location (i) and time (j).

2.5 Statistical analysis

In order to obtain an outlook on the possible sources of pollution and photochemical aging of BTEX, the inter-species ratios were calculated. Kruskal–Wallis non-parametric test ($\alpha = 0.05$) was conducted to investigate the intra-station differences, followed by Dunn's method post-hock analysis. The post-hock analysis was meant to compare the means between each pair of stations. The coefficient of divergence (COD) was used to examine the concentration change of each compound in monitoring stations in the second year of sampling interval compared to the first year. This criterion had been introduced in previous studies as the statistical index of intra-station changes of pollutants (Wongphatarakul et al. 1998; Wilson et al. 2005). Pearson correlation coefficient was utilized to evaluate inter-compound correlations as well as correlations between BTEX concentrations and weather conditions (average temperature (°C), relative humidity (%) and prevailing wind speed (km/h)). The calculations were performed using MS Excel and Real Statistics resource pack. Real Statistics resource pack is an easy-to-use add-in for Microsoft Excel which contains various statistical features to enhance Excel in terms of statistical capabilities. This complimentary add-in is available on real-statistics.com, where further information is provided.

3 Results and discussion

3.1 Concentration levels, spatiotemporal variations, and mass distribution of BTEX

Table 1 presents the BTEX levels measured in 2 yearly sampling intervals in different monitoring stations. The average concentration of Benzene in the entire sampling period generally exceeded the standards approved by the European Union and India (5 µg/m³) as well as Japan and China (Sekar et al. 2019). The violations from European and Indian standards can be seen in all stations except in RES 1 (Figure S3).

The BTEX levels are higher in traffic areas (TRS 1 and TRS 2) and suburbs (SUS) than in residential sites (RES 1 and RES 2). Toluene antecedes other species in terms of concentration (1.1 to ~ 5 times on average), which is consistent with other studies (Cruz et al. 2020; Ghaffari et al. 2021; Alahabadi et al. 2021). Table 1 also shows that the coefficients of variation are higher in the second period. The only exception is the greater fluctuations of Benzene concentration in 2018–2019 in RES 2, TRS 2, and SUS. Overall, the highest concentration fluctuations belonged to Toluene.

According to Fig. 2, The comparison of measured concentrations (in 2018–2019 and 2019–2020) with the average concentrations of five reference sites monitored by Tehran air quality control company during 2015–2016 (Amini et al. 2017) shows the gradual increase in the average concentration of all compounds except Benzene. Meanwhile, the concentration of Toluene experienced a more substantial accretion than that of other ones, as it was almost doubled in one year. The trend of Ethylbenzene concentration experienced an initial ascent and a sudden descent afterwards. The homogeneity of methods, protocols, and sampling instruments in these two studies make this comparison highly accurate.

As presented in Fig. 3, in all monitoring stations in 2019–2020, the highest mass percentage among BTEX species belongs to Toluene followed by m,p-Xylene, Benzene, o–Xylene, and Ethylbenzene. A comparison between two years demonstrate that this distribution has changed significantly over the study interval, and the amount of Toluene participation has increased in a way that its fraction leaped from about 30—40 percent in 2018–2019 to even more than 60 percent in some stations in 2019–2020. It is perceivable that in 2019–2020 period,

Table 1 BTEX concentrations (µg/m^3) and their basic descriptive statistics in monitoring locations

Station	Statistic	Year	Benzene	Toluene	Ethyl Benzene	m,p-Xylene	o-Xylene
RES 1	Mean	2018–2019	3.93	11.77	3.00	9.77	3.93
		2019–2020	3.56	39.64	4.31	14.68	4.98
	Max	2018–2019	6.29	17.00	4.40	14.00	4.90
		2019–2020	7.40	140.80	7.70	27.50	8.30
	Min	2018–2019	1.90	5.20	1.50	4.90	1.90
		2019–2020	1.70	5.80	1.40	3.90	1.10
	SD	2018–2019	1.25	3.07	0.67	2.11	0.85
		2019–2020	1.49	36.93	1.68	5.86	1.85
	CV	2018–2019	31.88	26.11	22.38	21.54	21.55
		2019–2020	41.91	93.17	38.93	39.92	37.21
RES 2	Mean	2018–2019	5.42	15.99	3.47	11.19	3.92
		2019–2020	4.68	32.67	4.16	13.68	4.48
	Max	2018–2019	8.31	25.00	4.90	16.30	5.90
		2019–2020	8.20	102.10	6.90	23.90	7.80
	Min	2018–2019	2.30	5.90	1.50	5.20	1.80
		2019–2020	2.40	8.50	1.60	5.60	1.80
	SD	2018–2019	1.74	4.92	0.88	2.84	1.08
		2019–2020	1.77	22.67	1.39	4.57	1.46
	CV	2018–2019	32.05	30.75	25.26	25.42	27.66
		2019–2020	37.72	69.39	33.36	33.44	32.66
TRS 1	Mean	2018–2019	9.18	30.04	6.79	22.47	7.82
		2019–2020	7.65	46.87	7.16	24.15	8.10
	Max	2018–2019	13.50	49.90	11.80	39.20	12.80
		2019–2020	13.70	112.60	14.00	49.90	16.60
	Min	2018–2019	4.30	12.20	3.50	10.30	3.70
		2019–2020	3.30	13.00	2.80	9.90	3.30
	SD	2018–2019	2.62	9.99	2.11	7.56	2.35
		2019–2020	3.01	28.23	2.91	10.22	3.33
	CV	2018–2019	28.50	33.24	31.08	33.63	30.06
		2019–2020	39.35	60.24	40.65	42.33	41.15
TRS 2	Mean	2018–2019	6.96	22.87	4.67	15.87	5.36
		2019–2020	5.80	42.31	5.46	18.61	6.07
	Max	2018–2019	11.40	47.00	8.10	29.80	9.20
		2019–2020	10.00	152.80	11.70	41.30	13.00
	Min	2018–2019	3.00	9.20	1.80	7.40	2.50
		2019–2020	2.80	9.40	2.40	7.20	2.80
	SD	2018–2019	2.06	8.04	1.41	4.98	1.68
		2019–2020	1.92	32.36	2.23	7.85	2.42
	CV	2018–2019	29.63	35.13	30.16	31.36	31.42
		2019–2020	33.11	76.49	40.74	42.19	39.94
SUS	Mean	2018–2019	8.23	25.89	5.12	17.73	6.01
		2019–2020	6.62	50.16	6.03	20.56	6.55
	Max	2018–2019	13.90	52.30	9.50	33.20	9.80
		2019–2020	12.20	152.70	11.90	42.30	14.50
	Min	2018–2019	4.10	12.30	2.60	10.40	3.20
		2019–2020	2.20	8.50	1.90	5.80	1.80
	SD	2018–2019	2.81	9.38	1.52	5.07	1.57
		2019–2020	2.66	39.23	2.54	9.10	2.92

Table 1 (continued)

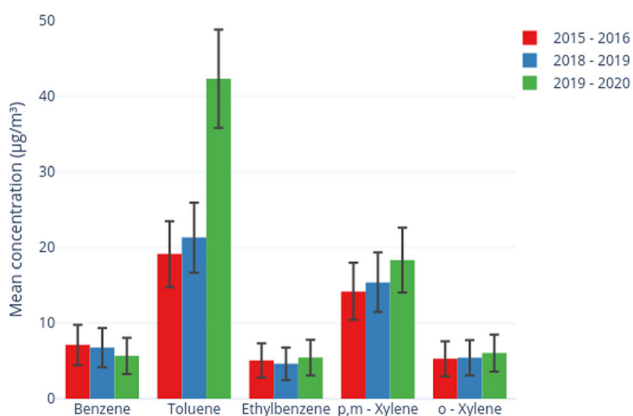| Station	Statistic	Year	Benzene	Toluene	Ethyl Benzene	m,p-Xylene	o-Xylene
	CV	2018–2019	34.16	36.23	29.67	28.58	26.12
		2019–2020	40.15	78.20	42.03	44.27	44.52
Average	Mean	2018–2019	6.74	21.31	4.61	15.41	5.41
		2019–2020	5.66	42.33	5.43	18.34	6.04
	Max	2018–2019	9.96	37.50	7.12	24.78	7.70
		2019–2020	9.14	95.04	9.48	33.44	10.98
	Min	2018–2019	3.12	8.96	2.18	7.64	2.62
		2019–2020	3.00	11.00	2.50	7.78	2.68
	SD	2018–2019	1.89	6.36	1.14	3.97	1.27
		2019–2020	1.92	26.16	1.82	6.37	2.01
	CV	2018–2019	0.28	0.30	0.25	0.26	0.24
		2019–2020	0.34	0.62	0.34	0.35	0.33

Fig. 2 The comparison of the mean concentrations of BTEX compounds between three different sampling periods

the share of o-Xylene preceded Benzene, and Ethylbenzene had the lowest share.

Figure 4 indicates the seasonal variations of BTEX species from autumn 2018 to summer 2020. Considering the trend of seasonal changes in the concentration of BTEX species in different stations, it can be seen that except Benzene, other pollutants have oscillated during different seasons, which eventually led to an increase in their concentration in the summer of 2020.

Figure 4 shows that in the summer of 2020, unexpected growth of concentration levels of Toluene occurred, which was also unprecedented in Amini et al. (2017) examinations. It is noteworthy that factors such as evaporation and temperature inversion have been mentioned before as influential phenomena involved in increasing VOCs concentration (Abbasi et al. 2020; Maleki et al. 2022).

A detailed correlation analysis (by means of Spearman rank correlations) revealed that an almost strong positive correlation exists between average temperature and Toluene, Ethylbenzene and Xylene in 2019–2020. The opposite was true in 2018–2019 period, as the mentioned correlations ranged from $0.75 – 0.79$ on average, with stronger correlations in traffic stations ($r \sim 0.7 – 0.79$) and
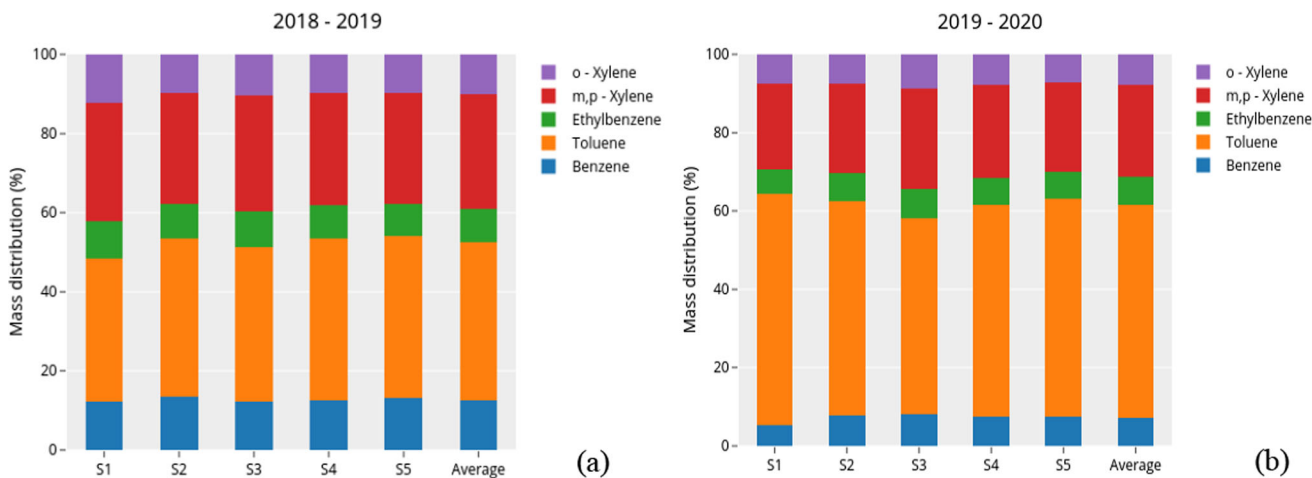

Fig. 3 Comparison of BTEX mass distribution between different sampling stations in 2018–2019 (a) and 2019–2020 (b)
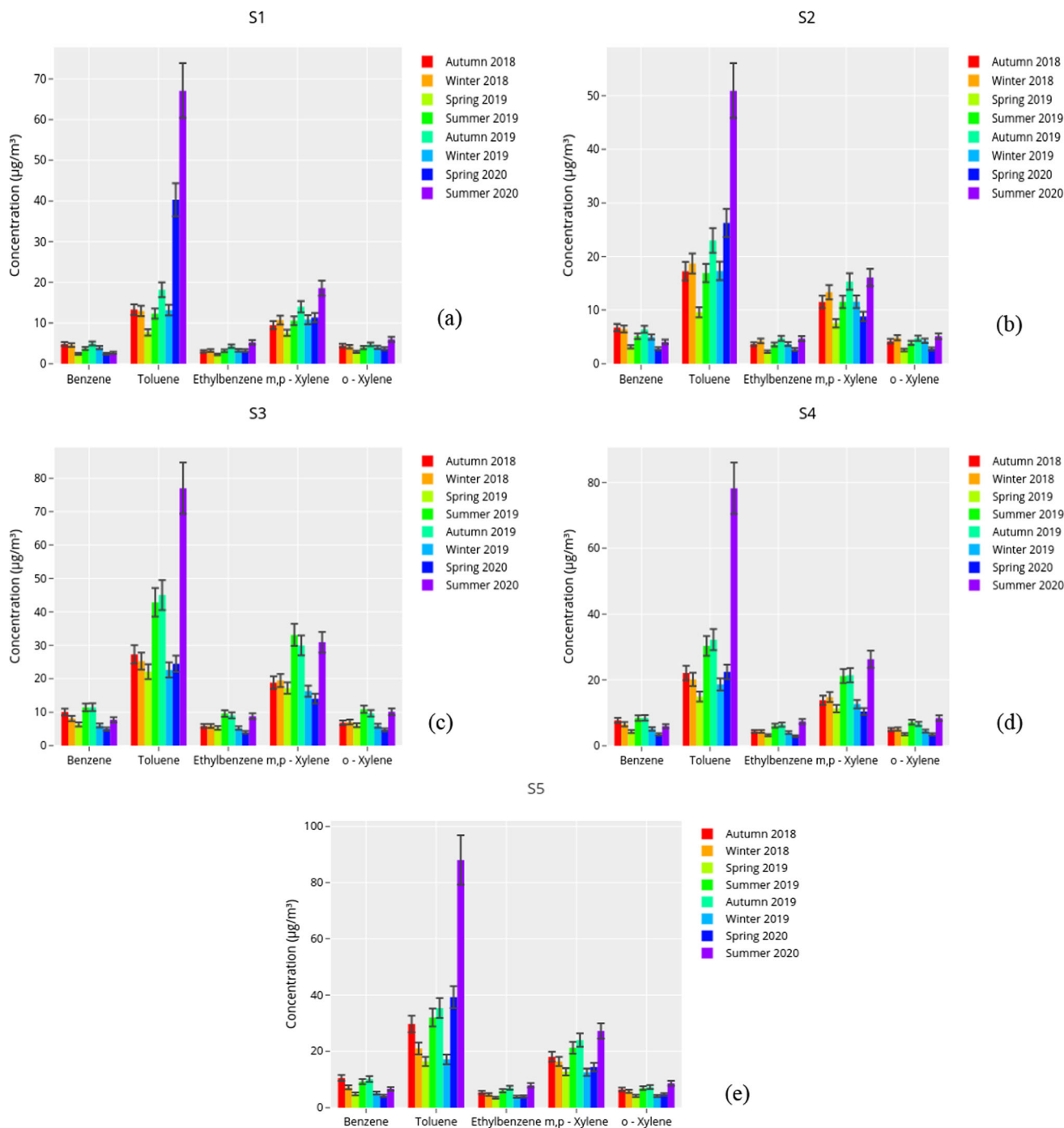
Fig. 4 Seasonal variations of BTEX species in 5 sampling points from 2018 to 2020, (a):RES 1, (b):RES 2, (c): TRS 1, (d): TRS 2, and (e): SUS

suburban site (r $\sim$ 0.65 – 0.72) respectively. Weaker correlations were observed in residential sites (r $\sim$ 0.26 – 0.56). These results suggest that evaporation rates were moderately strong determinants in high traffic and industrial – traffic suburban sites.

The trend of seasonal changes in this study also emphasizes that evaporation may be a synergic driving force in the peak of BTEX concentration in summer. In opposition, temperature inversion may not be a considerable interferer in increasing the concentration of BTEX as the trend of seasonal changes demonstrates that in the last two years, a downward trend bechances upon the arrival of winter. On the other hand, evaporation reduction can be suspected as one of the causes of concentration depletion in winter. In the period spanning from spring to winter 2019, the highest levels of BTEX concentration are visible in the

fall. This situation can be occurred due to changes in the traffic length data (m) (Figure S4, extracted from the Tehran Traffic Control Company archives). Traffic length is the length of the queue of motor vehicles in urban highways and main routes (in meters) which represents the amount of traffic, therefore pointing at the amount emissions from mobile sources.

The average length of traffic in spring, summer, autumn and winter 2019 was about 87,578, 100,896, 107,319, and 89,052 m, respectively. Thus, the maximum length of traffic in the fall of 2019 can be directly related to the leap of concentrations in this period. In these two years, seasonal comparisons emphasize on spring as the season in which the lowest concentrations occur. Concerning the traffic length diagram, the occurrence of minimal traffic in April following the Nowruz holiday may elucidate this downfall. The interference of intensified evaporation in gas stations shall be recalled as another factor in the inconsistency between the trend of changes in Benzene concentration and other pollutants (Allahabady et al. 2022). Furthermore, a source apportionment study in Tehran confirmed the emissions from the rubber, plastic, and leather industries as sources with significant contributions (Dehghani et al. 2017). In order to further examine the extent of urban traffic congestion effects on the dissemination of BTEX, the trend of monthly changes in BTEX concentration in high-traffic, residential and southern suburbs of Tehran is provided in Figure S5. The observation of traffic length changes is also helpful in assessing the variability of BTEX concentration during the global pandemic. Widespread quarantine in Tehran began in February 2020. With respect to the monthly traffic length variations, since the beginning of the pandemic and quarantine, urban traffic has decreased significantly, and in parallel, all monitoring stations have experienced a temporary decrease in BTEX levels until March and April. However, despite the relative stability of the Urban traffic length and its lower amounts in 2020 (compared to 2019), the concentration of compounds suddenly increased with a sharp slope in all sites. Hence the assumptions regarding the increase of emissions from fixed sources arise.

From January 2020 onwards, changes in traffic length are not consistent with ambient BTEX levels, especially with the changes in Toluene concentration, which shows that urban traffic may not be the sole determinant of BTEX levels in the 2019–2020 period.

According to previous studies, Toluene is the primary derivative of catalytic conversion of oil in power plants, gasoline pyrolysis, aromatization of aliphatic hydrocarbons, and a byproduct of fuel combustion and coking industry processes which are common in Iran (Shao et al. 2019; Yu et al. 2022). On the other hand, vehicle emissions are regarded as the primary source of Benzene, while both fixed and mobile sources are more involved in emissions of other species (Miri et al. 2016). The gradual decrease of Benzene may be the result of traffic plan, bus rapid transit and subway development. As a possible source, the contribution of coal combustion in industries has recently become of great concern in similar megacities (Li et al. 2020). These sources may explain the reason behind the temporal leap of Toluene concentration during the pandemic period as well, especially when considering the decline of traffic congestion (Figure S4) after the start of the lockdown and viral outbreak in early 2019. At the time when natural gas consumption reaches its peak in households, the consumption of gasoline and fuel oil in Tehran's industries increases (as a substitute fuel considered for the lack of natural gas in industries), which leads to the intensification of urban air pollution.

Therefore, sharp fluctuations in Toluene concentrations from late spring 2020 onwards can be related to fixed sources including industries. The usage of industrial solvents in various industries such as paints and resins can also cause a sharp increase in the concentration of species, which along with mobile sources, led to a significant increase in concentrations (Martins et al. 2016). In addition, a sharp rise in temperature from late spring to late summer intensifies evaporation, especially in gas stations, which may also be recalled as an influential factor.

As described in previous sections, the coefficient of divergence (COD) was used to compare the rate of change of each compound between two-yearly intervals. According to the results, the difference in Benzene concentration during the two years was greater in downtown (TRS 1) (COD = 0.11), whereas the least difference was observed in residential areas (COD = 0.06). It should be highlighted that the concentration of Benzene was more focused on the city center congestion and motor vehicle traffic. The coefficient of divergence of Toluene was higher in residential areas (0.37 > COD > 0.23), high-traffic sites (0.12 > COD > 0.17) and the southern suburbs (COD = 0.17), respectively. Ethylbenzene and Xylene isomers also experienced the largest concentration changes in RES 1 during the entire study period (0.15 > COD > 0.11) followed by the high-traffic area of the city center (COD = 0.1). Table S1 and Table 2 confirm the considerable increase of concentration fluctuation in 2019–2020 by means of interquartile ranges, coefficients of variation and standard deviations. In general, it can be claimed that the presence of suspicious sources in residential areas is possible, but the role of meteorological events and the reactivity of the pollutants may not be neglected.

Kruskal – Wallis and Dunn's post hock test were used to detect the intra location difference between the mean concentration of the species. The results demonstrated that in 2018–2019, more significant difference between stations

Table 2 Ratios between BTEX species at monitored locations

Station		Toluene/ Benzene	Ethyl Benzene/Benzene	m,p-Xylene/Benzene	o-Xylene/Benzene
RES 1	Mean	8.58	1.07	3.62	1.29
	Max	52.15	2.85	10.19	3.22
	Min	2.51	0.56	1.82	0.58
	SD	12.14	0.59	2.13	0.62
RES 2	Mean	5.58	0.8	2.62	0.87
	Max	37.81	2.15	7.3	2.07
	Min	2.48	0.51	1.63	0.58
	SD	6.26	0.29	1.04	0.28
TRS 1	Mean	4.85	0.85	2.83	0.97
	Max	19.28	1.61	5.65	1.86
	Min	2.48	0.51	1.69	0.62
	SD	3.29	0.2	0.74	0.23
TRS 2	Mean	5.31	0.81	2.77	0.92
	Max	22.14	1.7	5.99	1.88
	Min	2.71	0.53	1.7	0.6
	SD	4.12	0.23	0.88	0.26
SUS	Mean	5.62	0.79	2.72	0.89
	Max	30.25	1.78	7.33	1.94
	Min	2.51	0.5	1.45	0.58
	SD	5.55	0.27	1.06	0.29
Average	Mean	5.62	0.84	2.84	0.96
	Max	23.61	1.57	5.8	1.68
	Min	2.62	0.53	1.71	0.63
	SD	4.76	0.25	0.93	0.26

were present. However, the difference between the stations decreased in the second 12 months. With respect to the inter-station differences, it was observed that the difference in Benzene concentration levels in the second year remained the same as in the first year, except that there was no statistically significant difference between traffic stations. Such a result could indicate that Benzene emissions were mostly related to urban traffic over the past two years. In the case of Toluene, the result was quite the opposite. In the residential stations, Toluene levels were considerably different from the traffic stations and the suburbs in the first year. There was a similar difference between the two traffic stations, while the situation was contrary in the second year. This outcome may also point at the source diversion of Toluene emissions by the pass of time.

In the case of Ethylbenzene, there was a statistically significant concentration difference between monitoring stations in the first year except between two residential stations as well as between TRS 2 and SUS. However, it was observed that there is no statistically significant difference between TRS 1 and SUS in the second year, unlike the first 12 months of sampling. Such an alteration may

indicate a more homogenous dispersion of Ethylbenzene emissions over time.

Xylene isomers also experienced a decreased mean concentration difference in the second year. In general, it can be concluded that in 2019–2020 period, the decline in the difference of intra location average concentrations shows that the land use of stations became a minor determinant, and factors such as mobile sources had a minor role in BTEX pollution.

3.2 BTEX inter-compound relationships

3.2.1 Interspecies ratios

Each of the BTEX species have different degradation rates (Gaur et al. 2016). Therefore, given the higher decomposition rate of Toluene than Benzene, T/B ratio is considered as the measure of proximity to the emission source of BTEX (Abd Hamid et al. 2019). On the other hand, a T/B ratio higher than 4 indicates that the primary source of Benzene and Toluene are emissions from point sources, and studies have concluded that when this ratio is below 4,

Table 3 Pearson's correlation coefficients indicating the linear correlations of BTEX in the monitored sites

Station		Benzene	Toluene	Ethyl Benzene	p,m—Xylene	o-Xylene
RES 1	Benzene	1				
	Toluene	− 0.26	1			
	Ethyl Benzene	0.24	0.82	1		
	m,p-Xylene	0.12	0.82	0.96	1	
	o-Xylene	0.15	0.88	0.98	0.96	1
RES 2	Benzene	1				
	Toluene	− 0.06	1			
	Ethyl Benzene	0.63	0.66	1		
	m,p-Xylene	0.52	0.64	0.92	1	
	o-Xylene	0.54	0.75	0.97	0.91	1
TRS 1	Benzene	1				
	Toluene	0.34	1			
	Ethyl Benzene	0.79	0.74	1		
	m,p-Xylene	0.74	0.73	0.98	1	
	o-Xylene	0.75	0.79	0.98	0.98	1
TRS 2	Benzene	1				
	Toluene	0.17	1			
	Ethyl Benzene	0.64	0.81	1		
	m,p-Xylene	0.56	0.8	0.95	1	
	o-Xylene	0.58	0.86	0.98	0.96	1
SUS	Benzene	1				
	Toluene	0.11	1			
	Ethyl Benzene	0.62	0.78	1		
	m,p-Xylene	0.51	0.79	0.95	1	
	o-Xylene	0.6	0.81	0.98	0.95	1

traffic congestion may be suspected as their primary source (Abd Hamid et al. 2017; Moola and Johnson 2019). Furthermore, E/B and X/B point at the photochemical aging of the collected samples and values above 1 indicate that the samples are photochemically young due to the lack of hydroxyl radicals to react with the species (Baghani et al. 2019).

The interspecies ratios are shown in Table 2. The highest average T/B ratio was observed in RES 1, contrary to TRS 1. Another point worth mentioning is the fluctuation of this ratio in different stations, which is more unstable in residential stations (due to the higher standard deviation), suggesting that the pollution in residential areas may have been affected by a variety of BTEX sources in different times.

Considering that Tehran is one of the busiest cities in terms of urban traffic rate, changes in the cited ratios were plotted during the sampling interval to clarify the reason behind such unusual proportions.

Monthly changes of interspecies ratios (Figure S6) are excellent examples of how the integrity of BTEX emission sources has changed over the entire sampling period. Comparing the monthly changes of the T/B and X/B ratio

in the two periods, it was seen that in 2018–2019, T/B was relatively higher in traffic areas, whereas in 2019–2020, this fraction inflated in residential sites, especially in RES 1. It may be suspected that despite fluctuations of T/B ratios in the range of 1.5 to 4.3 in 2018–2019, the primary sources of BTEX dissemination have been mobile sources. However, the levels of this ratio had changed over time, and the role of fixed sources became more prominent in 2019–2020. This issue becomes more apparent from the end of spring 2020, and in addition, the increase in E/B ratio and X/B from late spring onwards indicates a decline in the photochemical age of the species, meaning that we might encounter fresh emission sources.

3.2.2 Interspecies correlations

As mentioned before, possible relationships between BTEX species were further investigated using Pearson correlation coefficients. The strong correlation between BTEX species indicates that these pollutants originate from the same source (Bretón et al. 2022). As shown in Table 3, the correlation between Benzene and other species is weak, while the opposite is true among other substances. When

Table 4 The average Ozone formation potential and OH° reactivity of BTEX

VOC	MIR	OH°	Monitoring station	Ozone formation potential	OH° reactivity
Benzene	0.42	1.23	RES 1	1.58	1.43
			RES 2	2.12	1.93
			TRS 1	3.54	3.21
			TRS 2	2.68	2.43
			SUS	3.13	2.84
			Average	2.61	2.36
Toluene	2.7	5.96	RES 1	68.63	46.93
			RES 2	65.23	44.60
			TRS 1	103.37	70.68
			TRS 2	87.47	59.81
			SUS	102.01	69.75
			Average	85.34	58.35
Ethylbenzene	2.7	7.1	RES 1	9.83	8.01
			RES 2	10.29	8.38
			TRS 1	18.82	15.33
			TRS 2	13.65	11.12
			SUS	15.03	12.24
			Average	13.52	11.01
m,p–Xylene	8.2	23.6	RES 1	79.16	89.02
			RES 2	80.66	90.71
			TRS 1	151.39	170.26
			TRS 2	111.86	125.81
			SUS	124.25	139.74
			Average	109.46	123.1
o-Xylene	3.5	13.7	RES 1	36.45	18.86
			RES 2	34.36	17.78
			TRS 1	65.27	33.78
			TRS 2	46.80	24.22
			SUS	51.47	26.64
			Average	46.87	24.25

this analysis was conducted for 2018–2019 sampling sessions, significant and positive correlations were observed, whereas this relationship was utterly reversed, and a decrease in inter compound correlations was found.

Hence, the results demonstrate that several sources may be involved in BTEX emissions with decreasing statistical correlation over time. As a result, mobile sources shall not be considered as the only intervening factor in increasing the concentration and emission of BTEX in Tehran, especially in 2020. In addition, the different consumption rates of BTEX species (due to their reaction with NO_X and particulate matter) may explain the reason behind the alteration of concentration trend (Li et al. 2014). All in all, these results suggest that the major source of Benzene may differ from other species. According to past studies in Tehran, the main source of Benzene emission was most likely the urban traffic (Miri et al. 2016).

3.2.3 Ozone formation potential and OH° reactivity

Table 4 shows the estimated Ozone formation potential and the rate of OH° reactivity for BTEX species. According to the results, m,p-Xylene has the highest potential for tropospheric Ozone production in the ambient air of Tehran, followed by Toluene, o-Xylene, Ethylbenzene, and Benzene. The dominance of the Xylene group in the tropospheric Ozone formation was previously inferred (Mehta et al. 2020). The results of this analysis are similar to the study of Hajizadeh et al. (2018) in another city of Iran called Yazd. However, the exact order applies to the degree of reactivity with hydroxyl radicals, and the results of the calculations of this factor also emphasize the high reactivity of Xylene and Toluene with OH°. As a result, due to the high reactivity and drastic increase in the Toluene concentration in 2020, the Ozone production cycle may intensify and accelerate in the future.

Table 5 Results of health risk assessment of BTEX

VOC	Monitoring station	EC ($\mu g/m^3$)	RfC ($\mu g/m^3$)	HQ	CR	W_E ($\times 10^6$)
Benzene	RES 1	0.25	30	0.008	2×10^{-6}	3.35
	RES 2	0.34		0.011	2.7×10^{-6}	10.04
	TRS 1	0.57		0.019	4.5×10^{-6}	24.75
	TRS 2	0.43		0.014	3.41×10^{-6}	13.63
	SUS	0.5		0.016	3.98×10^{-6}	6.37
	Average	0.46		0.015	3.6×10^{-6}	10.94
Toluene	RES 1	1.74	5000	0.0003	–	22.71
	RES 2	1.65		0.0003	–	47.97
	TRS 1	2.62		0.0005	–	112.41
	TRS 2	1.65		0.0004	–	69.09
	SUS	2.58		0.0005	–	32.35
	Average	1.45		0.0002	–	55.66
Ethylbenzene	RES 1	0.24	1000	0.0002	6.23×10^{-7}	3.25
	RES 2	0.26		0.0002	6.52×10^{-7}	7.56
	TRS 1	0.47		0.0004	1.19×10^{-6}	20.46
	TRS 2	0.34		0.0003	8.56×10^{-7}	10.78
	SUS	0.38		0.0003	9.52×10^{-7}	4.76
	Average	0.31		0.0003	7.89×10^{-7}	8.82
Xylene	RES 1	1.13	100	0.011	–	14.85
	RES 2	1.13		0.011	–	32.96
	TRS 1	2.14		0.021	–	91.76
	TRS 2	1.56		0.015	–	48.87
	SUS	1.73		0.017	–	21.74
	Average	1.42		0.014	–	39.72

The maximum Ozone formation potential and OH° reactivity of pollutants were observed at the downtown station (TRS 1), followed by the southern suburban station. Traffic stations (TRS 2) and residential stations were at lower levels, respectively.

3.3 Health risk assessment

Table 5 summarizes the results of the health risk assessment. Given the estimated value of hazard index which was lower than unity (HI = 0.037), the chronic risk of the BTEX compounds was not critical. Hazard quotients show that the chronic risks of BTEX are much higher in downtown (TRS 1), suburban district, TRS 2, and residential sections respectively.

The cancer risk of Benzene was more than three times the EPA permissible limit ($> 1 \times 10^{-6}$). Benzene was therefore found to individually make the ambient air of Tehran unsafe for its inhabitants, especially for sensitive groups such as elders. It should be noted that this carcinogenic risk is much higher in downtown (TRS 2) and suburbs possess higher Benzene cancer risk compared to residential districts, pointing at the importance of industrial sections located in south of the city. However, the potential cancer risk of Ethylbenzene was acceptable. The higher concentrations of Xylene and Toluene (in comparison with Benzene and Ethylbenzene) also highlight their greater non-carcinogenic risk. Previous research in a landfill area in Turkey illustrated that the adverse health effects of Benzene are negligible (Durmusoglu et al. 2010). Therefore, it is unlikely that the landfill located in the southern suburbs of the city will be a threat to public health in terms of BTEX pollution. Past research on this topic had a common point with these results, which indicated that the most important related issue of BTEX is related to the cancer risk of Benzene, and the non-carcinogenic of BTEX risk does not pose a threat to the health of citizens. (Latif et al. 2019; Alsbou and Omari 2020).

Since the carcinogenic risk of Benzene and Ethylbenzene were not thoroughly uniform in studied locations, the weighted exposure of local residents was calculated to obtain a general overview on the amount of exposure concerning the neighboring population of each site. The adjacent residents of each location was computed as described in previous sections. Considering the population adjacent to each monitoring station, weighted exposure in traffic areas was the highest compared to other locations, while the weighted exposures in residential sites stood at lower levels in comparison with suburban areas (Figure S7). Besides, the weighted exposure of Toluene
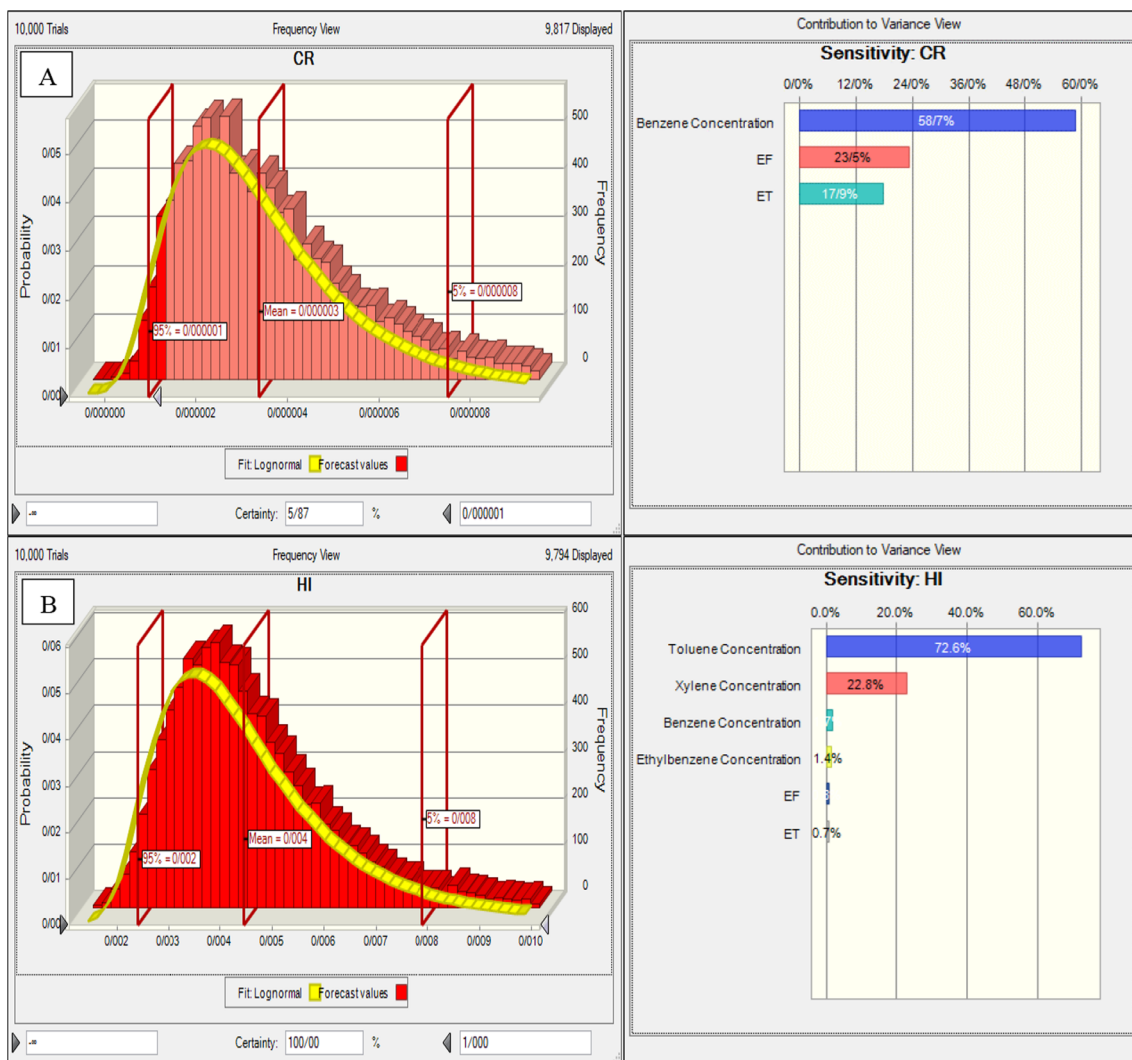
Fig. 5 Monte Carlo histogram of Benzene cancer risk (A) and BTEX hazard index (B)

surpassed other compounds and was followed by Xylene, Benzene, and Ethylbenzene, respectively, meaning that Toluene may threaten the public health with its overwhelming exposure levels.

To estimate the potential cancer risk of Benzene and the potential non carcinogenic risk of BTEX, sensitivity analysis and Monte Carlo simulation was conducted with 10,000 replications (Fig. 5). The results of the sensitivity analysis show that Benzene (58.7%) is the most influential factor in increasing the carcinogenic health risks of BTEX, while pointing at the determinant contribution of Toluene (72.6%) in increasing the non-carcinogenic risk of BTEX. The concerning rise of Toluene pollution and its potential non-cancer health outcomes on the exposed population of Tehran, may become of great concern if the emissions are not mitigated in the future. Additionally, the importance of Xylene concentration stands next to the Toluene in terms of BTEX hazard index variations (22.8%). The upper and

lower percentiles of potential cancer risk of Benzene were estimated to be 7.4×10^{-6} and 9.4×10^{-7}, respectively. These results indicate the high cancer risk of Benzene as it varies mostly above the standard enacted by USEPA (10^{-6}). The 5th and 95th percentile of BTEX non-carcinogenic risk were 0.008 and 0.002, respectively. The Monte Carlo simulation of HI revealed that the potential non-cancer risk of BTEX does not violate the contractual standard limit of 1, as the frequency distribution of HI data fluctuates well below unity.

4 Conclusion

The findings of this study not only compared BTEX concentrations before and after the Covid-19 outbreak, but investigated the effects of these aromatic compounds on public health and the urban environment, as the Ozone

formation potential and weighted exposures of BTEX were discovered in different urban backgrounds. Disregarding the effects of meteorological conditions in winter and summer, traffic congestion and transportation fleet were not found to be the only effectual factor in the leap of BTEX concentrations in Tehran. Findings emphasize on the potentially important role of point sources, especially after the beginning of the pandemic period, as the most concerning compound were found to be Toluene. The concentration of Benzene exceeding the EU threshold and its high cancer risk of warn that more attention is required to this pollutant in Tehran megacity.

The results of interspecies relationships and spatiotemporal analysis raised suspicions on BTEX source variety. Furthermore, the lack of significant correlations between Toluene and Benzene in 2020 highlighted the role of other pollution sources rather than the urban traffic.

Lastly, our findings suggest the importance of mitigation of each of the compounds based on different approaches, with Xylene possessing the highest Ozone formation potential, Benzene showing high cancer risk, and Toluene experiencing uprising concentrations after the viral outbreak.

It is recommended to control the pollution caused by urban traffic by means of developing the use of hybrid or electric vehicles in transportation fleet, as well as shifting the major focus on monitoring the industrial section in such megacities.

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Availability of data and materials Materials and data will be provided on reasonable request.**Ethical Approval.**The authors are committed that all ethical principles have been observed and taken into account in conducting this research. No human/animal(s) were involved in the provision of this study.

Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

Consent to participate Informed consent was obtained from all individual participants included in the study.

Consent to publish The consent to publish has been received from all authors.

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