

Characteristics and health effects of BTEX in a hot spot for urban pollution

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ABSTRACT

This study reports a spatiotemporal characterization of toluene, benzene, ethylbenzene, and xylenes concentrations (BTEX) in an urban hot spot in Iran, specifically at an bus terminal region in Shiraz. Sampling was carried out according to NIOSH Compendium Method 1501. The inverse distance weighting (IDW) method was applied for spatial mapping. The Monte Carlo simulation technique was applied to evaluate carcinogenic and non-carcinogenic risk owing to BTEX exposure. The highest average BTEX concentrations were observed for benzene in the morning (at 7:00–9:00 A.M. local time) ($26.15 \pm 17.65 \mu\text{g}/\text{m}^3$) and evening (at 6:00–8:00 P.M. local time) ($34.44 \pm 15.63 \mu\text{g}/\text{m}^3$). The benzene to toluene ratios in the morning and evening were 2.02 and 3.07, respectively. The main sources of BTEX were gas stations and a municipal solid waste transfer station. The inhalation lifetime cancer risk (LTCR) for benzene in the morning and evening were 1.96×10^{-4} and 2.49×10^{-4} , respectively, which exceeds the recommended value by US EPA and WHO. The hazard quotient (HQ) of all these pollutants was less than 1. The results of this work have implications for public health near ‘hot spots’ such as IGBT where large populations are exposed to carcinogenic emissions.

1. Introduction

Vehicular exhaust is one of the most important anthropogenic sources of air pollution in the ambient urban atmosphere (Bruno et al., 2008; Kalenge et al., 2013; Saxena and Ghosh, 2012; Yurdakul et al., 2013), a major constituent of which includes volatile organic compounds (VOCs) (Bruno et al., 2008; Esteve-Turrillas et al., 2007; Han et al., 2005; Jiang et al., 2017; Kim et al., 2012; Lau and Chan, 2003; Neghab et al., 2017; Özden et al., 2008; Parra et al., 2008a; Qiu et al., 2016). An important class of VOCs is the suite of BTEX (benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene) species, which have been the focus of many toxicological studies (Fazlzadeh Davil et al., 2011; Halliday, 2016; Hazrati et al., 2016a, 2015; Maré et al., 2016; Rad et al., 2014; Sairat et al., 2015). Ideal regions to study BTEX emissions and impacts include ‘hot spots’, which are typically urban areas where ambient levels significant exceed those of surrounding

remote areas (Zhu et al., 2008). Pollution in developing countries has significantly increased in recent years and fresh emissions especially are a major health concern for large populations in these areas (Bauri et al., 2016; Hazrati et al., 2016b; Masih et al., 2016; Rad et al., 2014; Saxena and Ghosh, 2012; Tunsaringkarn et al., 2014).

BTEX is an important class of compounds owing to the abundance of these species in the ambient atmosphere, their deleterious impacts on public health, and their function in atmospheric chemistry (Alghamdi et al., 2014; Parra et al., 2008a). Their sources, including in this work's study region, include vehicular exhaust, gas stations, industrial activity, landfill sites, municipal solid waste (MSW) stations, and combustion for domestic heating (Bruno et al., 2008; Carrieri et al., 2006; Chiriac et al., 2007, 2011; Correa et al., 2012; Durmusoglu et al., 2010; Jiang et al., 2017; Kim et al., 2008; Kountouriotis et al., 2014; Maré et al., 2016; Sairat et al., 2015; Terrés et al., 2010; Wu et al., 2006; Xiong et al., 2016). Past work has shown that more than 45% of total VOC

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emissions, such as for benzene and toluene, in Mexico City, the United Kingdom, and Los Angeles stemmed from gas stations, evaporation of petrol, and motor vehicle emissions (Correa et al., 2012; Durmusoglu et al., 2010). In terms of health effects, benzene is categorized as carcinogen, ethylbenzene is recognized as a potential carcinogen, while toluene and xylene are classified as Group D carcinogens or non-carcinogenic (Cancer, 2002; Demirel et al., 2014; Li et al., 2009; Tunsaringkarn et al., 2012; Von Burg, 1993). Furthermore, benzene impacts blood production, the lymphatic system, and the central nervous system (Correa et al., 2012; Duarte-Davidson et al., 2001; Moolla et al., 2015), while toluene impacts the reproductive and central nervous systems (Chen et al., 2011; Correa et al., 2012; Duarte-Davidson et al., 2001; Kalenge et al., 2013; Moolla et al., 2015; Tunsaringkarn et al., 2012). With regard to atmospheric chemistry, photochemical reactions of BTEX pollutants can generate secondary pollutants, such as ozone and secondary aerosol via gas-to-particle conversion processes (Alghamdi et al., 2014; Bell, 2006; Crosbie et al., 2014; Demirel et al., 2014; Han et al., 2005; Kourtidis et al., 2002; Maré et al., 2014; Ng et al., 2007; Saxena and Ghosh, 2012; Sorooshian et al., 2007; Srivastava et al., 2006; Zhao et al., 2004).

The major component of gasoline is benzene, which is released from gasoline engines (Weisel, 2010). The benzene-to-toluene (B/T) ratio is often applied as an index for determining the emission sources of BTEX compounds (Buczynska et al., 2009; Cheng et al., 2016; Elbir et al., 2007; Legay et al., 2011; Parra et al., 2008b). A ratio exceeding 0.5 suggests that the source of benzene is not only related to traffic but also other sources (Jiang et al., 2017; Yurdakul et al., 2013). Moreover, B/T ratios lower than 0.5 suggest that transportation is the predominant source of BTEX (Elber et al., 2007; Hartmann et al., 1997; Zhang et al., 2008). For instance, Hartmann et al. (1997) and Elber et al. (2007) showed that the B/T ratio in a suburban area was about 0.16–1, while next to congested roadways, the B/T ratio was about 0.5 (Elber et al., 2007; Hartmann et al., 1997). In addition to the B/T ratio, the xylenes/benzene (X/B) and ethylbenzene/benzene (Ebz/B) ratios are generally applied as indices of photochemical reactivity. For example, small X/B and Ebz/B ratios (< 1) suggest that sampled air masses are photochemically aged (e.g., via reactions with the hydroxyl radical) and that benzene has a relatively low reactivity as compared with ethylbenzene and xylenes; consequently, benzene can be transported to other regions without degradation (Bauri et al., 2016; Hoque et al., 2008).

The aim of this work is to investigate BTEX characteristics near a congested intercity bus terminal, including the effects of their emissions on public health. More specifically, the subsequent discussion focuses on a report of concentrations, spatial and temporal characteristics, photochemical aging, and risk assessment of BTEX in the ambient air of the Intercity Karandish Bus Terminal (IKBT) area in Shiraz, Iran. This is the first such study examining BTEX in this understudied, yet largely populated, region in the Middle East with attention geared towards spatial and diurnal trends.

2. Material and methods

2.1. Study area

Shiraz is the capital of the Fars Province in the semi-arid and southwestern part of Iran (29°36' N, 52°32' E). It has a population of ~1.8 million, based on the last census report in 2016, which qualifies it as the fifth most populated city in Iran (Statistical Centre of Iran (SCI), 2016). Shiraz covers 240 km² of area and consists of 11 urban districts with an average population density of approximately 6890 residents per km² (Statistical Centre of Iran (SCI), 2016). Shiraz is one of the most polluted cities in Iran (Arfaeinia et al., 2017), with the IKBT hot spot being one of the main reasons (Statistical Centre of Iran (SCI), 2016). This area has the largest intercity bus terminal (Karandish) in the southwest of Iran. Fig. 1 shows a spatial map of Shiraz and the sampling stations. The stations were chosen based on several factors such as

proximity to gas stations, level of congestion, population characteristics, and convenience for sampling. The study area is located between a longitude of 52°33'20" and 52°34'20" and latitudes of 29°37'20" and 29°36'20" (Fig. 1).

2.2. Sampling and analysis

Sampling of BTEX compounds was carried out according to NIOSH Compendium Method 1501 (Pendergrass, 2003; Schlecht and O'Connor, 1994). BTEX concentrations were measured over the duration of two hours in the morning (7:00–9:00 A.M. local time) and evening (6:00–8:00 P.M. local time) via active sampling (SKC, Model 222-ml/COUNT) using a charcoal glass tube at a flow rate of 0.21 per minute (Muezzinoglu et al., 2001; Pendergrass, 2003; Schlecht and O'Connor, 1994). Sampling was carried out every third day in all 18 locations. Sampling was conducted above street level (at a height of 2 m). The final set of 180 samples (90 for morning and 90 for evening) was collected over four consecutive weeks in November 2016. After sampling, the charcoal tubes were tagged, covered, and stored at 4 °C to minimize contamination and desorption.

Samples were analyzed within 72 h after collection. Before analysis, the main and second sections of the charcoal tube were placed into two vials and BTEX compounds were extracted by adding 1 ml carbon disulfide (ASTM, 1995; Hydrocarbons, 2003). The vials were subsequently shaken via ultrasonication for 20 min. Next, all samples were centrifuged until a clear phase was acquired at the top of the micro tube (10 min). BTEX compounds were examined using gas chromatography–mass spectrometry (GC-MS) (GC 7890N, AGILENT-MS 5975C, MODE EI). Helium was the carrier gas at 1 ml/min with a split ratio of 1:5 and inlet temperature 200 °C, respectively.

Data were analyzed using the SPSS statistical software (Version 22). The relationship between target compounds were evaluated by Spearman's rho correlation coefficient. Benzene to toluene (B/T), xylenes-to-benzene (X to B), and ethylbenzene-to-benzene (Ebz to B) ratios were calculated for the morning and evening in order to evaluate photochemical aging and to determine emission sources of target compounds. Additionally, the student's *t*-test was applied to find the level of statistical significance of correlation coefficients.

2.3. Quality assurance/quality control (QA/QC)

In order to check for possible artifacts, such as breakthrough in the two sections of the charcoal tubes, analysis was done for both the primary and back-up tubes. There was no evidence of BTEX contamination in the charcoal tube sections. The recovery of analytical method was measured by spiking the charcoal tubes with 10 µg of BTEX compounds. The limits of detection (LOD) were quantified as three times the standard deviation (SD) of the blank values. Limits of quantitation (LOQ) were calculated as ten times the SD of the blank values. Eighteen samples were gathered as blank samples and the concentrations (µg/m³) of BTEX compounds in blank samples ranged from 0.00 to 0.022 for benzene, 0.00 to 0.021 for toluene, 0.00 to 0.008 for ethylbenzene and 0.00 to 0.008 for xylene. The LOD and LOQ of these components were as follows (µg/m³): 0.021 and 0.068 (benzene), 0.022 and 0.072 (toluene), 0.008 and 0.027 (ethylbenzene), 0.012 and 0.039 (m, p-xylene) and 0.008 and 0.027 (o-xylene); also, recovery values of BTEX constituents ranged from 95.3 ± 2.2% to 99.8 ± 2.6% with relative SDs less than 3.5%. The calibration was achieved in six levels (0.01–60 µg/m³) of standard solutions and R² values of 0.998 for benzene, 0.987 for ethylbenzene, 0.989 for toluene, and 0.988 for xylene were acquired. A diagram of the steps of the procedures work are shown in Fig. 2.

2.4. Spatial distributions

ArcGIS software (Version 10.3) was used to conduct spatial analysis. The IDW interpolator method was employed to make raster layers for

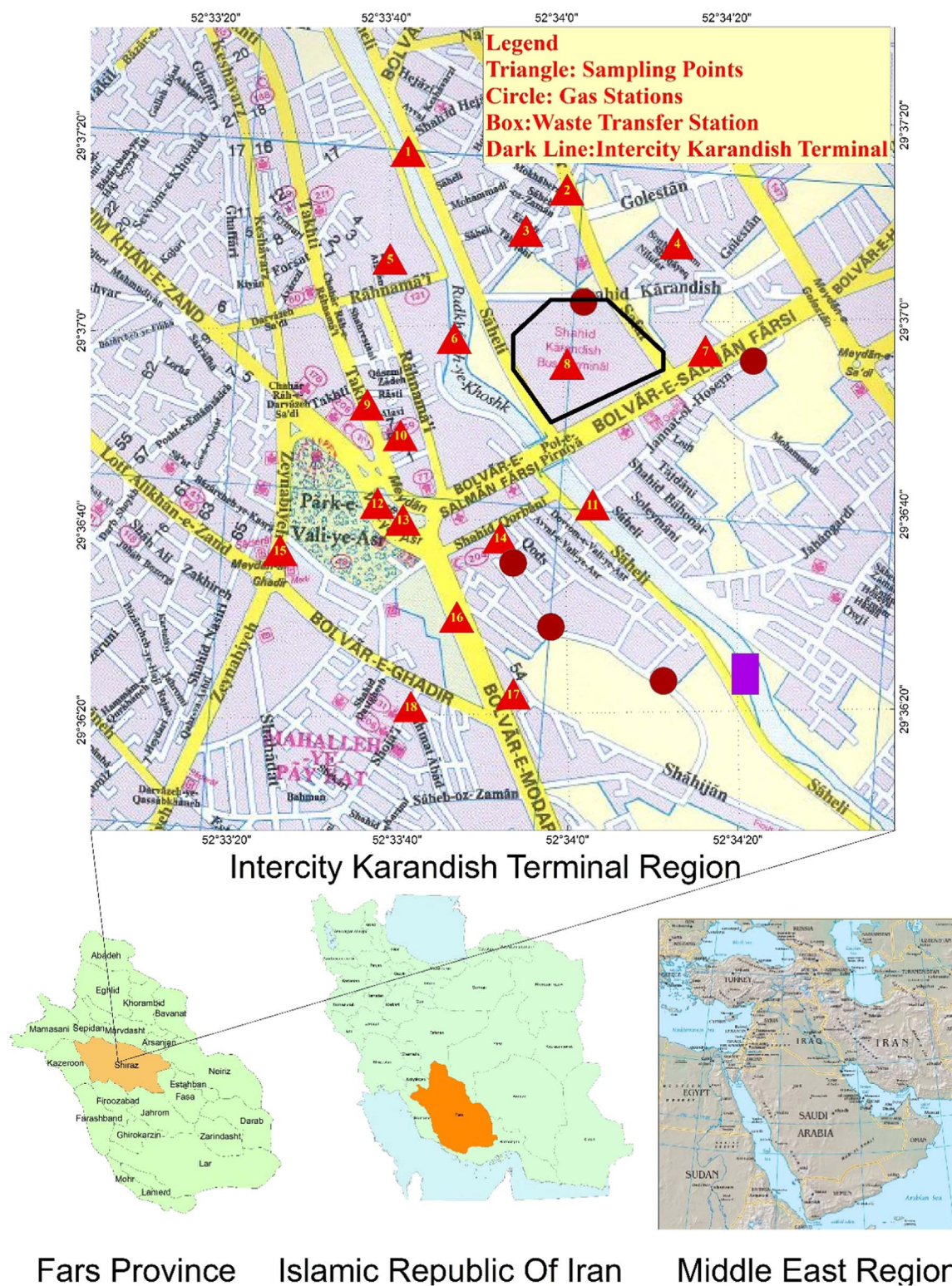


Fig. 1. Map of the study area and air monitoring stations.

the average concentration of BTEX components and to show the distribution of all the targeted pollutants in the IKBT region. Subsequently, the raster calculation function was applied to overlay each layer and generate mean maps of target pollutants. The IDW model equation is as follows (Miri et al., 2016; Wang et al., 2014; Xie et al., 2011):

$$\lambda_i = \frac{D_i - \alpha}{\sum_{i=1}^n D_i - \alpha} \quad (1)$$

where λ_i is the weight of the i sample point, α is the weighting power, and D_i is the distance between the station i and uncertain point, which was variable in our study.

Higher values were allocated to values closer to the interpolated point; in this regard, Miri et al. (2016) reported that as the distance increases, the weight decreases. The number of stations used in the interpolation is n , which was 10 in this study.

Numerous studies have applied the IDW technique for spatial

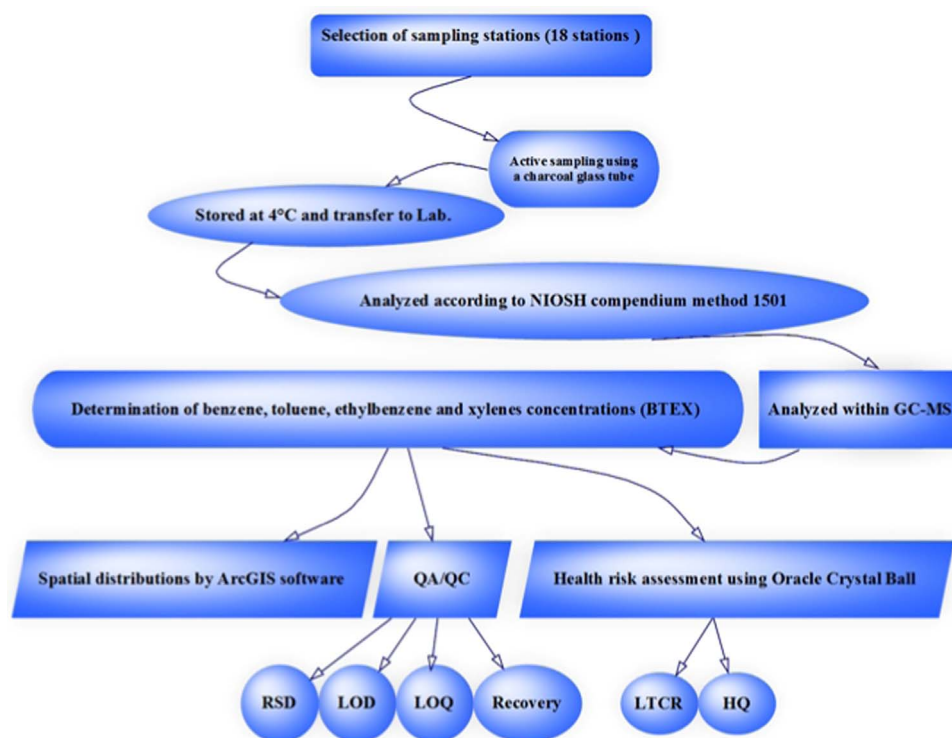


Fig. 2. A diagram of the steps of the procedures work.

mapping of pollutants such as polycyclic aromatic hydrocarbons (PAHs) in Pennsylvania, USA (Witter et al., 2014), O₃ in northern Georgia, China, and Belgium (Bell, 2006; Hooyberghs et al., 2006; Wang et al., 2014), PM₁₀ and PM_{2.5} in USA and China (Wang et al., 2014; Yanosky et al., 2008), and CO, SO₂, and NO₂ in China (Wang et al., 2014). The IDW technique has been expanded in the environmental field to forecast ambient air pollutants' concentration. Furthermore, IDW is beneficial when the distribution of the computed variables is unusual.

2.5. Health risk assessment

Benzene has harmful impacts on human health and it is a suspected carcinogen (Dutta et al., 2009; EPA, 1999). In order to assess the risk to the human health created by BTEXs, the non-carcinogenic risk of target components and inhalation lifetime cancer risk (LTCR) of benzene was calculated using the data obtained in this study.

The LTCR was computed based on the following equation (Li et al., 2008; Miri et al., 2016):

$$\text{LTCR} = \text{CDI} \times \text{CSF} \quad (2)$$

where CSF and CDI are the cancer slope factor (mg/kg-day) and chronic daily intake "air intake" (mg/kg-day), respectively. In addition, the chronic daily intake was determined by the following equation (Li et al., 2008; Miri et al., 2016):

$$\text{CDI} = (\text{C} \times \text{IR} \times \text{CF} \times \text{ED} \times \text{EF}) / (\text{AT} \times \text{BW}) \quad (3)$$

where C represents ambient concentration of pollutants (µg/m³), CF and IR are the conversion factor (mg/µg) and the human inhalation rate (m³/day), respectively, and ED, EF, BW, and AT are exposure duration (yr), exposure frequency (days/yr), body weight (kg), and average lifetime (yr), respectively (Li et al., 2008; Miri et al., 2016).

In order to address uncertainties in the calculations related to health risk estimates, Monte Carlo simulations were conducted using Oracle Crystal Ball 11.1.2.3 (sensitivity analysis). Table 1 displays the selected parameters utilized for risk assessment and sensitivity analysis.

Risk assessment for the non-carcinogenic of target components is represented in terms of the hazard quotient (HQ) parameter, which is

expressed as the ratio of chronic daily intake (CDI) (mg/kg-day) and the reference concentration (RfC) (mg/kg-day) (Li et al., 2008; Miri et al., 2016):

$$\text{HQ} = \text{CDI} / \text{RfC} \quad (4)$$

HQ > 1 indicates that the potential risk may be important, while HQ values less than and equal to one indicate is a more acceptable level as the dose level is lower than the RfC (Demirel et al., 2014; Miri et al., 2016; Moolla et al., 2015; Tunsaringkarn et al., 2012; Zhang et al., 2012). For computing the chronic daily intake, the mean concentrations of BTEX were used. The cancer slope factor for benzene is 0.029 mg/kg-day (EPA, 1999; Moolla et al., 2015) and RfD for benzene, toluene, xylenes, and ethylbenzene were 0.03, 5, 0.01, and 1 mg/kg-day, respectively (EPA, 1999; Moolla et al., 2015). It should be noted that the LTCR for other BTEX species such as xylenes, toluene and ethylbenzene (TEX) cannot be calculated since there are no cancer slope factors for these pollutants (Miri et al., 2016; Moolla et al., 2015).

3. Results and discussion

3.1. BTEX concentrations

The mean and standard deviation concentrations of benzene (B), toluene (T), ethylbenzene (Ebz), m/p-xylene ((m & p)-X), and o-xylene (O-X) concentrations in the morning hours were 26.15 ± 17.65, 12.97 ± 7.12, 7.50 ± 2.50, 19.34 ± 6.49, and 23.38 ± 8.28 µg/m³, respectively. In evening hours, the average and standard deviation concentrations for the same species were 34.44 ± 15.63, 11.20 ± 5.56, 6.58 ± 1.95, 16.81 ± 5.76, and 21.25 ± 7.13 µg/m³, respectively. These findings display that benzene was the most abundant of the four species, regardless of time of day.

Reasons for benzene being highest in concentration in this region could be linked to differences in the benzene content of the petrol in Shiraz as compared to other cities of Iran, and emissions from gas/petrol stations and the municipal solid waste (MSW) transfer station. Hence, the results of this study are in line with the findings from

Table 1

Risk parameters employed for Monte Carlo simulations and comparison of BTEX concentrations and B/T, (M + P)-X/B, O-X/B, and Ebz/B ratios in the current study and other studies.

Description	Parameters	Units	Value	Refs.
Body weight	BW	kg	71 ± 13.6	(Miri et al., 2016; Moolla et al., 2015)
Inhalation rate	IR	m ³ day ⁻¹	15–20	(Demirel et al., 2014; Moolla et al., 2015; Tunsaringkarn et al., 2012; Zhang et al., 2012)
Exposure duration	ED	yr	70	(Miri et al., 2016; Moolla et al., 2015; Zhou et al., 2011a)
Averaging time	AT	days	25,500	(Demirel et al., 2014; Miri et al., 2016; Tunsaringkarn et al., 2012)
Exposure frequency	EF	days yr ⁻¹	350–365	(Demirel et al., 2014; Miri et al., 2016; Tunsaringkarn et al., 2012; Zhou et al., 2011a)
B/T, (M + P)-X/B, O-X/B, and Ebz/B ratios				
B/T ratio	(M + P)-X/B ratio	O-X/B ratio	Ebz/B ratio	City
2.01	0.84	0.89	0.28	Shiraz, Iran-in the morning
3.07	0.49	0.62	0.19	Shiraz, Iran-in the evening
1.55–1.78	–	–	0.004–0.005	Mumbai, India
2.89	–	–	0.07	Yazd, Iran
2.48	–	–	0.12	Monterrey, Mexico
1.05	–	–	0.21	Zhengzhou, China
1.11	–	–	1.35	Ardabil, Iran
0.56	–	–	0.24	Gorakhpur, India
0.09	1.16	0.83	1.42	Tainan and Taipei, Taiwan
0.69	–	–	0.4	Gdansk, Poland
0.75	–	–	0.36	Gdynia, Poland
0.75	–	–	0.20	Sopot, Poland
0.19	0.54	0.40	0.51	Hong Kong, Japan
0.23	9.45	2.72	3.27	Rio de Janeiro, Brazil
0.07	1.5	0.53	1.08	Seoul, Korea
0.27	1.01	0.18	0.38	Ankara, Turkey
3.22	0.07	0.02	0.03	Orleans, France
				Ref.
				This study
				This study
				(Srivastava et al., 2006)
				(Mosaddegh Mehrjerdi et al., 2014)
				(Cerrón-Bretón et al., 2015)
				(Wang et al., 2008)
				(Hazrati et al., 2016b)
				(Masih et al., 2016)
				(Hsu and Huang, 2009)
				(Marć et al., 2014)
				(Marć et al., 2014)
				(Marć et al., 2014)
				(Ho et al., 2004)
				(Martins et al., 2007)
				(Kim et al., 2012)
				(Yurdakul et al., 2013)
				(Jiang et al., 2017)

Mumbai (India) and Monterrey (Mexico), gasoline and CNG refueling stations in Ardabil (Iran), a gas station in Yazd (Iran), and MSW landfills in France where benzene was the most abundant among the species examined here (Chiriac et al., 2007; Hazrati et al., 2016b; Mosaddegh Mehrjerdi et al., 2014; Srivastava et al., 2006). Moreover, Srivastava et al. (2006) and Cerrón-Bretón et al. (2015) in Mumbai and in Monterrey, respectively, showed the following order of abundance: benzene > toluene > ethylbenzene > xylenes.

Fig. 3 illustrates a statistical summary of BTEX species, and total BTEX concentrations in the morning and evening. The maximum and minimum concentrations for mornings and evenings were $55.28 \pm 5.35 \mu\text{g}/\text{m}^3$ for B and $4.16 \pm 0.30 \mu\text{g}/\text{m}^3$ for T in the morning and $56.58 \pm 5.76 \mu\text{g}/\text{m}^3$ for benzene and $3.99 \pm 0.28 \mu\text{g}/\text{m}^3$ for ethylbenzene in the evening, respectively. These findings are opposite of previous studies since benzene was the most abundant as compared to other components of BTEX in ambient air (Cerrón-Bretón et al., 2015; Mohamed et al., 2002; Moolla et al., 2015; Mosaddegh Mehrjerdi et al., 2014; Srivastava et al., 2006). The mean values of benzene observed by Moolla et al. (2015) (South Africa), Hazrati et al. (2016a, 2016b) (Ardabil, Iran), Mosaddegh Mehrjerdi et al. (2014) (Yazd, Iran), Mohamed et al. (2002) (United States), Srivastava et al. (2006) (Mumbai, India), and Cerrón-Bretón et al. (2015) (Monterrey, Mexico) were, 313.16, 1690, 1932, 18.94, 539.95, and $55.24 \mu\text{g}/\text{m}^3$, respectively (Cerrón-Bretón et al., 2015; Hazrati et al., 2016b; Mohamed et al., 2002; Moolla et al., 2015; Mosaddegh Mehrjerdi et al., 2014; Srivastava et al., 2006). A factor affecting the diurnal profile of benzene is time-dependent emissions in the vicinity of either gas stations (Kountouriotis et al., 2014; Rattanajongjitakorn and Prueksasit, 2014) or heavily congested roadways (Correa et al., 2012; Kourtidis et al., 2002; Lin et al., 2011). In addition, the results of this study reveal that the average concentration of BTEX was more than other studies, specifically those conducted in the Tri-City area (Gdansk, Gdynia, Sopot), Poland (Marć et al., 2014), Ardabil, Iran (Hazrati et al., 2016b), and Gorakhpur, India (Masih et al., 2016). This can most likely be explained by the combination of heavy traffic, fuel quality standards, old cars, and vicinity to five gas stations in the sampling region of IGBT. In addition, previous studies reported that different refineries in Iran generate petrol with different qualities in terms of aromatic compounds (Hazrati et al., 2016b). Benzene included in gasoline varies from 1% to 5%,

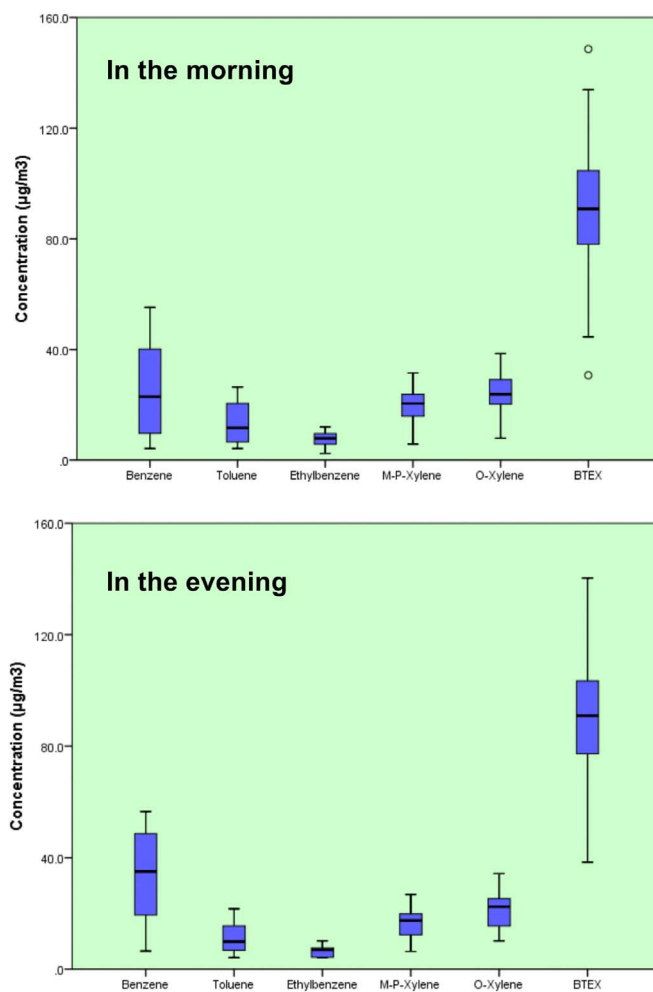


Fig. 3. Descriptive statistics of BTEX concentrations ($\mu\text{g}/\text{m}^3$) in the morning (7–9 A.M.) and evening (6–8 P.M.).

depending on the countries' legislation, fuel quality and season (Karakitsios et al., 2007). Consequently, BTEX compounds, especially benzene, measured in gas stations in the region of IGBT reach very high levels. An additional source of BTEX emission around IGBT is a nearby a MSW transfer station. Past work has also linked emissions from MSW landfills (MSWLF) to high levels of BTEX components (Chiriac et al., 2007, 2009, 2011; de Sá Borba et al., 2017; Durmusoglu et al., 2010; Kim et al., 2008).

3.2. The ratios between target components

3.2.1. The ratio of Benzene to toluene (B to T)

The ratio of B to T is generally utilized as an identifier for emission sources of target compounds (Hazrati et al., 2016b; Jiang et al., 2017; Masih et al., 2016; Miri et al., 2016). Table 1 compares BTEX concentrations and its various ratios in the current study versus other regions. B/T ratios in the morning and evening were 2.02 ± 0.55 and 3.07 ± 1.12 , respectively. These high ratio values of benzene to toluene are attributed to multiple sources of benzene such as gas and petrol stations, emissions related to traffic and irregular sources, and MSW emissions that produce leachate containing BTEX (Chiriac et al., 2011; Durmusoglu et al., 2010). B/T (2.02–3.07) ratios in this study were similar to those in Orleans, France (3.22), Monterrey, Mexico (2.48), Mumbai, India (1.55–1.78), and Yazd, Iran (2.89) (Bauri et al., 2016; Jiang et al., 2017; Mosaddegh Mehrjerdi et al., 2014; Srivastava et al., 2006). In contrast, lower ratios were observed in the region of La Plata (Argentina) (0.36) (Massolo et al., 2010), Carmen (Mexico) (0.39–0.36) (Ceron et al., 2013), Rome (Italy) (0.36), Izmir (Turkey) (0.53–0.5) (Muezzinoglu et al., 2001), and Delhi (India) (0.5–0.39) (Hoque et al., 2008). Differences in the B/T ratio between these studies is due to the diversity in the vehicular fleets, fuel formula, and industrial activities.

3.2.2. Ratios of xylenes to benzene (Xs to B) and ethylbenzene/benzene (Ebz /B)

The mean values of the (M&P)-X to B (0.49–0.74), O-X to B (0.62–0.89), and Ebz /B (0.19–0.28) are presented in Table 1. Small X/B and Ebz/B ratios in our study suggest that the sampled air masses were photochemically aged (e.g., via reactions with hydroxyl radicals) and that benzene has a relatively low reactivity as compared with ethylbenzene and xylenes. Therefore, M&P-xylene, ethylbenzene and o-xylene could be included in photochemical reactions with hydroxyl radicals (Bauri et al., 2016; Jiang et al., 2017; Masih et al., 2016; Muezzinoglu et al., 2001). These results emphasize the findings of previous research, in which the minimum concentration of BTEX species was for ethylbenzene and xylenes (Bauri et al., 2016). In addition, higher benzene and toluene concentrations were measured in past work over the United States in line with our findings (Pankow et al., 2003). Also, the X/B ratio (0.49–0.89) in this study is comparable to Orleans, France (0.28–1.09) (Jiang et al., 2017) and Delhi, India (0.34–0.87) (Hoque et al., 2008). Moreover, X/B and Ebz/B ratios could also be indicative of air mass age (Tunsaringkarn et al., 2014). According to Jiang et al. (2017) small X/B and Ebz /B ratios indicate that xylenes stem from transport.

3.3. Spatial analysis of BTEXs

The spatial distribution of benzene, BTEX components, and the sum of BTEX for morning and evening is shown in Fig. 4. The spatial distribution (Figs. 1 and 4) displays that the highest BTEX concentrations in the morning and evening were at points 4, 7, 16, and 17. This can be explained by proximity to several sources including IGBT, roads with heavy traffic, the MSW station, and five gas stations. In addition, the results revealed that ethylbenzene and isomers of xylene exhibited a similar distribution, while benzene, toluene, and total BTEX were different in the morning (Fig. 4a). Furthermore, spatial mapping in the

evening showed that distribution of TEX species and total BTEX were similar, while benzene was different. The concentrations of benzene in sampling points 16 and 17 in the south (three gas stations) were about 1–2.2 times higher than that in sampling points 4 and 7 (two gas stations). The wind direction is mainly northerly, which is the main reason why BTEX can migrate from the petrol station and bus terminal in the north to points 16 or 17 and accumulate in the southern area. Furthermore, Parra et al. (2006) mentioned that benzene had different distribution than TEX pollutants because benzene has a relatively low reactivity with OH; consequently, this pollutant can be transported to other regions without degradation. The spatial analysis indicated that BTEX levels decreased with increasing distance from strong emissions sources such as gas stations and the MSW station; this is in line with the findings of another study in Tehran, Iran (Miri et al., 2016) and in Gothenburg, Sweden (Thorsson and Eliasson, 2006).

3.4. The correlations among BTEX species

Table 2 reports on correlations between the BTEX species based on mean concentrations in both the morning and evening. There were significant positive correlations between BTEX species in the morning as well as in the evening. This result suggests that the emission sources of BTEX species are similar in both the morning and evening. Besides, Hoque et al. (2008), Rad et al. (2014), and Miri et al. (2016) reported that a strong correlation was obtained between BTEX compounds. Similarly, in this study a strong correlation was obtained between TEX compounds. The correlation coefficients (r) for TEX compounds were high in the morning as compared with the evening. The minimum correlation coefficient ($r = 0.005$, P-value = 0.984) was observed between benzene and m/p-xylene. This can be attributed to the various sources of BTEX species. The main source of benzene in the study region is gas stations. Nevertheless, the other sources of TEX could be related to bus traffic, gas stations, as well as the MSW station. No statistically significant differences were found between the BTEX species in the morning and evening based on the following p-values: 0.157 for benzene, 0.424 for toluene, 0.239 for ethylbenzene, 0.237 for (m + p)-xylene, 0.414 for o-xylene.

3.5. Health risk assessment

The LTCR between 1×10^{-5} and 1×10^{-6} has been regarded as "acceptable" by the WHO while the US EPA has suggested a LTCR under 1×10^{-6} (Gong et al., 2017; Miri et al., 2016). As can be observed in Fig. 5 and Table 3, the average LTCRs of benzene in the morning and evening were 1.96×10^{-4} and 2.49×10^{-4} , respectively, which exceed the recommended value by US EPA and WHO. Similar findings have been obtained by Li et al. (2014) in the ambient urban atmosphere of Beijing (China) (Li et al., 2014), in the north urban atmosphere of India (Masih et al., 2016), and by a gas station in Bangkok, Thailand (Tunsaringkarn et al., 2012) with mean LTCR values of benzene reported at 1.34×10^{-5} , 4.6×10^{-6} , and 1.75×10^{-4} , respectively. In addition, different results have been obtained by Miri et al. (2016) in the ambient air in Tehran, Iran and Hu et al. (2010) in the ambient air in Nanjing, China with mean LTCR values of benzene reported at 3.93×10^{-7} and 1×10^{-7} , respectively.

Results from the model simulations focused on sensitivity analysis of benzene LTCR are summarized in Fig. 5. Factors examined included body weight, inhalation rate, exposure duration, averaging time, and exposure frequency. The percentage value relevant to each variable represents the amount of the LTCR accounted for by that variable. The concentration of the pollutant had the highest positive contribution and body weight (BW) exhibited the most negative contribution to affect the average lifetime cancer risk for both the morning and evening. Furthermore, Miri et al. (2016) reported that BW was the most negative portion (– 51.6%) to the average lifetime cancer risk (Miri et al., 2016).

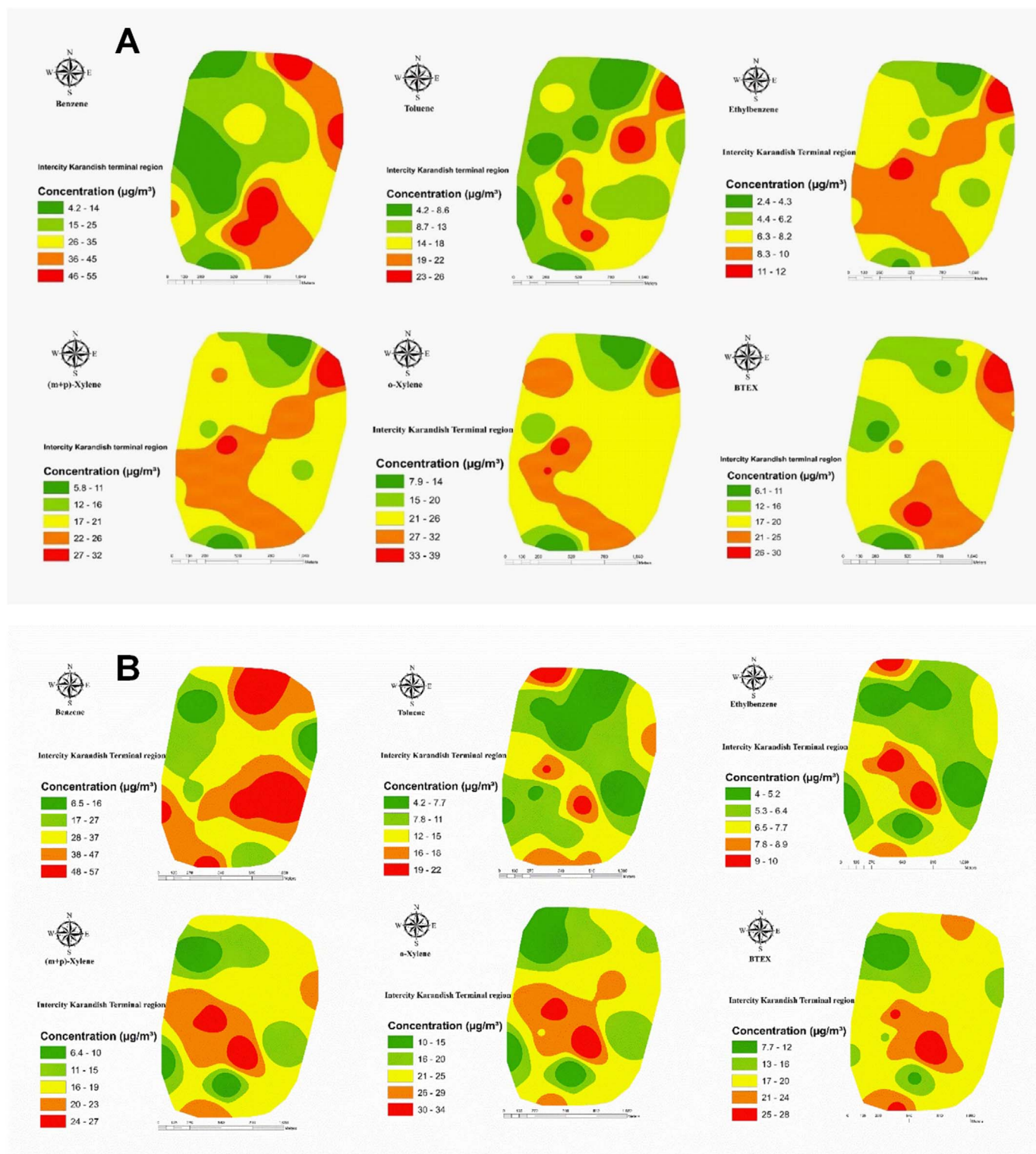


Fig. 4. Spatial distribution of average concentrations (µg/m³) of target components in the morning (A) and in the evening (B).

The results of hazard quotient (HQ) are introduced in Table 3. The results of present study displayed that the hazard quotient of all BTEX pollutants are less than 1. Therefore, there is less concern about non-carcinogenic risk of these pollutants in the study area.

4. Conclusion

This study reports on ambient measurements of BTEX pollutant

concentrations in the ambient urban atmosphere in the morning and evening in a busy bus terminal region of Shiraz, Iran. Spatial analysis showed revealed that BTEX levels decreased with increasing distance from the municipal solid waste (MSW) transfer station and that maximum BTEX concentrations were observed in the surrounding gas/petrol stations. High B:T ratios are attributed to emissions of traffic sources. Maximum diurnal mean concentrations of benzene were observed in the evening, while maximum levels of the ETX components

Table 2
Spearman's correlation coefficients (r) between target compounds.

Pollutant		Benzene	Toluene	Ethylbenzene	m/p-xylene	o-xylene
Morning						
	Benzene	r	1.000			
		P-value				
Toluene		r	0.055	1.000		
		P-value	.828			
Ethylbenzene		r	0.007	0.799**	1.000	
		P-value	.977	0.000		
m/p-xylene		r	0.055	0.844**	1.000	
		P-value	.829	0.000		
o-xylene		r	0.069	0.754**	0.926**	1.000
		P-value	.785	0.000	0.000	
In the evening						
	Benzene	r	1.000			
		P-value				
Toluene		r	0.251	1.000		
		P-value	.316			
Ethylbenzene		r	0.127	0.799**	1.000	
		P-value	.616	0.000		
m/p-xylene		r	0.005	0.608**	1.000	
		P-value	.984	0.007		
o-xylene		r	0.127	0.740**	0.917**	1.000
		P-value	.616	0.097	0.000	

** Correlation is significant at the 0.01 level.

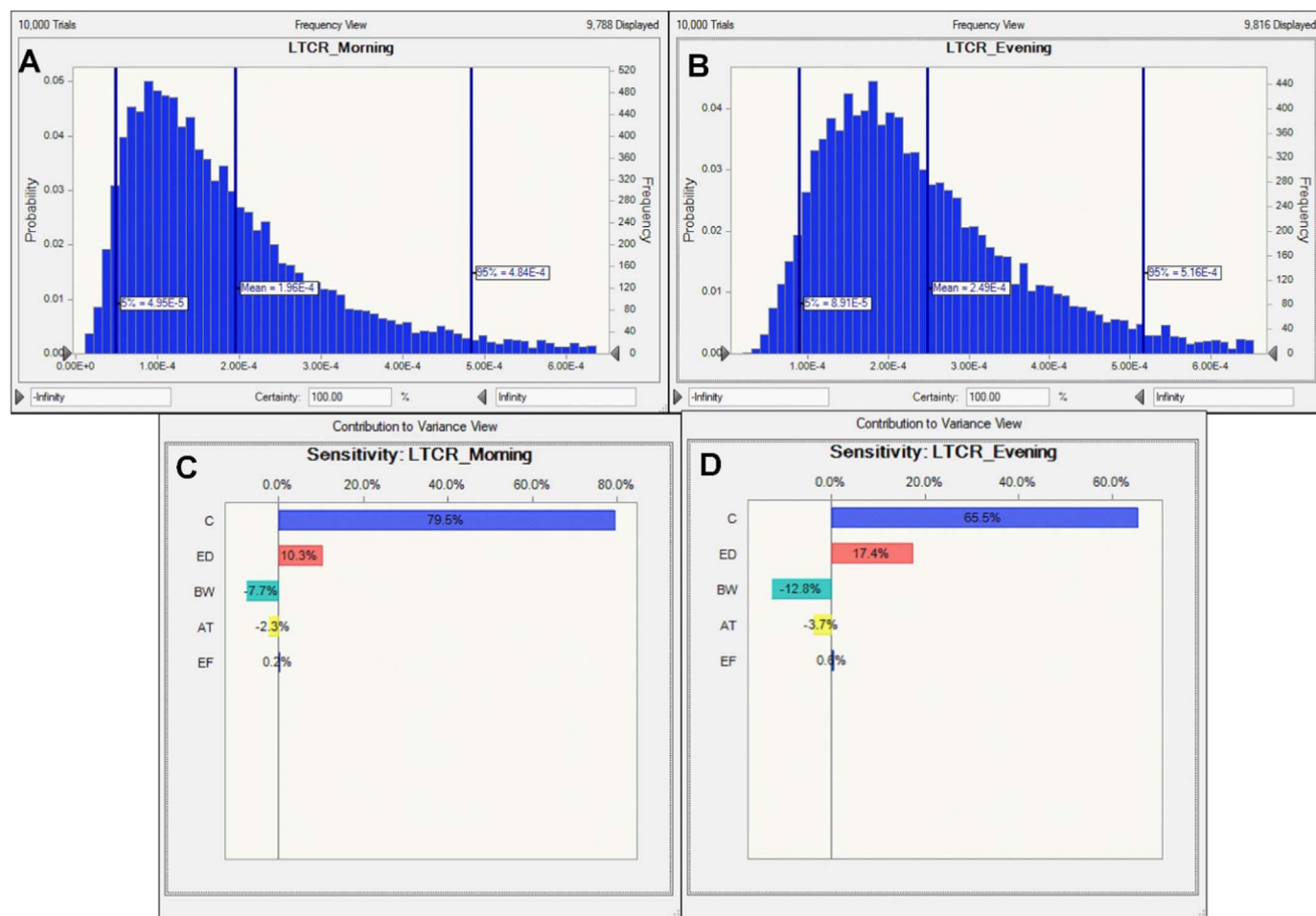


Fig. 5. Forecasted possibility of LTCR for benzene in the morning (A) and evening (B) and sensitivity analysis of LTCR model for benzene in the morning (C) and evening (D), (C: concentration of the pollutant, IR: inhalation rate, ED: Exposure duration, BW: body weight, AT: Averaging time, and EF: Exposure frequency).

Table 3

Comparison of the results of health risk assessment in the current and other related studies.

HQ and LTCR		Benzene	Toluene	Ethylbenzene	M/P-xylene	O-xylene	Reference	Ref.
HQ	Mean	8.71×10^{-1}	2.59×10^{-3}	7.50×10^{-3}	1.93	2.33	Shiraz, Iran	This study, in the morning
	SD	5.88×10^{-1}	1.42×10^{-3}	2.50×10^{-3}	6.49×10^{-1}	8.05×10^{-1}		
LTCR		2.77×10^{-7}	–	–	–	–		
HQ	Mean	1.14	2.24×10^{-3}	6.58×10^{-3}	1.68	2.12	Shiraz, Iran	This study, in the evening
	SD	5.21×10^{-1}	1.11×10^{-3}	1.95×10^{-3}	5.76×10^{-1}	6.93×10^{-1}		
LTCR		3.35×10^{-7}	–	–	–	–		
HQ	Mean	4.37×10^{-2}	1.06×10^{-3}	1.75×10^{-3}	4.45×10^{-2}	1.65×10^{-2}	Tehran, Iran	(Miri et al., 2016)
	SD	7.32×10^{-3}	3.70×10^{-4}	8.06×10^{-4}	1.17×10^{-2}	5.01×10^{-3}		
LTCR		3.93×10^{-7}	–	–	–	–		
HQ	Mean	0.29	8×10^{-3}	5×10^{-3}	7×10^{-2}	–	Ardabil, Iran	(Hazrati et al., 2016b)
	SD	0.22	7×10^{-3}	4×10^{-3}	6×10^{-2}	–		
LTCR		7.1×10^{-5}	–	–	–	–		
HQ	Mean	7.74×10^{-1}	2.17×10^{-2}	2.01×10^{-2}	4.72×10^{-1}	–	Kolkata, India	(Majumdar et al., 2008)
LTCR		9.66×10^{-5}	–	–	–	–		
HQ	Mean	1.57×10^{-1}	2.39×10^{-2}	3.29×10^{-3}	8.06×10^{-3}	3.53×10^{-3}	Beijing, China	(Zhang et al., 2012)
LTCR		4.19×10^{-5}	–	–	–	–		
HQ	Mean	0.38	5×10^{-3}	9×10^{-3}	2×10^{-3}	–	Bangkok, Thailand	(Tunsaringkarn et al., 2012)
LTCR		8.71×10^{-5}	–	–	–	–		
HQ	Mean	5.73×10^{-2}	1.08×10^{-3}	1.19×10^{-3}	2.09×10^{-2}	5.32×10^{-3}	Northeastern urban area of Beijing, China	(Li et al., 2014)
LTCR		1.34×10^{-5}	–	–	–	–		
HQ	Mean	–	–	–	–	–	Tianjin, China	(Zhou et al., 2011a)
LTCR		2.18×10^{-5}	–	–	–	–		
HQ	Mean	9.43×10^{-2}	2.30×10^{-2}	2.0×10^{-3}	5.61×10^{-2}	–	Hangzhou, China	(Li et al., 2014)
LTCR		9.43×10^{-6}	–	–	–	–		
HQ	Mean	1.58×10^{-1}	–	1.69×10^{-2}	7.76×10^{-3}	–	Urban-rural juncture belt area in Beijing, China	(Zhou et al., 2011b)
LTCR		2.21×10^{-5}	–	–	–	–		

HQ: hazard quotient; LTCR: integrated lifetime cancer risk.

The values of RFC in this study for benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene were 30, 5000, 1000, 10, 10 $\mu\text{g}/\text{m}^3$, respectively (EPA, 1999; Moolla et al., 2015).

were measured in the morning. The average inhalation lifetime cancer risk (LTCR) of benzene in the morning and evening exceeded the recommended value by the US EPA and WHO, while a hazard quotient (HQ) less than one indicated harmful impacts on the exposed population.

The results of this work have implications for public health near areas such as IKBT where large populations are exposed to carcinogenic emissions. One potential way to minimize exposure of large populations to high concentrations is to move an emissions hot spot, such as IKBT, which has gas stations and a MSW station, to areas outside the urban centre.

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