

CHARACTERISTIC OF ATMOSPHERIC BTEX CONCENTRATIONS AND THEIR HEALTH IMPLICATIONS IN URBAN ENVIRONMENT

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(Received 30th Aug 2018; accepted 8th Nov 2018)

Abstract. The atmospheric concentrations of BTEX (benzene, toluene, ethylbenzene, m,p-xylene and o-xylene) were measured in five different urban cities in Kuwait through the year of 2016. The overall mean of total BTEX in all sites tested in this study was 5.21 $\mu\text{g}/\text{m}^3$ and it was found that the toluene level was the highest in all monitored sites. In terms of seasonal variations, BTEX concentrations were slightly higher in the winter than in the summer. This is plausibly due to higher chemical removal reaction rates of BTEX and to dust storm in the summer that eventually removes BTEX from the atmosphere. The diurnal patterns showed high records of BTEX concentrations in the morning (07:00–8:00 h) and during rush hours (19:00–21:00 h) in the evening, due to high volume of traffic and weak atmospheric dispersion and photochemical reactivity. Low records of BTEX concentrations were detected during midday, probably due to the high rate of photochemical reactions, to the increased mixing depth, to the upshifting of the urban boundary layer, and to the decreased traffic volume. Benzene/Toluene (B/T) and Xylene/ethylbenzene (X/E) ratios suggested that vehicular emissions were the main source of BTEX. Since individual pollutant exposure is associated with cancer risk (CR), BTEX concentrations are far from being safe for the population residing in these urban cities. According to individual hazard quotient (HQ), there is no serious threat of chronic non- cancer health effects in specific target organs for the urban cities population. A quite extensive review of BTEX in atmosphere was presented and it was found that the amount of BTEX in Kuwait was among the lowest compared with that of other cities in the world.

Keywords: *BTEX in ambient air, seasonal and diurnal variations, source apportionment, health risk assessment, spatial distribution*

Introduction

Several epidemiological studies have proven the harmful impacts of volatile organic compounds (VOCs) in urban ambient air. Over the last several decades, importance in determining the VOCs in the atmosphere has increased. VOCs play a vital role in the formation of ozone (Berezina et al., 2017; Olumayede et al., 2014) and photochemical oxidants (Derstroff et al., 2017). Recently many researchers have focused on the VOCs BTEX compounds (benzene, toluene, ethyl benzene and xylene) due to their toxicity and well correlated with each other (Bretón et al., 2017; Baek et al., 2015; Kerchich et al., 2012; Miller et al., 2010, 2009; Hoque et al., 2008).

BTEX can be found in both outdoor and indoor environments (Bolden et al., 2015; Fazlzadehdavilb et al., 2016; Le ha et al., 2017). They are generated from different sources such as vehicles, gasoline evaporation, heating systems, tobacco and aerosols (Xu et al., 2018; Hamid et al., 2017; Gennaro et al., 2015; Environment Australia, 1999). Also, it can be found in used items such as glues, cleaning products, paints, cosmetics and solvents (Holgate et al., 1999). The most important source of benzene for both indoor and outdoor exposure is the traffic (Gennaro et al., 2013; Jo et al., 1999). The concentration of VOCs and BTEX can vary between seasons and year to year due to the effect of source emissions, environmental conditions in the city, vehicle types, flow rates

and speeds of traffic (Buczynska et al., 2015; Borgie et al., 2014; Tager et al., 2009; Truc and Oanh, 2007; Paul et al., 1997).

Several attempts have been made all over the world to identify, quantify and characterize the level of VOCs BTEX in various environments. Lee et al. (2002) studied the concentrations of VOCs in urban atmosphere of Hong Kong. VOCs range was from undetectable to $1396 \mu\text{g}/\text{m}^3$ and the BTEX were the major constituents, approximately more than 60% in composition of total VOC detected. In another study done by Hinwood et al. (2007), the geometric mean (GM) of daily BTEX concentrations documented for the study population from four Australian cities were benzene $0.80 \text{ mg}/\text{m}^3$, toluene $2.83 \text{ mg}/\text{m}^3$, ethylbenzene $0.49 \text{ mg}/\text{m}^3$ and xylenes $2.36 \text{ mg}/\text{m}^3$. Zhang et al. (2012) measured the level of BTEX during autumn, winter, spring, and summer seasons in Beijing, China. The average concentrations of the total measured BTEX during the four seasons were 27.2, 31.9, 23.2, $19.1 \mu\text{g}/\text{m}^3$, respectively. Miller et al. (2012) studied the BTEX levels in the urban industrial city of Windsor in Canada. The three-year mean concentrations in $\mu\text{g}/\text{m}^3$ were: benzene (0.76), toluene (2.75), ethylbenzene (0.45), o-xylene (0.47), (m-p)-xylene (1.36) and the total mean concentrations of BTEX were $5.64 \mu\text{g}/\text{m}^3$. Duan et al. (2017) investigated the atmospheric concentrations of BTEX in China and researchers observed that BTEX species were higher in the winter than in the summer and toluene was more abundant compared with BTEX species. Pourfarzi et al. (2016) reported that the BTEX concentrations present in refueling stations in Iran are generally higher than typical outdoor air levels and ethylbenzene has the highest average concentration followed by benzene.

Numerous studies used benzene/ benzene (B/T), toluene/ benzene (T/B), and xylene/ethylbenzene ($\Sigma \text{X/E}$) ratios as indicatives of emission sources or photochemical age. In one study reported by Wang et al. (2012), benzene to toluene ratio range was 0.4–1.0 in the urban area of Beijing, China. In another study (Liu et al., 2005), the B/T ratio from roadside in Beijing was 0.61. Barletta et al. (2005) concluded that an average B/T value of 0.6 might be used to characterize vehicle emissions. Miller et al. (2012) considered the mobile emission is the major source of toluene to benzene (T/B) ratio, with the highest observed ratio occurring in the summer, the lowest in winter, and fall and spring values fell in between in the city of Windsor in Canada. Similarly, Khoder (2007) found from different areas in Cairo that the average toluene/benzene ratio (T/B) was 2.45 and 2.42 for the urban areas and 1.29 for the rural area, suggesting that motor vehicle emission is the main source of emission. Likewise, xylene/ethylbenzene ($\Sigma \text{X/E}$) ratio is used as an indicative of photochemical age and in most studies it ranged from 1.1 to 4.8 regardless of the geographic location (Rad et al., 2014; Hsieh et al., 2011; Truc and Oanh, 2007; Ho, et al., 2004). Low X/E ratio suggests an aged air parcel as these species are removed from air via different mechanisms including dispersion, deposition, and chemical reaction. Other studies done by Parra et al. (2006), Smith et al. (2007) and Su et al. (2010) reported significant proportional correlations among the BTEX species. They suggested that the high correlations ($r > 0.74$) between ethylbenzene and the two xylene species means that the species were originating from common sources and the relatively lower correlation coefficients ($r < 0.60$) seen between benzene and the other BTEX species were due to fact that benzene is emitted from vehicles whereas the other species are emitted from both vehicles and industrial activities.

Previous epidemiological studies have related the BTEX levels to several health outcomes. Benzene has been correlated with increased rates of leukemia and solid tumors (Vigliani et al., 1976). Some studies linked benzene from traffic emissions and cancer in members of the community especially children (Nordlinder et al., 1997). Exposure to toluene and xylenes has been associated with adverse effects on the nervous

system, liver and kidneys (ATSDR, 2003; USEPA, 2004). Exposure to ethyl benzene has a negative impact on the respiratory system and the kidneys (ATSDR, 2003; NTP, 1999). Several other studies highlighted the harmful effects of BTEX on human beings as well as the entire ecosystem. Up to the knowledge of the author, this study is the first thorough study investigating diurnal, seasonal, and spatial variations of BTEX level in ambient air of Kuwait. Additionally, source apportionment of atmospheric BTEX and cancer risks and non-cancer effects associated with exposure to atmospheric BTEX were also examined. This study was conducted during the year of 2016 at five representatives and spatially distributed sampling locations in Kuwait. This study is an attempt to control atmospheric concentrations of BTEX in ambient air of Kuwait and reduce their detrimental health outcomes.

Materials and methods

Study area and sampling

The atmospheric concentrations of BTEX (benzene, toluene, ethylbenzene, m,p-xylene and o-xylene) were measured in five different urban cities in Kuwait through the year of 2016. The five representative urban cities in Kuwait selected from south to north were Ali Sabah Al-Salem (Latitude: 29° 17.373'N, Longitude: 48° 9.291'E), Fahaheel (Latitude: 29° 4.818'N, Longitude: 48° 6.969'E), Al-Salam (Latitude: 29° 4.818'N, Longitude: 48° 0.426'E), Saad Al-Abdullah (Latitude: 29° 18.916'N, Longitude: 47° 43.347'E), and Al-Jahra (Latitude: 29° 19.927'N, Longitude: 47° 39.699'E) (*Fig. 1*). Ali Sabah Al-Salem city is situated at the south part of urban development of Kuwait with a population around 50,237 residents. This city is surrounded by main oil refineries (Mina Al-Ahmadi and Mina Abdullah) of the country. Moreover, it is proximate to petrochemical industrial plants such as ammonia, urea, polyethylene polypropylene plants and wastewater treatment plant. The city is also fronting express highway (No.30) that spreads from downtown of Kuwait to the borders of Saudi Arabia. Fahaheel city is located in the south of Kuwait just after Ali Sabah Al-Salem city toward the Kuwait city, and has a population twice that of Ali Sabah Al-Salem city (around 105,000). This area is surrounded by numerous emission sources including three large petroleum refineries, Greater Burgan field, several small, medium, and large petrochemical industrial plants, and the largest highway (Road No.30). Al-Salam city was selected because of its unique location as it is exposed to the many sources of various air pollutants. It lies approximately in the center part of Kuwait and bordered by two large highways (Road No.40 and 50) in the east and west, respectively. In the south, north, and in the middle of the city, there are numerous roads, government establishments, and stores, which are considered as emission sources. Saad Al-Abdullah city is located in the north part of Kuwait and surrounded by several industrial companies and workshops, involved in a wide range of activities such as petro chemical, farms army forces establishments, construction/recycling, insulation and fiber glass, mechanical and chemical plants. Al-Jahra city is situated at the north part of the residential band of Kuwait followed Saad Al-Abdullah city toward boarder between Kuwait and the Kingdom of Saudi Arabia and it is one of the largest populated city with a population of about 490,000 residents. The city is bounded by various small-medium industrial, commercial areas, industrial, powers plant, desalination plants as well as wastewater treatment plants. Additionally, several road network are available in this city including highway# 80, highway# 70, and it is fronting the largest express highway, 6th ring road.



Figure 1. Sampling sites for ground-level BTEX samples collected in Kuwait

Measurements of the atmospheric concentrations of BTEX (benzene, toluene, ethylbenzene, m,p-xylene and o-xylene) were performed from 1st January 2016 until 31st December 2016 on an hourly basis (8760 hourly data were recorded per year for each location), simultaneously in five different urban cities in Kuwait. Measurements of the atmospheric concentrations of BTEX were carried out by HORIBA Air Quality Monitoring Station (AQMS), which are located in the center of the five urban cities in Kuwait. BTEX species were analyzed with automatic sampling throughout all year. Analyzers were calibrated before the start-up and data were cross checked and

verified. Kuwait is witnessed by two distinct seasons: winter and summer. Summer season extends from April to October and is characterized as hot and humid. While winter season spreads from November to March, and is experienced as cooler with minimal rainfall. Regarding the wind characteristics, the most prevailing wind direction throughout the year is northwesterly winds followed by southeasterly winds, which was observed more often from February to April. Wind speed varied from 2.8 to 5.9 m/s with an average of 4.2 m/s during the studied period.

Exposure and risk assessment

The health risk assessment of BTEX consists of two parts; one quantifies the cancer effects of the chemicals, while the second addresses the non-cancer effects of the chemicals. Cancer risks are expressed as a probability of suffering an adverse effect (cancer) during a life time (assumed to be 70 years). To assess cancer risks, integrated lifetime cancer risk (ILTCR) due to the exposure to BTEX was estimated.

Only those substances that are known or suspected human carcinogens were considered in calculating integrated lifetime cancer risk (ILTCR). Formaldehyde, acetaldehyde, benzene, and ethylbenzene are believed to be carcinogenic (Dutta et al., 2009; Tunsaringkarn et al., 2012; Zhou et al., 2015). For non-carcinogens, hazard quotient (HQ) was used to assess non-cancer effects of BTEX. The daily exposure (E) of an individual by intake process (only inhalation was considered) was calculated from *Equation 1*:

$$E = \frac{C \times I_{ra} \times E_{da}}{B_{wa}} \quad (\text{Eq.1})$$

where the description of the variables used is tabulated below.

Variable	Description	Value	Units
E	Daily exposure		mg/kg-day
C	Concentration of the pollutant		mg/m ³
I _{ra}	Inhalation rate*, adult	0.83*	m ³ /h
E _{da}	Exposure duration, adult	24	hr/day
B _{wa}	Body weight, adult	65	kg

*The value of inhalation rate (adult) is taken from USEPA (1997)

The integrated lifetime cancer risk (ILTCR) was calculated from *Equation 2*:

$$\text{ILTCR} = E \text{ (mg Kg}^{-1} \text{ day}^{-1}) \times \text{SF (mg}^{-1} \text{ Kg day)} \quad (\text{Eq.2})$$

where SF is the carcinogenic potency slope or a slope factor of inhalation unit risk for toxics when the exposure-carcinogenic effect is considered as linear, taking from EPA (<http://www.epa.gov/iris>).

Human health risk estimates for inhalation of non-carcinogens are expressed as hazard quotient (HQ). It is defined as the ratio of yearly average daily received concentration (C_y) and the reference concentration, RfC (a level below which adverse health effects are not likely to occur). HQ was calculated from *Equation 3*:

$$HQ = \frac{C_y}{RfC} \quad (\text{Eq.3})$$

The reference concentration (RfC) for each pollutant was obtained from EPA (<http://rais.ornl.gov>) and California Office of Environmental Health Hazard Assessment (<http://www.arb.ca.gov/toxics/healthval/acute.pdf>).

Statistical analysis

To evaluate the differences among sites, One-way ANOVA analysis was employed using STATISTICA software. Statistical significance was considered once p -value < 0.05 . Statistical Software R programming language, with package open-air version 2.13.2, was utilized for other statistical tests and plotting graphs.

Results and discussion

Diurnal, seasonal, and spatial variations of BTEX concentrations

The atmospheric levels of BTEX in five different urban cities in Kuwait during the year of 2016 were quantified and descriptive statistics are presented in *Table 1*. Among the BTEX compounds, toluene showed the highest concentrations in all sites, with an average varied between $6.96 \pm 2.71 \mu\text{g}/\text{m}^3$ to $14.85 \pm 4.41 \mu\text{g}/\text{m}^3$ followed by MP-Xylene ($1.82 \pm 0.54 - 9.88 \pm 1.22 \mu\text{g}/\text{m}^3$), and o-xylene ($1.00 \pm 0.34 - 9.79 \pm 0.49 \mu\text{g}/\text{m}^3$). Ethylbenzene ($0.78 \pm 0.27 - 8.88 \pm 0.28 \mu\text{g}/\text{m}^3$) and benzene ($2.49 \pm 0.83 - 3.80 \pm 0.33 \mu\text{g}/\text{m}^3$) were present at lower concentrations. The overall mean of total BTEX in all sites tested in this study was $5.21 \mu\text{g}/\text{m}^3$. These observations are consistent with several previous studies where toluene was found the highest in the atmosphere of urban cities (Duan et al., 2017; Hoque et al., 2008; Johnson et al., 2010; Miller et al., 2009; Parra et al., 2006; Smith et al., 2007; Srivastava et al., 2005). Higher concentrations of toluene might be due to human activities such as fuel burning, the use of glues, cleaning products, paints, cosmetics and solvents (Holgate et al., 1999).

The diurnal variations of BTEX concentrations of benzene, toluene, ethylbenzene, and xylene in five different urban cities in Kuwait during the year of 2016 are shown in *Figure 2a-d*. The diurnal variations of BTEX concentrations followed similar arrangement: increased at 07:00–8:00 h, then decreased at 9:00–16:00 h and thereafter increased and reached a peak at 21:00 h, and finally decreased slightly at 1:00–6:00 h. The similar pattern of BTEX species suggested a common source of the pollutants. This BTEX profile is consistent with the diurnal trends found in other urban areas (Alghamdi et al., 2014; Tang et al., 2007; Filella and Peñuelas, 2006; Yang et al., 2005; Ho et al., 2004). High records of BTEX concentrations in the morning (07:00–8:00 h) and during rush hours (19:00–21:00 h) in the evening were due to high volume of traffic, the main contributor of VOC emissions, and other evaporative emissions sources (Martins et al., 2016; Song et al., 2008; Ho et al., 2004; Na et al., 2003;). Additionally, atmospheric dispersion and photochemical reactivity are weak during these periods. Conversely, low records of BTEX concentrations during midday can be possibly attributed to the high intensity of solar radiation that induces photochemical reaction, increases the mixing depth, and shifting up the urban boundary layer. In addition to that, traffic volume in midday decreases and thus the contribution of vehicle-related sources becomes trivial.

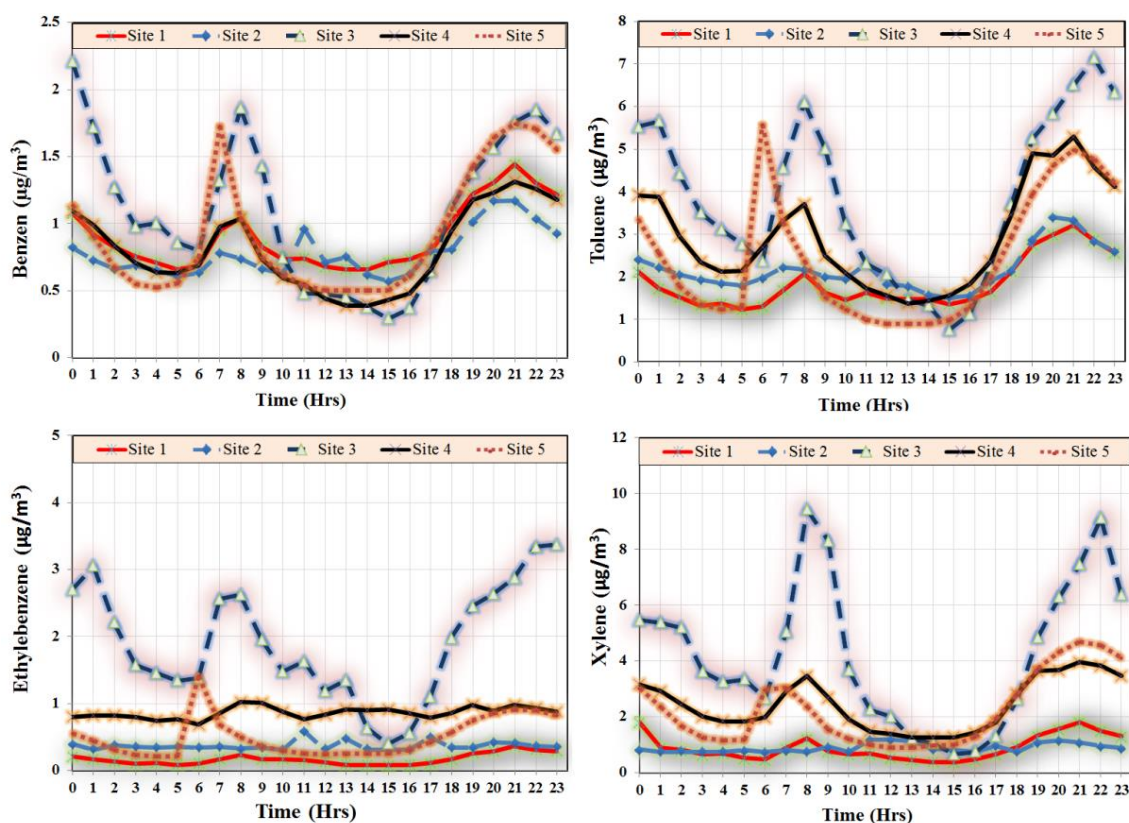


Figure 2. Diurnal BTEX average concentrations at five sites in Kuwait; (a) benzene, (b), toluene, (c) ethyl benzene, and (d) xylene. These data are the average hourly concentrations per year

Table 1. Descriptive statistics of average daily concentration of BTEX in ($\mu\text{g}/\text{m}^3$)

BTEX	Descriptive statistics	Site 1	Site 2	Site 3	Site 4	Site 5
Benzene	Max.	27.1	46.8	109.4	90.3	96.9
	Min.	0.02	0.22	0.005	0.03	0.01
	Ave.	2.49	2.87	3.80	2.58	3.51
	Med.	2.33	1.47	1.59	1.66	1.4
	SD	0.30	0.83	0.43	1.00	0.33
Toluene	Max.	40.9	85.5	171.9	48.30	75.5
	Min.	0.004	0.150	0.038	0.038	0.105
	Ave.	6.96	8.16	14.85	11.09	9.14
	Med.	5.04	1.880	5.716	5.453	3.61
	SD	2.71	3.43	4.41	3.41	2.21
Et-benzene	Max.	29.55	42.73	98.83	44.97	27.32
	Min.	0.004	0.173	0.043	0.043	0.004
	Ave.	0.78	1.60	8.88	3.73	2.12
	Med.	0.30	1.04	3.16	1.65	0.65
	SD	0.27	0.85	0.28	0.51	0.62

MP-Xylene	Max.	64.3	34.2	188.4	128.50	39.4
	Min.	0.009	0.217	0.043	0.043	0.009
	Ave.	1.82	2.82	9.88	6.07	6.67
	Med.	1.4	1.17	0.95	2.56	2.17
	SD	0.54	0.72	1.22	0.66	0.49
O-Xylene	Max.	44.80	35.5	179.20	51.30	35.90
	Min.	0.004	0.173	0.043	0.043	0.004
	Ave.	1.00	1.99	9.79	4.55	3.03
	Med.	0.52	1.39	2.08	2.38	1.04
	SD	0.34	0.94	0.49	0.46	0.18

Site 1: Ali Sabah Al-Salem, Site 2: Al-Fahaheel, Site 3: Al-Salam, Site 4: Saad Al-Abdullah, Site 5: Al-Jahra

Table 2 illustrates the seasonal variations of BTEX between winter and summer months among the five locations. Temperature in Kuwait is usually between 6 °C in winter and 45 °C in the summer. Overall, in all five tested sites, BTEX levels in the winter were higher than that of the summer. Seasonal variation of BTEX level in some sites (site 1, 3, and 5) was statistically significant (p -values < 0.05). Similar observations were also reported in the previous studies where BTEX concentrations in the winter were higher than those in the summer (Baek et al., 1997; Hartwell et al., 1987; Wathne, 1983). Low BTEX concentrations in the summer are possibly due to higher chemical removal reaction rates of BTEX compared with winter months. In the summer, the high temperatures combined with long daytime induces evaporation rate that would eventually promote BTEX dispersion in air. Another plausible reason to the decreasing level of BTEX in the summer is due to the frequent dust storms in Kuwait as in the case of other counties that witness arid and semi-arid climates. These dust storms remove the BTEX from the atmosphere during the summer time and thus reduce their concentrations.

Table 2. Seasonal variations of BTEX between winter and summer months among the five locations. The reading represents average value $\pm$ Standard deviation and units are in $\mu\text{g}/\text{m}^3$

Location/season	Benzene	Toluene	Et-benzene	Σ -Xylene
Site 1				
Winter	2.7 ± 0.92	9.9 ± 1.4	0.81 ± 0.41	3.43 ± 0.29
Summer	2.3 ± 0.92	5.5 ± 1.5	0.04 ± 0.001	1.98 ± 0.4
P-value	0.24	0.022*	0.016*	0.018*
Site 2				
Winter	3.8 ± 0.85	10.9 ± 5.0	1.66 ± 0.46	4.0 ± 0.7
Summer	2.6 ± 0.92	6.0 ± 0.86	1.63 ± 0.84	3.44 ± 0.8
P-value	0.24	0.26	0.94	0.33
Site 3				
Winter	5.0 ± 0.85	14.2 ± 5.8	8.2 ± 3.5	12.8 ± 2
Summer	4.4 ± 1.2	12.01 ± 4.2	7.2 ± 2.1	10.5 ± 1.9
P-value	0.15	0.20	0.12	0.11

Site 4				
Winter	2.96 ± 0.9	12.4 ± 2.4	4.7 ± 3.5	11.8 ± 2.1
Summer	2.22 ± 0.6	9.0 ± 1.9	1.8 ± 0.4	8.4 ± 2.4
P-value	0.16	0.06	0.009*	0.006*
Site 5				
Winter	3.5 ± 3.0	11.7 ± 4.2	2.9 ± 1.9	11.5 ± 1.0
Summer	2.3 ± 2.0	6.0 ± 3.0	0.94 ± 0.73	4.4 ± 3.4
P-value	0.026*	0.026*	0.026*	0.015*

*A p-value of < 0.05 was considered statistically significant. Site 1: Ali Sabah Al-Salem, Site 2: Fahaheel, Site 3: Al-Salam, Site 4: Saad Al-Abdullah, Site 5: Al-Jahra

Atmospheric BTEX levels were also spatially quantified in the five urban sites and results are shown in *Figure 3a-d*. The highest concentrations of BTEX compounds were detected in site 3 whereas the lowest concentrations were found in site 1 (*Fig. 3a-d*). This observation indeed indicates that BTEX compounds originated from similar emission source. Site 3 is surrounded by four main congested highways (40 and 50 roads and 5th and 6th ring roads) and several small roads inside the city. This indeed suggested that vehicle emission might be a prevailing source for BTEX compounds in this study.

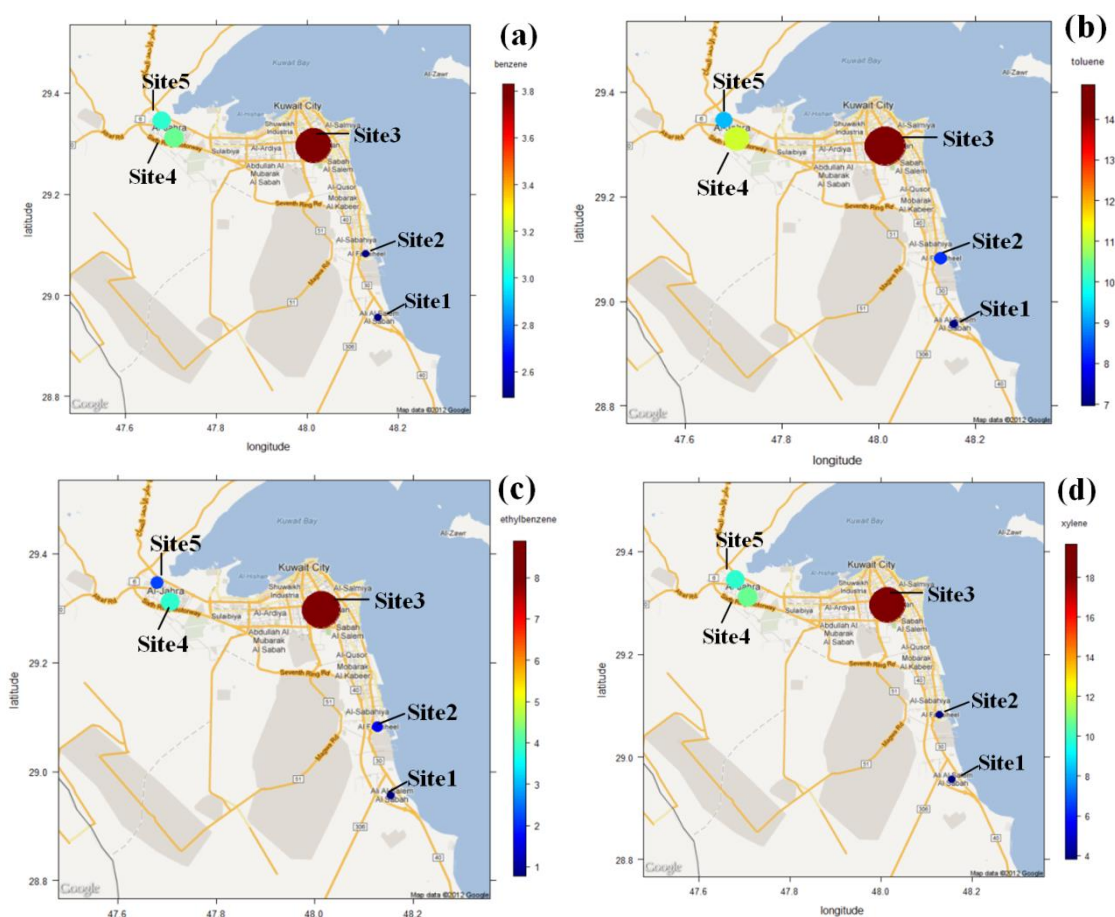
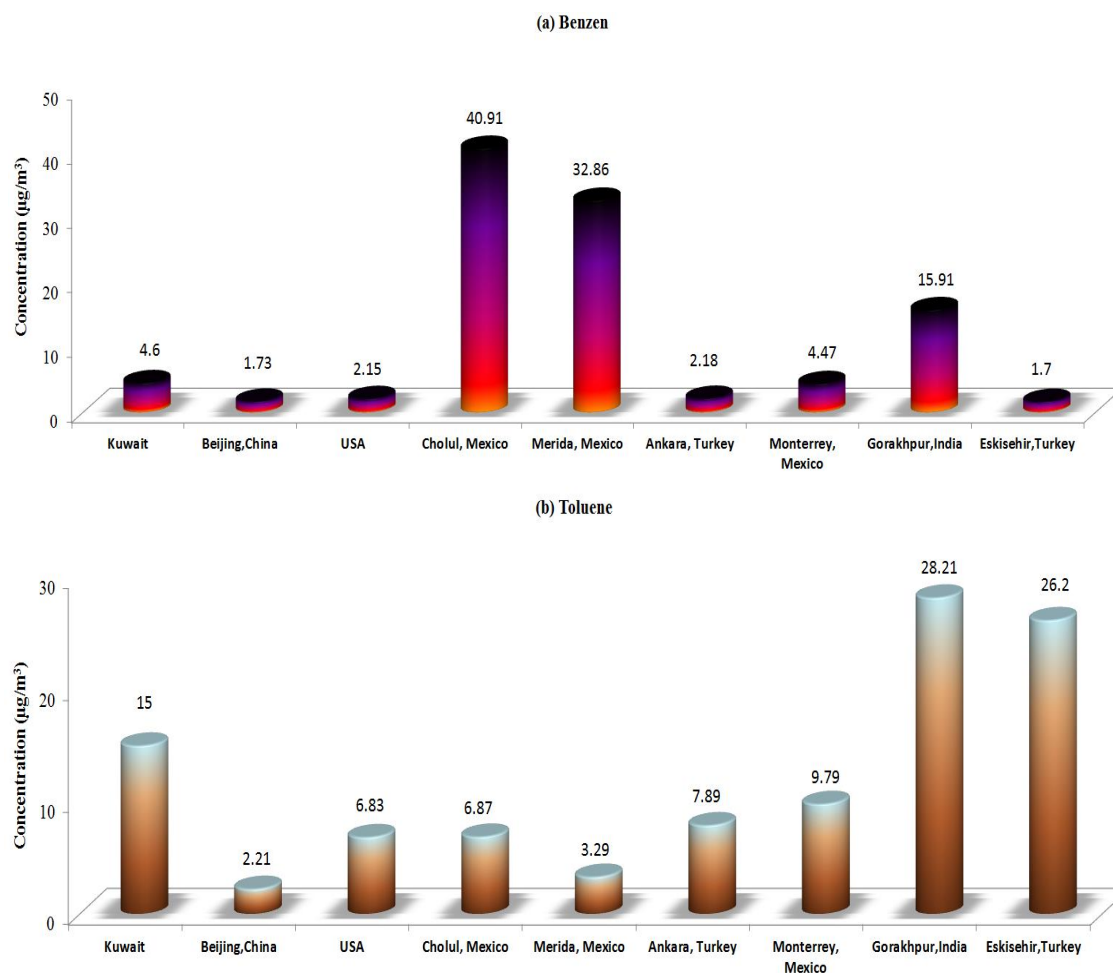


Figure 3. Mean hourly concentrations of (a) benzene, (b) toluene, (c) ethylbenzene, and (d) Σ -xylene. The units are in $\mu\text{g}/\text{m}^3$

Comparison of BTEX levels in Kuwait with other cities in the world

The concentrations of BTEX compounds measured in the five urban cities in this study (Fig. 1) were also compared with those found in other cities over the world (Gao et al., 2018; Bretón et al., 2017; Masih et al., 2016; Menchaca-Torre et al., 2015; Batterman et al., 2014; Demirel et al., 2014; Yurdakul et al., 2013). As shown in Figure 4a, the highest benzene levels were reported in Mexico (Cholul and Merida) (40.91 and 32.86 $\mu\text{g}/\text{m}^3$) and India (Gorakhpur) (15.91 $\mu\text{g}/\text{m}^3$). The average benzene concentration in Kuwait (4.6 $\mu\text{g}/\text{m}^3$) was similar to those in Mexico (Monterrey) (4.47 $\mu\text{g}/\text{m}^3$), Turkey (Ankara) (2.18 $\mu\text{g}/\text{m}^3$), and the USA (2.15 $\mu\text{g}/\text{m}^3$). The lowest levels of benzene were found in China (Beijing) (1.73 $\mu\text{g}/\text{m}^3$) and Turkey (Eskisehir) (1.7 $\mu\text{g}/\text{m}^3$). Toluene level, as shown in Figure 4b, was the highest in India (Gorakhpur) (28.21 $\mu\text{g}/\text{m}^3$) and Turkey (Eskisehir) (26.2 $\mu\text{g}/\text{m}^3$) followed by Kuwait (15 $\mu\text{g}/\text{m}^3$), Mexico (Monterrey) (9.79 $\mu\text{g}/\text{m}^3$), Turkey (Ankara) (7.89 $\mu\text{g}/\text{m}^3$), the USA (6.83 $\mu\text{g}/\text{m}^3$), and the others. The lowest toluene levels were detected in China (Beijing) (2.21 $\mu\text{g}/\text{m}^3$) and Mexico (Merida) (3.29 $\mu\text{g}/\text{m}^3$). For ethylbenzene level, it is clear from Figure 4c that it was the highest in Mexico (Cholul and Merida) (13.87 and 8.29 $\mu\text{g}/\text{m}^3$). The average ethylbenzene concentration in Kuwait (5 $\mu\text{g}/\text{m}^3$) was similar to those in India (Gorakhpur) (3.38 $\mu\text{g}/\text{m}^3$) and the USA (1.28 $\mu\text{g}/\text{m}^3$). Minimum levels of ethylbenzene were found in China (Beijing) (0.38 $\mu\text{g}/\text{m}^3$) and Mexico (Monterrey) (0.43 $\mu\text{g}/\text{m}^3$). Xylene level in different countries is shown in Figure 4d.



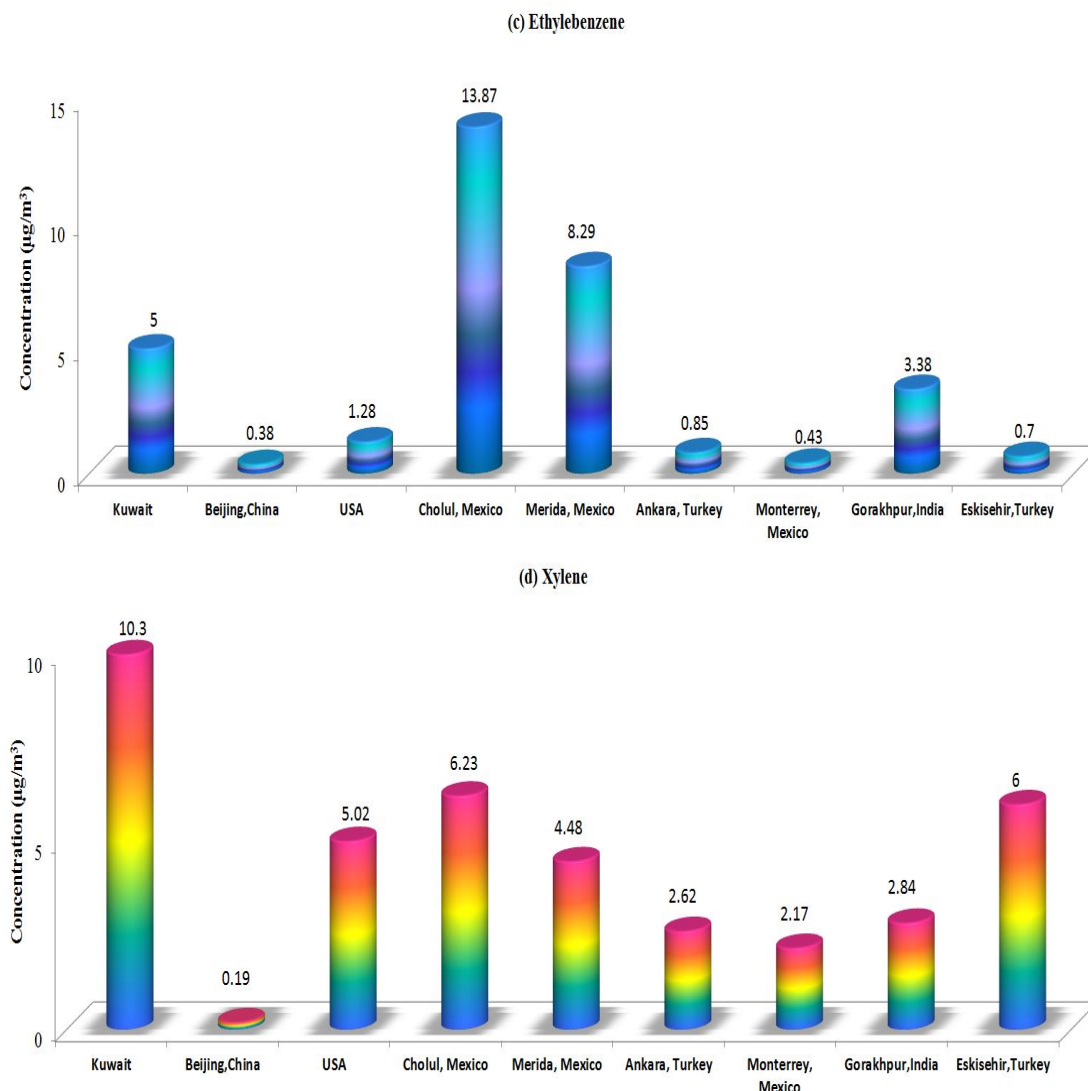


Figure 4. Comparison of BTEX concentrations for fourteen cities including Kuwait: (a) benzene, (b) toluene, (c) ethylbenzene, and (d) xylene (ΣX)

It is important to note that xylene level in Kuwait was reported as Σ (m-o-p) xylene, but in the most recent studies reported in this study, xylene was reported as either o-xylene or p-xylene. Therefore, direct comparison cannot be made and only higher differences in xylene level between countries should be considered. Relatively Kuwait has the highest xylene level ($10 \mu\text{g}/\text{m}^3$) followed by Mexico (Cholul) ($6.23 \mu\text{g}/\text{m}^3$), Turkey (Eskisehir) ($6 \mu\text{g}/\text{m}^3$), and the USA ($5.02 \mu\text{g}/\text{m}^3$). Xylene levels were the lowest in China (Beijing) ($0.19 \mu\text{g}/\text{m}^3$). It is noteworthy to mention that each city has particular region sources and they differ in fuel types, fuel consumption pattern, and meteorological conditions. These factors can significantly influence BTEX level in ambient air and induce differences among cities in different parts of the world.

Benzene/toluene (B/T) ratios

Average benzene-toluene (B/T) ratios were calculated for the five sampling urban cities to differentiate between vehicular emissions and other combustion sources.

Previous studies suggest that the ratio of different aromatic compounds (particularly benzene and toluene) can be useful in identifying VOC sources, and a B/T ratio of around 0.5 has been reported to be characteristic of vehicular emissions (Brocco et al., 1997; Perry and Gee, 1995). In this study, B/T ratio ranged from 0.4 to 0.8, 0.3 to 1.5, 0.3 to 0.4, 0.4 to 0.5, and 0.3 to 0.8 in Ali Sabah Al-Salem, Al-Fahaheel, Al-Salam, Saud Al-Abdullah, and Al-Jahra, respectively. Additionally, average B/T ratios in Ali Sabah Al-Salem, Al-Fahaheel, Al-Salam, Saud Al-Abdullah, and Al-Jahra were 0.5, 0.7, 0.35, 0.45, and 0.45, respectively. Higher average B/T ratio (0.7) was found in Fahaheel compared to other urban cities neighbourhoods, while Al-Salem had low average B/T (0.35) ratio. The high B/T ratio in Al-Fahaheel showed that large additional sources of benzene are emitted, possibly from industrial emissions, as Al-Fahaheel is adjacent to Al-Ahmadi petroleum refinery and other petrochemical industries. Previous studies reported that B/T ratio increases with increasing traffic volume, industrial emissions and other urban sources in denser areas (Lee et al., 2002; Brocco et al., 1997) found that the B/T ratio in the urban area of Rome ranged from 0.3 to 0.5. In Hong Kong B/T ratio was of about 0.2 (Lee et al., 2002) and 0.1 was reported in other Asian cities such as Manila and Bangkok (Gee et al., 1998). In southern Taiwan (Hsieh et al., 2006), the average B/T ratios in Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were 0.77, 0.59, 0.12, 0.38, 1.67 and 0.34, respectively. Our average (B/T) ratios in the five locations were between 0.35 and 0.7, suggesting vehicular emissions as the main source of VOCs.

Σ-xylene/ethylbenzene (X/E) ratio

In this study, xylene/ethylbenzene (Σ X/E) ratio is used to assess the relative age of the air parcels. Several studies used X/E ratio to evaluate the relative age of the air parcels (Hsieh et al., 2006; Monod et al., 2001; Truc et al., 2007). Conceptually, ethylbenzene is considered a low reactive species whereas xylenes are considered a highly reactive species. Hence, low X/E ratio suggests an aged air parcel. X/E ratios ranged from 2.9 to 11.5, 1.2 to 4.3, 2.2 to 2.6, 1.1 to 5.9, and 4 to 7.6 in Ali Sabah Al-Salem, Al-Fahaheel, Al-Salam, Saud Al-Abdullah, and Al-Jahra, respectively. Recently Rad et al., 2014 reported X/E ratios ranged from 1.13 to 4.95 in Ahvaz metropolitan city, Iran. Hsieh et al., 2011 stated that X/E ratios of five different traffic tunnels in southern Taiwan, where X/E ratios ranging from 2.4 to 12.1. Truc et al. (2007) investigated X/E ratios in three roadsides in Hanoi, Vietnam and X/E ratios ranged from 1.2 to 2.9. In Hong Kong, average values of X/E ratios were from 1.5 to 2.2 (Ho, et al., 2004). Other X/E ratios were also reported for different urban samples, ranging from 1.3 for Tokyo to above 4.8 in Athens (Truc et al., 2007); however, the most common values are between 2.0 and 3.0 (Monod et al., 2001). The X/E ratios found in our study are in the range of reported X/E ratios in the previous studies and therefore the contribution of vehicular emissions is still the foremost source of VOCs. However, this does not eliminate the possibility of other non-traffic sources. The average X/E ratios in Ali Sabah Al-Salem, Al-Fahaheel, Al-Salam, Saud Al-Abdullah, and Al-Jahra were 9.7, 2.6, 2.4, 4.2, and 5.4, respectively. Higher average X/E ratio (9.7) was found in Ali Sabah Al-Salem compared to other urban cities neighbourhoods (averages from 2.4-5.4). Such high value indicates that the freshly emitted xylene in the transportation decayed at different rates to OH-oxidation in the atmosphere. Conversely, the lower X/E ratio (2.4) in Al-Salam implies an aged air parcel.

Exposure and risk assessment

Numerous researchers have reported the detrimental impacts of BTEX on human health as illustrated in the introduction section. Thus, to assess cancer risks and non-cancer effects due to the exposure to measured atmospheric BTEX at the five representative sites (*Fig. 1*), the average daily exposure, individual Hazard Quotient (HQ) and integrated lifetime cancer risk (ILTCR) were estimated and the values are reported in *Table 3*. In term of exposure, toluene was found the highest in all sites compared with other individual components. With respect to sites, residents of site 3 received higher dose of exposure from the pollutants in comparison to other four sites and consequently probability of cancer risk was the highest in site 3.

Table 3. Estimate of individual pollutant exposure, associated non-cancer hazard and cancer risk

Compounds	Site	Yearly average concentration (mg/m ³)	Daily average exposure (mg kg ⁻¹ day ⁻¹)	HQ	ITLCR
Benzene	Site 1	2.49E-03	7.62E-04	8.29E-02	2.20E-05
	Site 2	2.87E-03	8.79E-04	9.56E-02	2.54E-05
	Site 3	3.83E-03	1.17E-03	1.28E-01	3.39E-05
	Site 4	2.58E-03	7.91E-04	8.61E-02	2.29E-05
	Site 5	3.51E-03	1.07E-03	1.17E-01	3.11E-05
Toluene	Site 1	6.96E-03	2.13E-03	1.74E-02	
	Site 2	8.16E-03	2.50E-03	2.04E-02	
	Site 3	1.49E-02	4.55E-03	3.71E-02	
	Site 4	1.11E-02	3.40E-03	2.77E-02	
	Site 5	9.14E-03	2.80E-03	2.28E-02	
Et-Benzene	Site 1	7.80E-04	2.39E-04	7.80E-04	9.23E-07
	Site 2	1.60E-03	4.91E-04	1.60E-03	1.90E-06
	Site 3	8.88E-03	2.72E-03	8.88E-03	1.05E-05
	Site 4	3.73E-03	1.14E-03	3.73E-03	4.41E-06
	Site 5	2.12E-03	6.51E-04	2.12E-03	2.51E-06
m,p-Xylene	Site 1	1.82E-03	5.58E-04	2.60E-03	
	Site 2	2.82E-03	8.63E-04	4.02E-03	
	Site 3	9.88E-03	3.03E-03	1.41E-02	
	Site 4	6.07E-03	1.86E-03	8.67E-03	
	Site 5	6.67E-03	2.04E-03	9.53E-03	
o-Xylene	Site 1	1.99E-03	6.11E-04	2.57E-03	
	Site 2	9.97E-04	3.05E-04	1.28E-03	
	Site 3	9.79E-03	3.00E-03	1.26E-02	
	Site 4	4.55E-03	1.39E-03	5.86E-03	
	Site 5	3.03E-03	9.29E-04	3.91E-03	

Site 1: Ali Sabah Al-Salem, Site 2: Fahaheel, Site 3: Al-Salam, Site 4: Saad Al-Abdullah, Site 5: Al-Jahra

Except ethyl benzene at site 1, estimated ILTCR in all sites, as shown in *Table 3*, exceeded the threshold value of 1E-06, indicating significant risk. The highest estimated

ILTCR for ethyl benzene was 1.05×10^{-5} and was found in site 3. As for benzene, the highest ILTCR value (3.39×10^{-5}) was found in site 3 while the lowest value (2.20×10^{-5}) was found in site 1. It was reported that for benzene exposure of $1 \mu\text{g}/\text{m}^3$, the lifetime risk of chronic leukemia is $4.4\text{--}7.6 \times 10^{-6}$ (Crump, 1994). The calculated cancer risk in this study offers insights that exposure level of BTEX is far from being safe for population residing in these urban cities, with the highest threat in site 3.

According to estimated hazard quotient (HQ), non-cancer effects, it is evident from *Table 3* that individual HQs did not exceed unity for any pollutant. If the $\text{HQ} > 1$, it indicates long term exposure may result in detrimental health effects. Again benzene showed highest HQs in all sites compared with other individual chemicals and site 3 is labelled as the highest susceptible site for non-cancer effects. Based on individual HQs, which did not exceed unity in all sites, it shows no serious threat of chronic non-cancer health effects in specific target organs for the urban cities population.

It is imperative to mention that BTEX were considered as precursors for various atmospheric reactions, which would indeed make their indirect health impact on residents as well as ecosystems still viable. Thus, further control measures are urgently needed for mitigating the emissions of these toxic compounds in Kuwait. In line with the results of this study and previous studies, vehicle emission was identified as a prevailing source for BTEX. Therefore, to mitigate BTEX emission, vehicles numbers driven by individual should be reduced, as cars in Kuwait has exceeded 1.5 million. Additionally, stricter emission standards should be enacted. Furthermore, the current traffic status of prevailing traffic congestion with high pollutant's emission is urgently needed to be improved. These suggestions collectively might effectively reduce BTEX emission into atmosphere and subsequently reduce their health impacts on population.

Conclusions

BTEX compounds were measured during the year 2016 in five different urban cities from Kuwait. It was found that toluene was the most abundant amongst the BTEX compounds, followed by MP-xylene, o-xylene, ethylbenzene and benzene during the period of the study. ΣBTEX showed a seasonal variation, with higher concentrations during the winter than in the summer, probably due to higher chemical removal reaction rates of BTEX and dust storm in the summer that ultimately eliminates the BTEX from the atmosphere. BTEX compounds showed diurnal variations, high records in the morning and during rush hours in the evening, which possibly attributed to weak atmospheric dispersion and photochemical reactivity and high volume of traffic. While decreased concentrations of BTEX were observed during midday, perhaps as a result of decreased traffic volume, shifting up the urban boundary layer, high rate of photochemical reaction, and the increased mixing depth. Benzene/Toluene (B/T) and Xylene/ethylbenzene (X/E) ratios proposed that vehicular emissions were the predominant source of BTEX. The individual hazard quotient (HQ) showed no serious threat of chronic non-cancer health effects in specific target organs for the urban cities population.

Acknowledgements. The authors would like to thank Kuwait University for supporting the completion of this study.

Conflict of interests. The corresponding author states that there is no conflict of interests.

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