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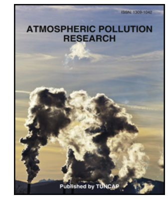

On the nature and health impacts of BTEX in a populated middle eastern city: Tehran, Iran

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ABSTRACT

This study describes a spatio-temporal characterization of concentrations of BTEX in ambient air of four hot spots (bus terminals) in the megacity of Tehran. Monte Carlo simulations were performed to evaluate cancer risk and non-cancer risk owing to BTEX exposure in three age groups (< 6, 6 to < 21 and 21 to < 81 years). The average toluene to benzene ratios for the four intercity bus terminals were 2.63 (summer) and 2.88 (winter). Furthermore, the mean xylenes to benzene and ethylbenzene to benzene ratios in the two seasons for all stations ranged from 3.33 to 4.40 (summer) and 2.13–2.80 (winter), respectively. There was insignificant difference in BTEX levels between working and non-working days owing to the lack of change in vehicular traffic during the full week. Factors promoting BTEX formation in the study region were fuel evaporation, gas stations, diesel bus emissions, and a lack of hydroxyl radicals (·OH) for reacting with the target compounds. Calculations suggested that cancer risk for benzene and ethylbenzene in three age groups at the four bus terminals exceeded values recommended by U. S. EPA. In addition, the hazard quotient for BTEX in both seasons for different age groups ranged between 1.23×10^{-5} and 3.58×10^{-1}, values of which were lower than reference levels. Carcinogenic emissions such as with benzene and ethylbenzene discharged by bus terminals impact the growing population in the study region, which requires additional action to reduce health effects.

1. Introduction

Intercity bus terminals are known as pollution ‘hot spots’ in major urban areas worldwide (Dehghani et al., 2018a; Moolla et al., 2015a; Parra et al., 2008; Qiu et al., 2016; Soldatos et al., 2003). This is largely due to the extensive emissions from diesel buses and petrol vehicles (Dehghani et al., 2018a; Hazrati et al., 2016b; Moolla et al., 2015a; Parra et al., 2008; Qiu et al., 2016; Soldatos et al., 2003). Air pollution in intercity bus terminals in developing countries has been exacerbated with time due to growing urban populations and reliance on buses as a form of transport, which poses major health risks (Cheng et al., 2011; Dehghani et al., 2018a; El-Fadel and El-Hougeiri, 2003; Wöhrnschimmel et al., 2008).

A major class of pollutants in the exhaust of buses and vehicles, including the evaporation of fuel, is volatile organic compounds (VOCs) (Faiz et al., 1996; Gupta et al., 2018; Jorquera and Rappenglück, 2004; Khoder, 2007; Lee et al., 2002; Liu et al., 2008; Sanchez et al., 2008; Zheng et al., 2017). The chief VOC components are benzene, toluene, ethylbenzene, and xylene, collectively referred to as BTEX, which have been the subject of many toxicology and various health effect studies (Baghani et al., 2018; Dehghani et al., 2018a; Delikhoon et al., 2018; Durmusoglu et al., 2010; Fazlzadeh et al., 2018; Hazrati et al., 2016a, 2016b; Hinwood et al., 2007; Liu et al., 2018; Neghab et al., 2017; Zhang et al., 2012). According to International Agency for Research on

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Cancer (IARC), benzene (group 1), ethylbenzene (group 2B), and toluene and xylenes (group 3) are categorized as human carcinogen, probable human carcinogen, and non-carcinogen for humans, respectively (IARC, 2014; Lim et al., 2014). In addition, benzene negatively impacts the blood-forming system and contributes to leukemia and hematological disorders (Moolla et al., 2015a; Smith, 2010), while toluene impacts the reproductive and neurobehavioral health (Foo et al., 1990; Greenberg, 1997; Tunsaringkarn et al., 2012b). Aside from public health, BTEX pollutants also have important effects also on atmospheric chemistry (Alghamdi et al., 2014; Parra et al., 2008; Zhu et al., 2008). For example, atmospheric reactions between BTEX and emitted nitrogen oxides (NOx) can produce ground level O_3 (Alghamdi et al., 2014; Parra et al., 2008; Zhu et al., 2008).

The ratio of toluene to benzene (T/B) (μg m^{-3}/μg m^{-3}) has been usually applied as an indicator for emission sources of pollution (Dehghani et al., 2018a; Jiang et al., 2017; Parra et al., 2008). For example, ratios of T/B between 1.50 and 4.30 and sometimes simply less than 3 have been considered as an identifier of traffic emissions (Alghamdi et al., 2014; Hoque et al., 2008; Jiang et al., 2017; Liu et al., 2009; Matysik et al., 2010). In addition to the T/B ratio, the ratios of xylenes/benzene (X/B) and ethylbenzene/benzene (Ebz/B) are mostly used as indices of photochemical reactivity (Bretón et al., 2017; Dehghani et al., 2018a; Kerchich and Kerbachi, 2012). For instance, large X/B and Ebz/B ratios (> 1) suggest that sampled air masses were not photochemically aged due to a lack of hydroxyl radicals (•OH) reacting with isomers of ethylbenzene and xylene (Kerchich and Kerbachi, 2012).

Tehran, Iran represents a major urban center with many bus terminals and thus is a hotspot for BTEX emissions. The goal of this work is to characterize BTEX levels and to conduct a health risk assessment (carcinogenic and non-carcinogenic risk of BTEX compounds) for three different age groups (birth to < 6, 6 to < 21 and 21 to < 81 years) using Monte Carlo simulations four intercity bus terminals in Tehran. Discussion is focused on a report of concentrations, spatio-temporal characterization of BTEX levels, concentrations of BTEX as a function of day of week, and the possibility of photochemical aging in the ambient air of the four bus terminals. Lastly, interrelationships between BTEX species and environmental air parameters such as temperature (°C), relative humidity (%) and wind speed (m s^{-1}) are summarized.

2. Material and methods

2.1. Study area

Tehran is the capital city of Iran (35.6892° N, 51.3890° E) (Marzouni et al., 2017; Tayyebi et al., 2018) (Fig. 1). This city has 22 regions have covering more than 613 km^2. The climate in Tehran can be characterized as semi-arid, with dry and hot summers, mild conditions in fall and spring, and cold conditions in the wintertime (Crosbie et al., 2014). The annual average daily temperature is 19 °C. July is the hottest month in Tehran with a mean temperature of 30 °C, while the coldest month is January at 4 °C. The mean annual precipitation in this area study is 225 mm. This megacity's population is around 13.3 million (2018 values) (Statistical Centre of Iran (SCI), 2016). Tehran has four intercity bus terminals, which transfer passengers between buses that travel to different parts of Iran. These intercity bus terminals include the following: Beyhaghi bus terminal; Jonoob bus terminal; Tehranpars-Shargh bus terminal; Azadi bus terminal (Fig. 1). In addition, environmental air parameters such as temperature (°C), relative humidity (%) and wind speed (m s^{-1}) were also simultaneously recorded using a portable instrument (Preservation Equipment Ltd, UK and Campbell Scientific, Inc., USA) to determine the relationship between BTEX concentration and environmental air parameters at each sampling location.

2.2. Sampling and analysis

Sampling of BTEX species were performed according to the National Institute for Occupational Safety and Health (NIOSH) 1501 procedure (Dehghani et al., 2018b; NIOSH, 2003a; Schlecht and O'Conner, 1994; Wang et al., 2005). Sampling was conducted over 3 h (9:00–12:00 a.m. local time) in the summer (22 May 2018 to 21 June 2018) and winter (20 January 2017 to 19 February 2017) using active sampling (SKC 222 Series Low Flow Pump) with a charcoal glass tube at a flow rate of 0.1 L min^{-1} (Dehghani et al., 2018a; Pendergrass, 2003). Sampling was performed every sixth day for 30 days at all four intercity bus terminals during the two seasons. Sampling was conducted at a height of 1.5 m. We collected 24 samples in summer (June) (6 for intercity Beyhaghi bus terminal, 6 for intercity Jonoob bus terminal, 6 for intercity Tehranpars-Shargh bus terminal, and 6 for intercity Azadi bus terminal) and 24 samples in winter (January) (6 for Beyhaghi bus terminal, 6 for Jonoob bus terminal, 6 for Tehranpars-Shargh bus terminal, and 6 for Azadi bus terminal). Before analysis, the two parts of the sampling tubes (the front and back) were placed into two separate vials and the BTEX pollutants were extracted using 1 mL carbon disulfide from charcoal tubes (ASTM, 1995; NIOSH, 2003b). The vials including carbon disulfide and charcoal were slowly shaken for 30 min. The solvent was moved in GC vials and target compounds were measured by a GC (Chrompack-Netherlands (NL)-CP9001) equipped with an FID detector using a capillary column (CP-Sil 8 CB-Chrompack, 30 m × 0.32 mm, 0.20 μm in film thickness). The injector was kept in split mode with a ratio of 1–5 and at a temperature of 250 °C. Nitrogen (99.999%) was used as the carrier gas at a flow rate of 2.5 mL min^{-1}. One μL aliquots were derived from GC vials and injected in a capillary column. The temperature of the injector was adjusted at 250 °C. The oven temperature was programmed at 40 °C for 10 min and then 10 °C min^{-1} to 200 °C.

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

In this work, two parts of tubes were analyzed individually for the potential of breakthrough for samples. There were no signs of BTEX contamination in the tube sections. Six samples for summer and six samples for winter were gathered as blank samples and concentrations of BTEX in these tubes for both seasons ranged from 0.00 to 0.016, 0.00–0.019, 0.00–0.104, and 0.00–0.102 (μg m^{-3}) for benzene, toluene, ethylbenzene, and xylene, respectively. The average recovery of 95% (90–112%) was obtained for BTEX contaminants with standard deviations (SDs) less than 4.00%. Calibration curves were developed using six levels of standard solutions (1–50 ppm), with coefficients of determination (R^2) being 0.997, 0.995, 0.998, and 0.994 for benzene, toluene, ethylbenzene, and xylene, respectively.

2.4. Statistical analysis

SPSS analytical software (Version 22.00) was used for statistical analysis. The relationships between concentrations of BTEX in each bus terminal and environmental air parameters such as temperature (°C), relative humidity (%) and wind speed (m s^{-1}) were assessed by Spearman's rho correlation coefficient. The ratios of B/T, X/B, and Ebz/B were computed for the four terminals for winter and summer in order to assess photochemical aging and to find emission sources of BTEX. Three-way ANOVA was used to find the effects of three variables (days, seasons, terminals) for the target compounds. Working days in Iran, are from Saturday to Wednesday. Non-working days are Thursday and Friday. Since the day of week did not impact the concentration of target pollutants, two-way ANOVA was used to find the effects of two variables (between variables of seasons and terminals) for the target compounds. Finally, the one-way ANOVA (Tukey post hoc) was used in the comparative analysis between the average concentrations of target compounds in different seasons for the four terminals.

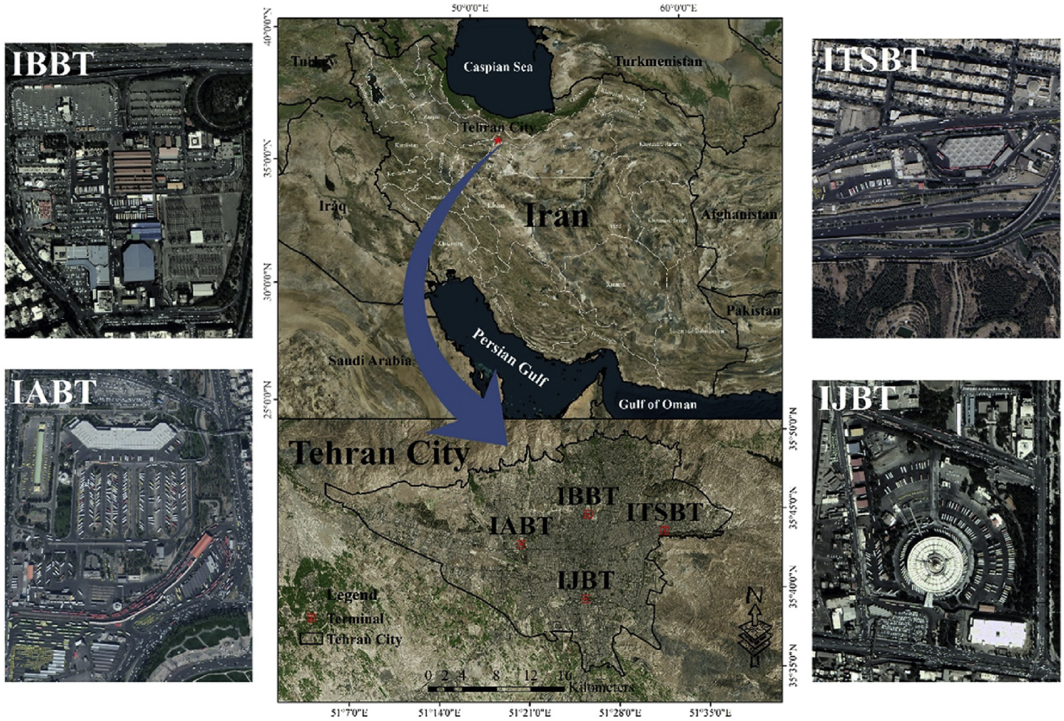

Fig. 1. Map of the study region and sampling locations: intercity Beyhaghi bus terminal (IBBT); intercity Jonoob bus terminal (IJBT); intercity Tehranpars-Shargh bus terminal (ITSBT); intercity Azadi bus terminal (IABT).

2.5. Health risk assessment

According to previous studies, benzene can cause cancer risk and promote diseases such as polycythemia, leukemia, hematological disorders, and aplastic anemia (Correa et al., 2012; Duarte-Davidson et al., 2001; Durmusoglu et al., 2010; Moolla et al., 2015b; Robinson et al., 1997). According to the International Agency for Research on Cancer (IARC), benzene and ethylbenzene were categorized as a carcinogen (group 1) and a potential carcinogen (group 2B), while xylene and toluene were not classified as carcinogenic (group 3) (IARC, 2014; Lim et al., 2014). Health risk assessment is the best procedure to determine the carcinogen and non-carcinogen health effects of BTEX in ambient air (Durmusoglu et al., 2010; Edokpolo et al., 2014). For calculating cancer risk (CR) for benzene, Eq. (2) was used, while Eq. (3) was applied to assess the non-carcinogenic risk or hazard quotient (HQ) for the toluene, ethylbenzene and xylene species.

According to the United States Environmental Protection Agency (U. S. EPA), cancer risk values considered as “an acceptable risk for humans” are recommended to be lower than $1 \times 10-6$ (EPA, 2003).

The cancer risk was estimated according to following equation (Gong et al., 2017; Hazrati et al., 2015a, 2016a; Ho et al., 2016; Rovira et al., 2016; Tunsaringkarn et al., 2012a):

$$CR = CDI \times CSF \quad (1)$$

Where CDI and CSF are chronic daily intake (mg kg^{-1} day^{-1}) and the cancer slope factor (mg kg^{-1} day^{-1})$^{-1}$), respectively.

In addition, the hazard quotient was calculated according to following equation:

$$HQ = \frac{CDI}{RfD} \quad \text{where; (Unsafe)} 1 < HQ \le (Safe) \quad (2)$$

Where HQ and RfD are hazard quotient (mg kg^{-1} day^{-1}) and reference dose (mg kg^{-1} day^{-1}), respectively.

Furthermore, chronic daily intake (mg kg^{-1} day^{-1}) was calculated according to following equation:

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

Where C and IR represent pollutant concentrations (μg m^{-3}) and human inhalation rate (m^3 day^{-1}), respectively, ED and EF represent the exposure duration (year) exposure frequency (days year^{-1}), and BW and AT are the body weight (kg) and the average lifetime (days),

Table 1
Exposure variables applied for Monte Carlo simulations for estimating hazard quotient, cancer risk, and sensitivity analysis for target components.

Parameters/Description	Age groups (year)			References
	Birth to < 6	6 to < 21	21 to < 81	
IR = Inhalation rate (m^3 day^{-1})	9 ± 1.05	14.40 ± 2.12	14.93 ± 1.59	((EPA), 2011)
BW = Body weight (kg)	10.16 ± 4.86	53.4 ± 20.11	80	((EPA), 2011)
ED = Exposure duration (year)	3	5	49	((EPA), 2011)
EF = Exposure frequency (day year^{-1})	365	365	365	((EPA), 2011)
AT = Averaging time (day)	1095	1825	17885	((EPA), 2011)
CSF = Cancer slope factor	0.00273 (mg kg^{-1} day^{-1}) for benzene (RAIS), 0.00385 (mg kg^{-1} day^{-1}) for ethylbenzene (RAIS)			Young (2014)
RfC = Inhalation reference concentration	30 for benzene, 5000 for toluene, 10 for xylene, 1000 for ethylbenzene (μg kg^{-1} day^{-1})			(EPA, 1999; Moolla et al., 2015a)

Note: Cancer slope factor for toluene and xylene did not exist due to the controversy of human carcinogenicity. There are not enough data to prove its carcinogenicity.

respectively.

Hazard quotients exceeding one (1 < hazard quotient (HQ)) indicate unsafe risk, while HQ ≤ 1 indicates safe risk. Table 1 displays selected factor values used for health risk assessment for three different age groups (birth to < 6, 6 to < 21 and 21 to < 81 years) with corresponding results for a sensitivity analysis for values used to calculate chronic daily intake, hazard quotient, and cancer risk. For estimating the chronic daily intake, the mean value for the target components was applied. It should be also taken into consideration that we selected different age groups (birth to < 6, 6 to < 21 and 21 to < 81 years) based on EPA (2011) because in Iran various variables such as inhalation rate (IR), body weight (BW), exposure duration (ED), exposure frequency (EF), and averaging time (AT) are not classified based on different age groups. In addition, based on Table 1, the parameters used for sensitivity analysis of the Monte Carlo simulations for benzene and ethylbenzene included inhalation rate (IR), body weight (BW), exposure duration (ED), exposure frequency (EF), and averaging time (AT). The percentage value relevant to each variable demonstrates the amount of the cancer risk calculated for by that variable.

3. Results

3.1. Mean concentrations of benzene, ethylbenzene, toluene, and xylene and total BTEX in four intercity bus terminals during summer and winter

The mean ± SD concentrations of benzene, toluene, ethylbenzene and xylenes, total BTEX (μg m^{-3}), temperature (C°), relative humidity (%), and wind speed (m s^{-1}) in four bus terminals during winter and summer are described in Table 2 and Fig. 2. The maximum seasonal mean concentrations of BTEX and total BTEX among the four terminals were detected in Jonoob bus terminal for both seasons. This is due to Jonoob bus terminal being the terminal with the most buses and traffic. According to Fig. 2, the mean total BTEX discharged to the ambient air for the four intercity bus terminals was 1.43–2.12 times more in summer than winter.

3.2. Concentrations of BTEX as a function of day of week and temporal analysis of BTEX

Concentrations of BTEX components in the summer followed the same pattern in the winter as a function of day of week (Fig. 3), with the lowest concentrations being for benzene in the four bus terminals in the both seasons. The highest levels were measured for xylenes in the both seasons. The P-value corresponding to the level of significance in the difference of benzene, toluene, ethylbenzene, and xylene concentration between different pairs of terminals are shown in Table 3. The three-way ANOVA analysis revealed that there was no significant difference between days and the mean concentrations of BTEX ($p = 0.816$ for benzene, $p = 0.989$ for toluene, $p = 0.994$ for ethylbenzene, and $p = 0.415$ for xylene).

3.3. Comparison of BTEX concentrations with recommended guidelines

The findings the present works were contrasted with proposed guidelines for indoor and ambient (outdoor) air (Table 4).

3.4. Interrelationships between BTEX species and environmental air parameters

Table S1 summarizes Pearson's correlations among BTEX constituent concentrations according to average concentrations in each intercity bus terminal in the winter and summer. Accordingly, the correlation coefficients (r) for BTEX compounds in the summer (for an intercity Beyhaghi bus terminal, Jonoob bus terminal and Tehranpars-Shargh bus terminal) were higher than winter.

Table 2
The mean (± SD) concentrations of BTEX (μg m^{-3}), temperature (C°), relative humidity (%), and wind speed (m s^{-1}) in four bus terminals during summer and winter and comparison of the mean concentrations of BTEX (μg m^{-3}) in this work with other studies.

Benzene	Toluene	Ethylbenzene	Xylenes	Temperature	Humidity	Wind speed	City	Reference
153.96 ± 17.87	386.20 ± 19.75	390.84 ± 52.35	447.53 ± 43.27	12.05 ± 0.157	74.83 ± 6.17	15.36 ± 0.56	Tehran, Iran (IBBT), in winter	This study (2017–2018)
296.32 ± 5.24	876.85 ± 7.51	821.20 ± 5.01	878.86 ± 32.58	13.44 ± 0.22	66.66 ± 2.42	18.18 ± 1.56	Tehran, Iran (IJBT), in winter	This study (2017–2018)
191.81 ± 5.85	574.54 ± 8.71	560.41 ± 14.6	798.23 ± 139.84	12.26 ± 0.08	74.16 ± 8.3	14.76 ± 1.62	Tehran, Iran (ITSBT), in winter	This study (2017–2018)
235.17 ± 19.11	686.71 ± 14.36	684.54 ± 19.53	800 ± 57.73	12.57 ± 0.13	69.33 ± 3.72	14.71 ± 0.41	Tehran, Iran (IABT), in winter	This study (2017–2018)
214.08 ± 30.48	565.07 ± 108.20	473.61 ± 111.33	950.88 ± 138.95	29.44 ± 1.2	26 ± 1.09	13.93 ± 0.23	Tehran, Iran (IBBT), in summer	This study (2017–2018)
348.63 ± 2.66	826.37 ± 3.57	628.75 ± 4.93	1320.26 ± 62.43	33.31 ± 0.54	23.16 ± 1.47	14.11 ± 1.02	Tehran, Iran (IJBT), in summer	This study (2017–2018)
215.68 ± 3.59	678.73 ± 116.87	489.27 ± 111.26	1161.09 ± 76.63	30.11 ± 0.71	24.33 ± 1.36	14.85 ± 1.78	Tehran, Iran (ITSBT), in summer	This study (2017–2018)
262.12 ± 2.48	664.43 ± 55.57	624.73 ± 10.52	1147.55 ± 54.06	31.69 ± 0.25	24.16 ± 0.75	14.38 ± 1.07	Tehran, Iran (IABT), in summer	This study (2017–2018)
100	250	136	348	–	–	–	Pamplona, Northern Spain	(Parra et al., 2008)
13.7	12.4	–	4.1	23.1 ± 5.8	53.1 ± 14.9	–	Beijing, China	Li et al. (2006)
0.3–210	0.5–69.20	0.1–12.20	0.4–38.40	–	–	–	Belgium, Hungary	Keymeulen et al. (2001)
54.14	209.24	45.87	118.93	–	–	–	Rio de Janeiro, Brazil	de Castro et al. (2015)
46.72–435.43	25.54–342.46	7.10–30.07	9.36–89.73	26.5–29.2	–	–	Salvador, Brazil	Cruz et al. (2017)
350	338	93	360	16.2–27.2	68.3–74.9	–	Athens, Greece	Soldatos et al. (2003)
2010	1800	2720	1650	–	–	–	Ardabil, Iran	(Hazrati et al., 2016b)
313,16	188,43	63,72	850,97		–	–	Johannesburg, South Africa	(Moolla et al., 2015a)

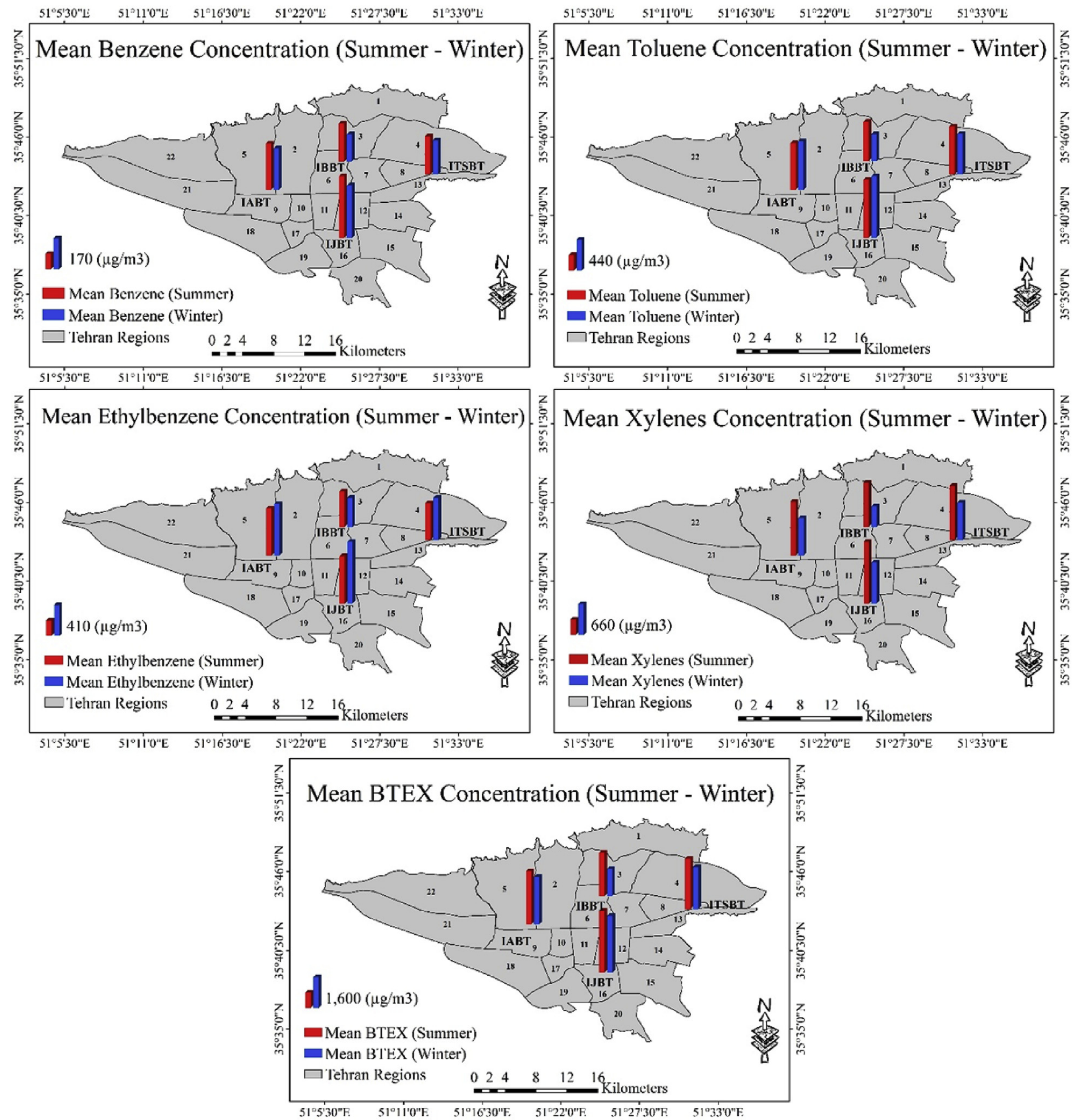

Fig. 2. The mean concentrations of benzene, ethylbenzene, toluene, and xylenes and total BTEX for four intercity bus terminals during summer and winter.

3.5. The ratios between target components (T/B, X/B and Ebz/B ratios)

In this work, the mean ratios of T/B for four terminals in the winter and summer were 2.63 and 2.88, respectively, indicative of the importance of traffic emissions (diesel buses or fresh emissions) as the main emission source of BTEX the study area. Furthermore, the average values of the X/B and Ebz/B ratios for the four bus terminals in the summer were 4.40 and 2.13, respectively. In addition, the mean values of the X/B and Ebz/B ratios for the four bus terminals in the winter were 3.33 and 2.80, respectively.

3.6. Health risk assessment

Table S2 summarizes findings related to cancer risk and hazard quotient and sensitivity analysis for model simulations for BTEX compounds in the ambient air of the four bus terminals. Accordingly, the average cancer risks computed for benzene and ethylbenzene in different age groups (birth to < 6, 6 to < 21 and 21 to < 81 years) at Azadi bus terminal, Beyhaghi bus terminal, Jonoob bus terminal, and Tehranpars-Shargh bus terminal exceeded the suggested value by U. S. EPA (Table S2).

4. Discussion

These findings display that xylene was more abundant as compared with other species. Moreover, Parra et al. (2008), Soldatos et al. (2003), and Moolla et al. (2015a) demonstrated the following order of abundance in public buses (Pamplona, Northern Spain), in car parking's and gasoline service stations (Athens, Greece) and in the diesel bus refuelling stations (Johannesburg, South Africa), respectively: xylenes > toluene > ethylbenzene > benzene. Such an order is generally consistent with our study findings (Moolla et al., 2015a; Parra et al., 2008;

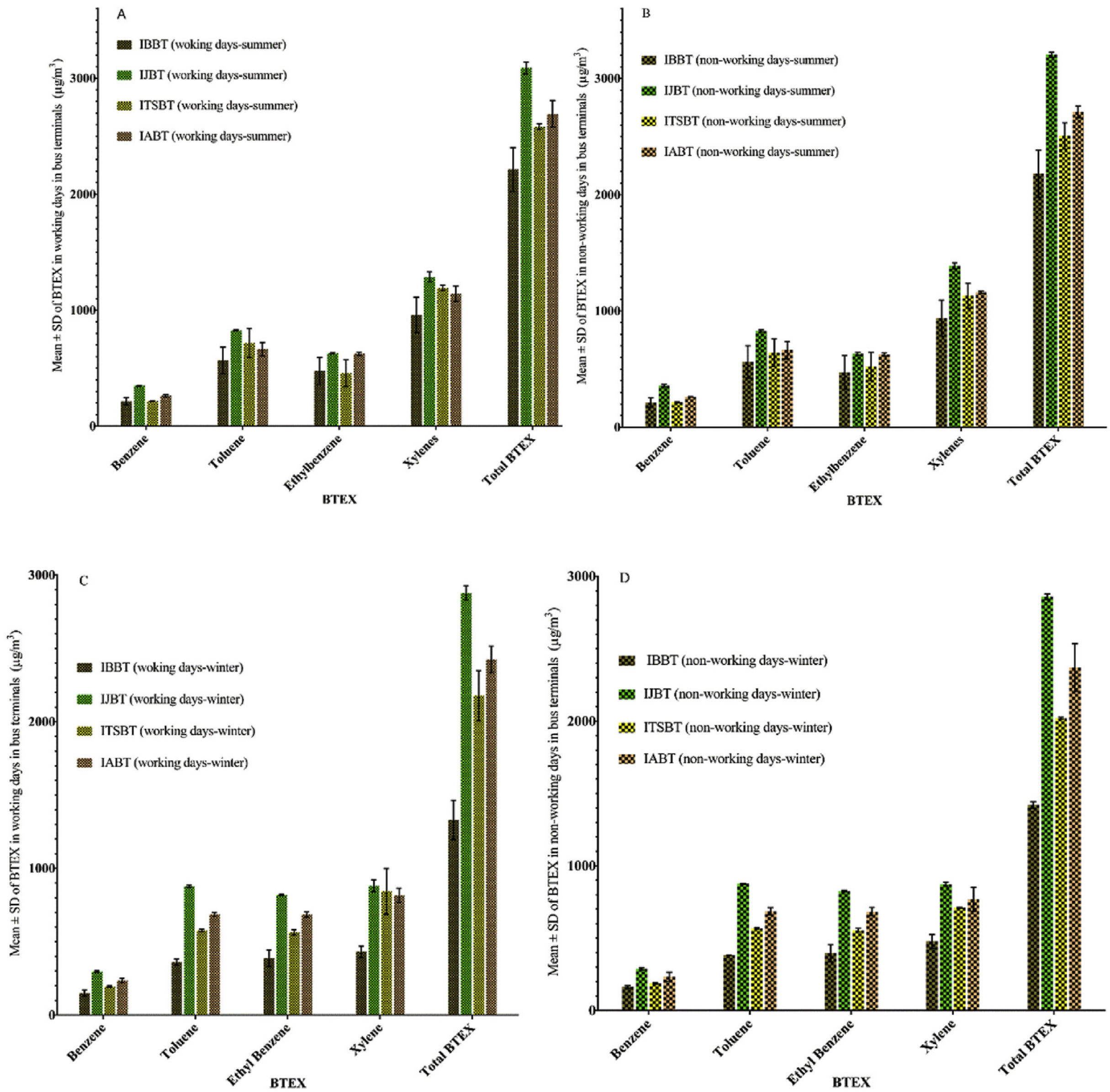

Fig. 3. Mean and SD of benzene, toluene, ethylbenzene, xylenes, and the total of BTEX (μg m^{-3}) for four intercity bus terminals based on working days in summer (A), non-working in summer (B), working days in winter (C), non-working in winter (D).

Soldatos et al., 2003). Reasons for concentration of isomers of ethylbenzene and xylene being highest in these terminals could be related to types of petrol and gasoline in Iran and the abundance of diesel buses in intercity bus terminals (Dehghani et al., 2018a; Hazrati et al., 2016b). In addition, the kind of fuels used in Iran include gas, petrol, gasoline, diesel fuel, compressed natural gas (CNG), and liquefied petroleum gas (LPG) (Delikhoon et al., 2018), while the main fuels consumed by diesel buses and vehicles in the four bus terminals examined were petrol,

Table 3
The P-value corresponding to the level of significance in the difference of benzene, toluene, ethylbenzene, and xylene concentration between different pairs of terminals.

Tukey post hoc	Summer				Winter			
	Benzene	Toluene	Ethylbenzene	Xylene	Benzene	Toluene	Ethylbenzene	Xylene
Terminal vs Terminal	P-value	P-value	P-value	P-value	P-value	P-value	P-value	P-value
Beyhaghi vs Jonoob	< 0.001	< 0.001	0.014	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Beyhaghi vs Tehranpars-Shargh	0.998	0.124	0.986	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Beyhaghi vs Azadi	< 0.001	0.207	0.017	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Jonoob vs Tehranpars-Shargh	< 0.001	0.031	0.029	0.007	< 0.001	< 0.001	< 0.001	0.007
Azadi vs Jonoob	< 0.001	0.016	0.990	0.004	< 0.001	< 0.001	< 0.001	0.004
Azadi vs Tehranpars-Shargh	< 0.001	0.991	0.035	0.998	< 0.001	< 0.001	< 0.001	0.998

Table 4
Recommended guidelines for BTEX concentrations (µg m^{-3}) in indoor and ambient air.

Component	Indoor and threshold limit values												Outdoor
	TWA[a] (µg/m^3)				STEL[b] (µg/m^3)				CE[c] (µg/m^3)	LTE[d] (µg/m^3)	STE[e] (µg/m^3)	STEL (µg/m^3)	
	[f] HSE (U.K.)	[g]MHMEI (Iran)	[h]NIOSH	[i]ACGIH	HSE (U.K.)	MHMEI (Iran)	NIOSH	ACGIH	[j]HKSAR	[k]French IAQGs	Health Canada	Health Canada	[l]IEPO
Benzene	0.325 × 10^4	0.16 × 10^4	.32 × 10^3	0.16 × 10^4	0.8 × 10^4	–	0.375 × 10^4	0.8 × 10^4	16.1	10	30	–	5
Toluene	19.1 × 10^4	7.5 × 10^4	37.5 × 10^4	7.5 × 10^4	38.4 × 10^4	–	56 × 10^4	–	1092	–	–	15 × 10^3	–
Ethylbenzene	44.1 × 10^4	8.7 × 10^4	43.5 × 10^4	8.7 × 10^4	55.2 × 10^4	–	54.5 × 10^4	–	1447	–	–	–	–
Xylene	22 × 10^4	43.4 × 10^4	43.5 × 10^4	43.4 × 10^4	44.1 × 10^4	65.1 × 10^4	65.5 × 10^4	65.1 × 10^4	1447	–	–	–	–
Reference	HSE (2011)	MHMEI (2012)	NIOSH (2000)	ACGIH (2007)	HSE (2011)	MHMEI (2012)	NIOSH (2000)	ACGIH (2007)	HKSAR (2003)	Keirsbulck et al. (2009)	Canada (2013)	Canada (2011)	IEPO (2012)

[a] Time weighted Average.
[b] Short-term exposure limit.
[c] Continued exposure.
[d] Long-term exposure.
[e] Short-term exposure.
[f] Health and Safety Executive.
[g] Ministry of Health and Medical Education Iran MHMEI.
[h] National Institute for Occupational Safety NIOSH.
[i] American Conference of Governmental Industrial Hygienists (ACGIH).
[j] Hong Kong Special Administrative Region Indoor Air Quality Management Group (HKSAR).
[k] French Indoor air quality guidelines (IAQGs).
[l] Iran's Environmental Protection Organization (IEPO).

gasoline and diesel fuel. The results of this work are similar to the findings from compressed natural gas (CNG) and gasoline stations in Ardabil (Iran) and intercity bus terminals in western Shaanxi (China) where BTEX levels are enhanced owing to significant diesel bus activity (Hazrati et al., 2016b; Qiu et al., 2016). Another reason why xylene and ethylbenzene concentrations for winter are higher than other species is the lack of OH^- radicals (·OH) that can react with and deplete isomers of xylene and ethylbenzene (Kerchich and Kerbachi, 2012). Also, the concentration of BTEX is likely higher in summer than winter due to increase temperatures, which promotes fuel evaporation (Cerón-Bretón et al., 2015a; Karakitsios et al., 2007; Sanchez et al., 2008).

Comparison of the average concentrations of BTEX (µg m^{-3}) in this study is compared to other studies in Table 2 for context. Accordingly, the average concentrations of BTEX (µg m^{-3}) in this study is higher than some studies since a function of sampling in the bus terminals is important (diesel buses or fresh emissions) and fuel composition in Iran is various which these findings are in line with previous studies (Amini et al., 2017; Cheng et al., 2011; Dehghani et al., 2018a; El-Fadel and El-Hougeiri, 2003; Hazrati et al., 2016b; Qiu et al., 2016). Amini et al. (2017) reported that the concentrations of benzene, toluene, ethylbenzene, xylene and total BTEX in Tehran during winter ranged from 0.4 to 20.7, 0.4 to 84.2, 0.4 to 11.2, 1.2 to 57.5, and 2.4–154.6 µg m^{-3}, respectively (Amini et al., 2017). The same study declared that the range of concentrations of target compounds in Tehran during summer were from 2.1 to 72.2, 6.9 to 287.6, 1.6 to 34.4, 5.5 to 151.3, and 17–538.1 µg m^{-3}, respectively (Amini et al., 2017). Another study was done in Tehran by Miri et al. (2016) showing that the annual mean concentrations of benzene, toluene, ethylbenzene, and xylenes were 3.44, 16.25, 3.63, and 17.26 µg m^{-3}, respectively (Miri et al., 2016). The mean concentration of benzene, toluene, ethylbenzene and xylene in Aghdasieh T-Junction in Tehran (Iran) were 16.57 ± 5.86, 9.11 ± 1.16, 5.08 ± 1.67 and 5.96 ± 1.89 ppb, respectively (Fazlzadeh et al., 2012). Furthermore, the mean concentrations of benzene, toluene, ethylbenzene and xylene compounds in Tehran, Iran using UNMIX receptor model were 28.96 ± 9.12, 29.55 ± 9.73, 28.61 ± 12.2 and 25.68 ± 10.58 µg m^{-3}, respectively (Dehghani et al., 2017). Hence, for comparison the results of this work with previous studies could be concluded that background ambient air levels in Tehran had slightly positive effects on the mean concentrations of BTEX in an intercity bus terminals.

Another reason why xylenes and ethylbenzene concentrations for winter are higher than other species is the lack of OH^- radicals (·OH) that can react with and deplete isomers of xylene and ethylbenzene (Kerchich and Kerbachi, 2012). Also, the concentration of BTEX is likely higher in summer than winter due to enhanced temperatures, which promotes fuel evaporation (Cerón-Bretón et al., 2015a; Karakitsios et al., 2007; Sanchez et al., 2008). In addition, the findings of this work shows that the mean total of BTEX in the working and non-working days in the summer were more than in the winter due likely to higher temperatures in the summer promoting fuel evaporation (Fig. 3) (Cerón-Bretón et al., 2015a; Ho et al., 2004; Karakitsios et al., 2007).

In addition, the three-way ANOVA analysis revealed that there was no significant difference between days and the mean concentrations of BTEX ($p = 0.816$ for benzene, $p = 0.989$ for toluene, $p = 0.994$ for ethylbenzene, and $p = 0.415$ for xylene) (Table 3). The reason why the day of week likely had no effect on the concentrations of BTEX was that the rate of migration into Tehran city during working days was equivalent to the rate leaving Tehran to surrounding areas on non-working days.

As the day was shown to not be a critical factor for BTEX concentrations, two-way ANOVA was applied to determine the effects of two other variables (season and terminal). Results indicated that there was no significant effect from the season or bus terminal on the concentration of xylene component ($p \geq 0.05$), while an interaction existed between season and terminal for the concentration of BTE components ($p \leq 0.05$) (Table 3).

One-way ANOVA (i.e., Tukey post hoc) was applied in the comparative analysis between the mean concentrations of BTEX compounds in different seasons for the four terminals (Table 3). There was no statistically significant difference between the Beyhaghi and Tehranpars-Shargh bus terminals in summer for benzene ($p = 0.998$), toluene ($p = 0.124$) and ethylbenzene ($p = 0.986$). In addition, there was no statistically significant difference between Beyhaghi and Azadi bus terminals in summer for toluene ($p = 0.124$). There was no statistically significant difference between Tehranpars-Shargh and Azadi bus terminals in summer for toluene ($p = 0.991$), while a statistically significant difference was observed between other terminals for target compounds ($p \leq 0.001$). Furthermore, the findings of this study shows which there was a statistically significant difference between all terminals in winter for target compounds (BTEX) ($p \leq 0.001$) except between Tehranpars-Shargh and Azadi bus terminals for xylene ($p = 0.998$) (Table 3).

According to Table 4, the only standard adjusted values for concentration of benzene in the urban ambient air near the study region were reported by Iran's Environmental Protection Organization (IEPO) as being $5\,\mu g\,m^{-3}$ (IEPO, 2012). This study's mean concentrations of benzene were higher than guidelines for indoor (Health Canada (2013); French IAQGs (Keirsbulck et al., 2009); HKSAR (HKSAR, 2003); NIOSH (NIOSH, 2000) and ambient air IEPO (IEPO, 2012), while the mean concentrations of TEX were lower than proposed guidelines such as HSE (HSE, 2011) and ACGIH (ACGIH, 2007).

Furthermore, Table S1 (interrelationships between BTEX species and environmental air parameters) showed that the major emitted sources of BTEX species are similar in four terminals in the summer and winter. Moreover, Dehghani et al. (2018) and Parra et al. (2008) described that a significant correlation was acquired among BTEX compounds. Hence, the main source of ethylbenzene and xylene in the regions of this study may be ascribed to abundance of diesel buses (fresh emissions) and the absence of ·OH for reacting with isomers of xylenes and ethylbenzene in the winter. However, the other sources of BTEX compounds in the summer could be affiliated with bus traffic (fresh emissions), gas stations near the bus terminals and fuel evaporation (higher temperature in the summer) in an intercity bus terminals; these findings are consistent with former studies (Cerón-Bretón et al., 2015a; Dehghani et al., 2018a; Karakitsios et al., 2007; Sanchez et al., 2008).

The T/B ($\mu g\ m^{-3}/\mu g\ m^{-3}$) ratio has been usually used as an indicator for emission sources of pollution (Dehghani et al., 2018a; Parra et al., 2008). The T/B ratio range of 1.50–4.30 is regarded as an identifier of traffic emissions (fresh emissions/bus emissions) (Hoque et al., 2008; Liu et al., 2009). In this work, the mean ratios of T/B for four terminals in the winter and summer were 2.63 and 2.88, respectively, indicative of the importance of traffic emissions (diesel buses or fresh emissions) as the main emission source of BTEX the study area. T/B (2.63–2.88) ratios in this work were comparable to those in Rome, Italy (2.80) (Brocco et al., 1997), La Plata, Argentina (2.70) (Massolo et al., 2010) and Carmen, Mexico (2.56–2.70) (Cerón et al., 2013). These differences in the B/T ratios could be related to differences in the areas studied, time of sampling, freshness of emissions, types of vehicles, and fuel formulas (Alghamdi et al., 2014; Bretón et al., 2017; Dehghani et al., 2018a; Hazrati et al., 2016b; Hoque et al., 2008; Kerchich and Kerbachi, 2012; Miller et al., 2011).

The average values of the X/B and Ebz/B ratios for the four bus terminals in the summer were 4.40 and 2.13, respectively. In addition, the mean values of the X/B and Ebz/B ratios for the four bus terminals in the winter were 3.33 and 2.80, respectively. Large ratios of X/B and Ebz/B (> 1) in the present study suggest that the sampled air masses were not photochemically aged (lack of hydroxyl radicals (·OH) for reacting with isomers of xylene and ethylbenzene) and that benzene has high reactivity as compared with ethylbenzene and xylenes; hence, benzene cannot be transported to regions farther downwind, consistent with previous work (Kerchich and Kerbachi, 2012). Additionally, due to the sampling sites being very close to the bus terminals, X/B and Ebz/B ratios could be indicators of emission sources of BTEX. Hence, fresh emissions may be more important than reactions (lack of hydroxyl radicals (·OH) for reacting with isomers of xylene and ethylbenzene). The ratio of X/B (3.33–4.40) in this work is higher in contrast to other areas such as Shiraz, Iran (0.49–0.89) (Dehghani et al., 2018a), Orleans, France (0.28–1.09) (Jiang et al., 2017), Tainan and Taipei, Taiwan (0.83–1.16) (Hsu and Huang, 2009), Seoul, Korea (0.53–1.50) (Kim et al., 2012), and Ankara, Turkey (0.18–1.01) (Yurdakul et al., 2013). Moreover, the ratio of Eb/B (2.13–2.80) in the present work is also higher than other regions such as Ankara, Turkey (0.38) (Yurdakul et al., 2013), Sopot, Poland (0.20) (Marć et al., 2014), Shiraz, Iran (0.19–0.28) (Dehghani et al., 2018a), Gorakhpur, India (0.24) (Masih et al., 2016).

According to Table S2, the average cancer risks computed for benzene and ethylbenzene in different age groups (birth to < 6, 6 to < 21 and 21 to < 81 years) at the four studied bus terminals exceeded the suggested value by US EPA. These results of exceedance of guideline values are consistent with other regions such as an intercity Karandish bus terminal in Shiraz (Iran) (Dehghani et al., 2018a), the Yucatan Peninsula (Mexico) (Bretón et al., 2017) and in Orizaba and Veracruz (Mexico) (Cerón Bretón et al., 2015b). Contrasting results were reported for Kolkata (a heavy traffic site) (India) (Dutta et al., 2009), Hazrati et al., 2015a, b) in indoor air of waterpipe cafés, Ardabil (Iran) and Cerón Bretón et al. (2017) in ambient air of San Nicolas de los Garza, Nuevo Leon, (Mexico) (Cerón Bretón et al., 2017) with the mean cancer risk values of 3.63×10^{-5}, 125×10^{-6} and 2.14×10^{-6} for benzene, respectively.

According to Table S2, body weight (BW) had the greatest positive effect on the mean cancer risk for two age groups (Birth to < 6 and 6 to < 21 years) for four intercity bus terminals. But, in age groups of 21 to < 81 years at the Beyhaghi bus terminal and the other three terminals (Jonoob, Tehranpars-Shargh, Azadi), respectively, benzene and ethylbenzene concentrations (C) and IR had the greatest positive effect on the mean cancer risk. Similarly, Baghani et al. (2018) reported that benzene and ethylbenzene concentrations accounted for the highest positive effect on the mean cancer risk in indoor air of beauty salons Ardabil (Iran) (Baghani et al., 2018). The results of this work revealed that the hazard quotient of BTEX in both seasons in different age groups (birth to < 6, 6 to < 21 and 21 to < 81 years) at four bus terminals were lower than reference levels. Hence, the hazard quotient for target compounds in both seasons were at acceptable limits for humans in the four bus terminals.

5. Conclusions

This work focused on concentrations and health effects of BTEX pollutants in the winter and summer in four hot spots (bus terminals) of Tehran, Iran. The average T/B ratios ranged between 1.50 and 4.30, suggesting that traffic emissions (fresh emissions), especially from diesel buses, were the major pollution source in bus terminals. The day of week (i.e., working versus non-working days) did not impact BTEX concentrations. The cancer risk (CR) for benzene and ethylbenzene in three age groups exceeded the suggested value by U. S. EPA. In addition, the hazard quotients (HQ) of BTEX in both seasons in different age groups were lower than recommended levels. The findings of this work have implications for a large urban population exposed to carcinogenic emissions such as ethylbenzene and benzene. It is important to decrease exposure of people to high BTEX concentrations in hot spots such as bus terminals and to move such facilities outside urban centers. Additionally, regulations to reduce pollution from diesel buses and other vehicular traffic is recommended.

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Appendix A. Supplementary data

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