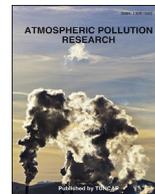


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Trends of BTEX in the central urban area of Iran: A preliminary study of photochemical ozone pollution and health risk assessment



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ABSTRACT

The Environmental Protection Agency (USEPA) has identified Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) as hazardous air pollutants. In this study, BTEX sampling was conducted at 20 sites during summer 2015 and winter 2016 in Yazd. Concentrations of BTEX were analyzed using a gas chromatograph with a flame ionization detector (GC-FID). In addition, ozone formation potential (OFP) and the health risks of BTEX were calculated. Spatial mapping was accomplished using the Kriging method. The obtained concentrations of total BTEX ranged from 8 to 560 $\mu\text{g}/\text{m}^3$. The highest average individual values belonged to toluene and xylene (38 ± 42 and 41 ± 45 $\mu\text{g}/\text{m}^3$, respectively). Seasonal variation showed a downward trend from summer to winter. The peak BTEX emissions occurred in the evenings, due to rush hour traffic and meteorological factors. Spatial analysis showed that the maximum levels of BTEX occurred on high traffic roads or near fuel stations. Significant correlation coefficients between benzene and other BTEX compounds revealed that BTEX were emitted from main sources including gasoline vehicles and stations. The mean ratio of toluene/benzene (T/B) in summer (1.8) was more than winter (1.4). The seasonal changes in T/B ratio possibly were attributed to photochemistry, meteorology, and emission aspects. The OFP values were 720 ± 729 and 375 ± 319 $\mu\text{g}/\text{m}^3$ in summer and winter, respectively. OFPs, ranked maximum to minimum, were as follows: xylene > toluene > ethylbenzene > benzene. Although the values of the non-cancer risk of BTEX were under permissible recommended level, a cancer risk still exists because of high values of airborne benzene.

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1. Introduction

The atmospheric pollutants, which have a major impact on the human health are increasing due to the population growth, increasing number of vehicles, and expansion of urbanization (da Silva et al., 2016; Fard et al., 2016). With the rapid increase of the vehicles and consumption of fossil fuels, a large amounts of hydrocarbons and nitrogen oxides (NOx) are released into the atmosphere (Atkinson, 2000). Volatile Organic Compounds (VOCs) are

an important group of air pollutants. These compounds have both anthropogenic and biogenic sources. Anthropogenic emissions of VOCs in the urban atmosphere consist vehicular exhaust, gasoline evaporation, solvent usage, leakage from the Compressed Natural Gas (CNG) and Liquefied Petroleum Gas (LPG) stations, petroleum refining, air fresheners, tobacco smoke, dry cleaners, municipal solid waste, bio-decomposition of the waste in landfills, and industrial processes. Biogenic VOCs (BVOCs) mainly come from the vegetation (forests), and wetlands and contribute minimally in the urban pollution compared to anthropogenic emissions (Bauri et al., 2016; da Silva et al., 2016). The United States Environmental Protection Agency (USEPA) has considered VOCs such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) as the air toxicants or hazardous air pollutants (HAPs). HAPs are pollutants known for causing cancer or having other serious detrimental health effects (Presto et al., 2016).

Some VOCs are toxic (benzene and 1,3-butadiene) and many participate in complex photochemical reactions in the presence of sunlight and hydroxyl radicals. The photochemical reactions can generate tropospheric ozone, peroxyacetyl nitrate (PAN), and Secondary Organic Aerosol (SOA) (Bauri et al., 2016; Marć et al., 2016; Atkinson, 2000).

In the urban areas, BTEX is responsible more than 60% of non-methane VOCs and can be used as an indicator of the organic pollutants in traffic. The main sources of BTEX include the mobile and stationary, particularly fuel combustion, evaporation of fuels and solvents, and fuel leakage from tanks (Lee et al., 2002; Tsai et al., 2006).

Benzene is carcinogenic to humans; therefore, the World Health Organization (WHO) and the USEPA do not recommend any safe level of exposure for it. However, a threshold for ambient air benzene levels has been defined in many countries. The European Commission (EC) guideline value for the annual average benzene concentration in Europe was $5 \mu\text{g}/\text{m}^3$ in 2000 (Su et al.), then decreased by $1 \mu\text{g}/\text{m}^3$ every 12 months, starting in 2006, to finally reach zero by January 2010. However, as yet, this goal has not been achieved. In Asia, the recommended annual thresholds for the ambient air benzene are 3, 5, 5, 20, 1.7, and $10 \mu\text{g}/\text{m}^3$, respectively, for Japan, India, Korea, Nepal, Thailand, and Vietnam (Lan and Binh, 2012). However, to the best of our knowledge, there is no recommended threshold level for the ambient air benzene in China and Singapore (Frank De Leeuw, 2017; Lan and Binh, 2012). Toluene affects the central nervous system, and ethylbenzene causes brain disorders and eye irritations. Xylene can cause skin inflammation and respiratory problems (Esmaelnejad et al., 2015; Mosaddegh Mehrjerdi et al., 2014).

Nowadays, the use of unleaded gasoline, which is rich in aromatic organic compounds like as BTEX, is increasing in the world (Miri et al., 2017; Nikoonahad et al., 2017). Therefore, monitoring of hydrocarbons is important in the urban areas.

Studies showed that xylene and toluene, as well as butane and ethylene, can produce one-third of the photocatalytic ozone (Derwent et al., 1996). In a two-year study, Majumdar (Majumdar et al., 2011) measured the concentration of benzene and toluene as $13\text{--}72 \mu\text{g}/\text{m}^3$ and $21\text{--}83 \mu\text{g}/\text{m}^3$, respectively, in Kolkata, India. Wang reported a daily average of BTX of $17.5 \mu\text{g}/\text{m}^3$ in China (Wang et al., 2010), and Kerbachi stated the mean concentration of BTEX in Algeria between 28 and $99 \mu\text{g}/\text{m}^3$ (Kerbachi et al., 2006). Based on studies in Iran, the average concentration of benzene and toluene was 63 and $9 \mu\text{g}/\text{m}^3$, respectively, in Tehran (Fazlzadeh et al., 2012) and the average concentration of BTEX in Ahvaz was $8.61 \mu\text{g}/\text{m}^3$ (Rad et al., 2014).

The BTEX has been commonly measured to evaluate the air quality in the urban area (Hoque et al., 2008), rural area (Liu et al., 2015), residential and commercial area (Schneider et al., 2001),

industrial environments and gas stations (Esmaelnejad et al., 2015; Baltrėnas et al., 2011). The differences between the results of these studies are related to sampling and analysis methods. Sampling methods include active and passive ones (Pekey and Yilmaz, 2011), both of which have good accuracy. Passive sampling is based on the diffusion mechanism and adsorbent tubes are used in it. This method needs more sampling time (Lan and Binh, 2012). Active sampling performs with low velocity pumps and other sampling equipment such as a flow meter, which makes it an expensive method (Yurdakul et al., 2017). Sampling time in active approach could be set in short periods. In most studies, a gas chromatograph with a flame ionization detector (GC-FID) or mass detector (GC-MS) is used for analyzing the BTEX. Another method for measuring hourly or daily values of BTEX in the air is on-line gas chromatograph, which is installed in urban or industrial areas (Pekey and Yilmaz, 2011; Martin et al., 2010).

Ozone formation potential (OFP) is generally used to estimate the maximum ozone formation capacity from VOCs, especially BTEX in cities (Wang et al., 2016). It could be calculated using maximum incremental reactivity (MIR) described by Carter (1994). Due to the intrinsic chemical behavior of each species, OFP of different VOCs varies. Therefore, qualitative and quantitative characterization of VOCs, as ozone precursors in a region, can help to understand the ozone formation process as well as evaluation of the best strategy for management and control of VOCs (Galvão et al., 2016).

Alghamdi et al. revealed photocatalytic OFP from BTEX of $260 \mu\text{g}/\text{m}^3$ in Jeddah, Saudi Arabia (Alghamdi et al., 2014). Fanizza et al. reported photocatalytic OFP from aromatic compounds of $197 \mu\text{g}/\text{m}^3$ in Rome, Italy (Fanizza et al., 2011).

Yazd is an industrial city located in Iran's central tropical desert, and the number of vehicles is increasing with the expansion of the city. Therefore, the release of BTEX compounds is inevitable, which increases urban air pollution and detrimental effects on human health. The monitoring of BTEX concentration is necessary for predicting the ambient air quality, especially in the middle-east cities such as Yazd. To the best of our knowledge, the research regarding OFP from BTEX in Iran has not yet been reported in detail. Therefore, this study is aimed to monitor the spatial and temporal trends of BTEX concentrations in the ambient air, their ratios, and OFP in the central urban area of Iran, Yazd. In addition, assessing the health risk of BTEX and determining their sources can be useful for the assessment of environmental health criteria in this city.

2. Materials and methods

2.1. Study area and sampling sites

Yazd is one of the oldest cities in Iran, established more than 2000 years ago, remaining intact throughout the centuries. The city ($31^\circ 88' \text{N}$, $54^\circ 36' \text{E}$) is the capital of Yazd Province, which is located east of Isfahan and south of the Lut desert, in the center of Iran (Fig. 1). Yazd has an area of 97 km^2 and a traffic network of approximately 240 km (Mahmoudi et al., 2014; Nejadkoorki et al., 2010). Industrial activities and local road traffic in the city and surrounding areas continue to grow.

The climate of Yazd is typical of a desert, with 300 sunny days per year and average annual precipitation of 50 mm. The absolute maximum and minimum air temperatures are 44°C and 10.17°C , respectively. June and July are the hottest months, with mean daily maximum temperature of 38.4°C . December and January are the coldest months, with temperatures in the range $6\text{--}18^\circ \text{C}$ (Mokhtari et al., 2015).

The wind rose for the sampling period was drawn using meteorological data taken from the Iranian Meteorological Department

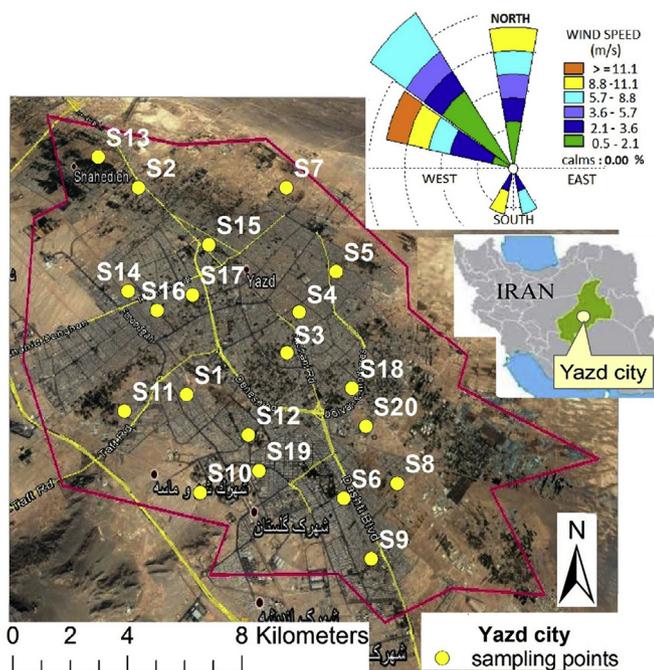


Fig. 1. Study area and monitoring sites, and wind rose plots showing the prevailing winds in Yazd.

(Fig. 1). The wind speed (m/s), wind direction, and frequency of wind speed are shown at a particular angle on the wind rose. As can be observed, the prevailing wind direction at the sampling sites was from the northwest most of the time.

The selected sampling sites were 20 points with different traffic density (Fig. 1), including sites with high traffic density (S3, S6, S7, S9, S15, and S17), intermediate traffic density (S2, S4, S8, S12, S13, S19, S20), and low traffic density (S1, S5, S10, S11, S14, S16, S18). S7, S8, S15, and S20 were located close to (~150 m) gas station.

2.2. Sampling and analysis

BTEX were sampled during two periods: summer (July 2015) and winter (January 2016). The sampling days were selected according to the local weather forecast with respect to wind speed and temperature, and sampling was not carried out in the unsuitable atmospheric conditions of high winds or rain. Daily meteorological data were obtained from the Yazd international airport weather station (Watson and Pletschke, 2006).

Two samples were taken from each sampling site per sampling period (8:00–10:00 in the morning and 19:00–21:00 in the evening, local time, each day). In addition, three samples were taken from S6 (high traffic density site), S8 (intermediate traffic density site), and S14 (low traffic density site) at off-peak times at noon (12:00–2:00).

Flow diagram of the study stages is shown in Fig. 2. Air samples were collected according to the NIOSH (National Institute for Occupational Safety and Health)-1501 method via active sampling during 2 h by means of a SKC personal sampling pump (SKC Inc., England, model 222-3) operating at level of human breathing (1.5 m above the ground) at a flow rate of 200 mL/min, at each site.

The ambient air was passed through charcoal sorbent tubes (SKC Inc., England, 226-01). The dimensions of these glass tubes were 7 cm long and 4 mm inner diameter, and the activated carbon inside the tubes was divided into two parts: 100 mg in front and 50 mg in back, which separated by 2-mm thick polyurethane foam.

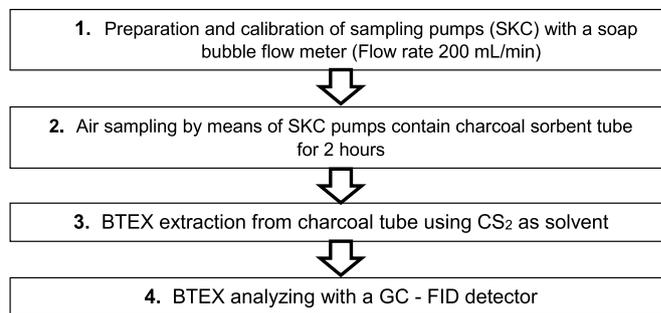


Fig. 2. Flow diagram of study stages.

In the laboratory, the charcoal sorbent tubes were placed in 2 mL vials, and 1 mL carbon disulfide (CS_2) was added to each vial as a solvent. For BTEX extraction, the vials were placed in a shaker for 30–60 min (Rad et al., 2014) and then the samples were immediately analyzed using a gas chromatograph equipped with a flame ionization detector (Agilent Technology, 7890, GC-FID) via the headspace method. Information regarding the GC-FID analysis is provided in Table 1.

2.3. Quality assurance and quality control

The chemicals used in this study, including carbon disulfide (CS_2) (Reagent Plus, redistilled, $\geq 99.9\%$, low benzene) and standards of BTEX were extra pure, GC grade and purchased from Sigma–Aldrich company. Before sampling, flow rate of the SKC pump was calibrated using a soap bubble flow meter manually (Niosh, 2016). After sampling, the charcoal sorbent tubes were covered with a plastic cap, stored at 4 °C to protect the samples from photo degradation or evaporation of BTEX, and then immediately transported to the laboratory for analysis. A charcoal tube was considered as a field blank (edges cutted and immediately capped without exposing to air) during each period of air sampling and analysed for BTEX along with the samples to identify possible background concentration. All samples were collected, prepared and measured in duplicate to confirm the precision and accuracy of the results. In addition, both front and back parts of the adsorbent tubes were measured to control possible penetration of the pollutants during sampling.

The calibration curves were made using a standard mixture of BTEX (2000 $\mu\text{g}/\text{mL}$ in methanol) to reach a response signal in GC-FID as standard concentrations in 10 points from 0.01 to 50 ppm. The recognized calibration curves for the BTEX compounds were obtained to have R-square-values ≥ 0.9994 . A calibration standard (25 ppm) was daily analyzed to check the GC performance. The precision of method was evaluated by Relative Standard Deviations (RSD). The RSD of each level of calibration (10 replicates) was not higher than 5%. The Method Detection Limit (MDL) for the benzene, toluene, ethylbenzene, and xylene were 0.052, 0.064, 0.067 and 0.057 $\mu\text{g}/\text{m}^3$, respectively. The limit of detection (LOD) and Limit of Quantitation (LOQ) were estimated to vary from 0.2 to 0.4 ppm and 0.6–1.2 ppm for BTEX compounds, respectively.

2.4. Spatial analysis

Concentration maps were drawn in ArcGIS 10.1 to display the spatial distribution. The Kriging method among the interpolation techniques is easy for characterizing the variance or precision of predictions. In this technique, the surrounding measured amounts are weighted to derive a forecast value for an unmeasured place. The base weight depends on the distance from the measured

Table 1
Details of the GC-FID analysis.

Characteristic	Condition
Sampling method	Headspace
Volume of injection	1 μ l with a split ratio of 1–5
Carrier gas	Helium (purity 99.995%) with flow rate of 1.11 mL/min
Fuel gas	H ₂ (30 mL/min)
Column model	HP5 MS
GC column characteristic	Agilent 19091S-433: 30 m \times 0.250 mm \times 0.25 μ m
Detector temperature	250 $^{\circ}$ C
Oven temperature	36 $^{\circ}$ C for 1 min and increased with rate of 10 $^{\circ}$ C/min to 90 $^{\circ}$ C and then increased up to 150 $^{\circ}$ C with rate of 25 $^{\circ}$ C/min for 6 min (total run time: 14.8 min)

points, forecast locations, and total spatial arrangement among the measured points (Xu et al., 2006).

In the present study, ordinary Kriging method was applied to generate independent raster layers for the average concentration of total BTEX compounds in the summer and winter. Then, the raster calculator function was used to overlay each layer to make maps of seasonal averages. Also, validation of Kriging method was done according to the evaluation of root mean square error (RMSE) in Equations (1) and (2) (Schneider et al.):

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (q_i - \hat{q}_i)^2} \quad (1)$$

$$\% \text{RMSE} = \left(\frac{\text{RMSE}}{\mu} \right) \times 100 \quad (2)$$

where n : the number of the measured values, q_i : measured value, \hat{q}_i : the value predicted by the Kriging method, and μ : mean of each factor. The RMSE could be used in a situation where both the measured and predicted amounts of data are equal to zero or in the optimum prediction condition. The RMSE should be smaller to obtain satisfactory interpolation. Acceptable value for % RMSE is 40% and more than 70% uncertainty between the predicted and measured values (Mehrzardi et al., 2008).

2.5. Ozone formation potential

Ozone formation in the troposphere is a worldwide air pollution concern. Ozone is not released directly but rather is made through the photochemical interactions between VOCs and NO_x. BTEX are homologues of VOCs and are emitted into the atmosphere, each reacts at the different rates and with diverse reaction mechanisms. Therefore, each VOCs has the different significant effects on ozone formation. MIR coefficient developed by Carter (1994) was used to calculate OFP that defined as the mass of ozone formed per mass of VOCs emitted. The MIR constants utilized in this study are those that were updated in 2010 by Carter (1990, 1994, 2010). The OFP was calculated using equation (3):

$$\text{OFP} = \text{BTEX} (\mu\text{g}/\text{m}^3) \times \text{MIR} (\text{g O}_3/\text{g VOCs}) \quad (3)$$

2.6. Health risk assessment and statistical analysis

The non-cancer risk of BTEX and the cancer risk of benzene through inhalation were calculated to obtain the human health effects of the BTEX series in the ambient air of Yazd. The EPA recommended a health risk assessment method for inhalable pollutants in 1989 (EPA/540/1-89/002), which was updated in 2009 (EPA-

540-R-070-002) (Li et al., 2014). According to this methodology, metric exposure (mg/m^3) is suggested for health risk assessment of the air pollutants instead of inhalation intake based on human Inhalation Rate (IR) and Body Weight (BW) ($\text{mg}/(\text{kg}\cdot\text{day})$). Cancer risk is described as the development of inhalation unit cancer risk (or cancer intension constant) and lifetime average exposure concentration.

Equation (4) describes the chronic and sub-chronic Exposure Concentration (EC, $\mu\text{g}/\text{m}^3$):

$$\text{EC} = (\text{CA} \times \text{ET} \times \text{EF} \times \text{ED}) / \text{AT} \quad (4)$$

where CA (mg/m^3) is the pollutant concentration in air, ET (24 h/d) is the exposure time, EF (365 d/y) is the exposure frequency, ED (70 y) is the exposure period, and AT ($70 \times 365 \times 24$ h) is the average time.

For non-carcinogenic compounds, the risk is determined as the Hazard Quotient (HQ), which is given in equation (5):

$$\text{HQ} = \text{EC}/(\text{RfC} \times 1000) \quad (5)$$

where RfC (mg/m^3) is the inhalation reference concentration.

Hazard Index (HI) is the sum of the HQs of various pollutants (equation (6)):

$$\text{HI} = \sum_{i=1}^n \text{HQ}_i \quad (6)$$

where HQ_i is HQ of the i th pollutant.

Lifetime cancer risk (R) for carcinogenic compounds is calculated using equation (7):

$$\text{R} = \text{EC} \times \text{IUR} \quad (7)$$

where IUR ($\text{m}^3/\mu\text{g}$) is the inhalation unit risk. Notice that HQ, HI, and R are dimensionless.

Spearman and Pearson tests were applied to identify the correlation between BTEX compounds in the summer and winter using SPSS v.16.0. A Kruskal-Wallis test was used for the statistical comparisons and the Least Significant Difference (LSD) calculations at an alpha level less than 0.05 ($\alpha < 0.05$).

3. Results and discussion

3.1. Ambient level of BTEX

The average concentrations of BTEX compounds in the ambient air of the study area are shown in Table 2. The results indicated that the average and the range of the mass concentrations of total BTEX were 114 ± 113 and 8–560 $\mu\text{g}/\text{m}^3$, respectively during the study period. Toluene and xylene had the highest average concentrations

Table 2
Mean concentrations of benzene, toluene, ethylbenzene, and xylenes ($\mu\text{g}/\text{m}^3$).

Sampling site	Benzene	Toluene	Ethylbenzene	Xylene	BTEX
S1	13 ± 1.8	22 ± 4.8	4 ± 0.6	21 ± 2.0	60 ± 6.9
S2	16 ± 10.2	26 ± 18.5	6 ± 2.0	25 ± 14.0	72 ± 44.7
S3	17 ± 3.5	26 ± 5.5	5 ± 1.1	28 ± 9.1	76 ± 17.3
S4	18 ± 5.3	31 ± 12.9	6 ± 1.7	31 ± 8.5	85 ± 28.3
S5	11 ± 6.1	17 ± 11.9	6 ± 1.5	18 ± 11.0	52 ± 28.6
S6	28 ± 11.8	55 ± 33.2	8 ± 3.3	48 ± 20.2	139 ± 68.3
S7	64 ± 36.3	133 ± 74.6	26 ± 15.3	138 ± 77.3	360 ± 189.9
S8	31 ± 27.7	82 ± 87.6	18 ± 14.2	94 ± 103.3	225 ± 232.2
S9	30 ± 7.1	54 ± 13.2	10 ± 3.1	63 ± 17.8	158 ± 39.4
S10	6 ± 1.3	8 ± 3.7	4 ± 1.5	9 ± 3.7	27 ± 8.4
S11	11 ± 4.7	19 ± 10.0	6 ± 0.7	29 ± 15.6	65 ± 29.7
S12	8 ± 4.2	11 ± 6.4	3 ± 1.7	11 ± 6.0	33 ± 17.0
S13	14 ± 6.7	24 ± 16.3	5 ± 2.6	28 ± 14.3	70 ± 38.3
S14	14 ± 5.1	15 ± 4.4	6 ± 2.2	28 ± 8.2	62 ± 12.1
S15	52 ± 25.5	104 ± 54.4	23 ± 13.0	118 ± 58.0	296 ± 143.7
S16	15 ± 2.4	15 ± 6.7	6 ± 0.6	24 ± 5.8	60 ± 11.7
S17	20 ± 2.4	40 ± 15.1	11 ± 3.9	34 ± 8.5	104 ± 28.6
S18	12 ± 6.1	18 ± 10.8	6 ± 1.3	19 ± 9.5	54 ± 25.5
S19	8 ± 2.6	12 ± 5.4	5 ± 0.6	12 ± 6.5	36 ± 14.8
S20	32 ± 5.0	51 ± 12.7	12 ± 3.4	62 ± 14.1	157 ± 34.6
Mean ± SD*	21±18	38±42	14±15	41±45	114±113
Range	2–108	2–211	2–85	2–234	8–560
N	80	80	80	80	80

*SD: Standard Deviation.

(38 ± 42 and $41 \pm 45 \mu\text{g}/\text{m}^3$, respectively). The lowest average concentrations were obtained by benzene and ethylbenzene (21 ± 18 and $14 \pm 15 \mu\text{g}/\text{m}^3$, respectively). Since the extreme values were observed for total BTEX concentration in some sampling sites, the data followed a non-normal distribution in summer and winter. In the studied urban areas of Canada, China, Spain, and Iran toluene and xylene had the highest concentrations compared to benzene and ethylbenzene (Li et al., 2014; Miller et al., 2012; Wang et al., 2010; Parra et al., 2009; Rad et al., 2014). These results are in agreement with our findings in Yazd. The concentrations of BTEX in this study are similar to the concentrations of BTEX in industrial cities in Turkey (3.7 – $335.5 \mu\text{g}/\text{m}^3$) (Pekey and Yilmaz, 2011) and India (150 – $400 \mu\text{g}/\text{m}^3$) (Hoque et al., 2008). In the UK (Derwent et al., 2000), Germany (Schneider et al., 2001), and Detroit, Michigan (Johnson et al., 2010), the concentrations of BTEX were reported to be less than $100 \mu\text{g}/\text{m}^3$, which is comparable to our observation in the present study. The difference in BTEX concentration in the diverse cities can be attributed to the fuel quality and concentration of aromatic compounds in fuels, traffic density, variety and number of industries, atmospheric conditions, and sampling strategy including period and points of sampling.

3.2. Temporal trends of BTEX

The temporal trend of the BTEX concentration in the ambient air is shown in Fig. 3. The results of the Kruskal-Wallis test revealed that statistically significant differences existed between the BTEX concentration in different seasons (summer and winter), and time of sampling (morning and evening) ($\alpha < 0.05$). Seasonal variation of benzene species showed a downward trend from the summer to winter, and the mean concentration of BTEX decreased from 137 ± 139 to $81 \pm 73 \mu\text{g}/\text{m}^3$.

In the coastal city of A Coruña, Spain, BTEX concentrations in the winter were lower than that of summer and found to be heavily influenced by traffic intensity (Perez-Rial et al., 2009). In another study conducted in the capital of Iran, Tehran, the minimum concentration of total BTEX was recorded in winter followed by autumn (Miri et al., 2016b). These results are consistent with our findings in Yazd.

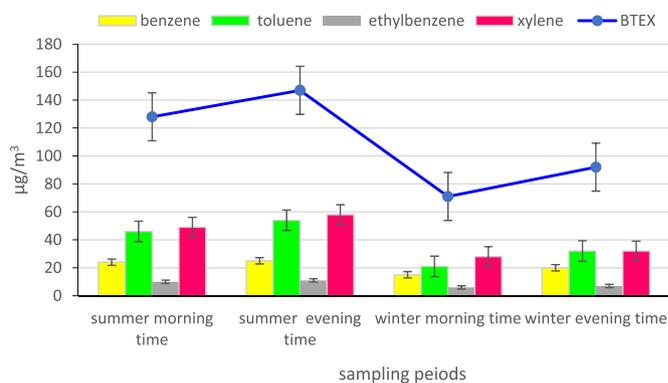


Fig. 3. Temporal trend of benzene species and total BTEX ($\mu\text{g}/\text{m}^3$).

However in other studies, BTEX compounds had the maximum concentration during the cold season (Mullaugh et al., 2015; Hansen and Palmgren, 1996; Rad et al., 2014; Pankow et al., 2003), which are inconsistent with our results.

Different factors can affect the seasonal concentrations of BTEX. In winter, they might reach a maximum level because of the higher atmospheric stability (Rad et al., 2014). On the other hand, reduction in winter can be attributed to the atmospheric precipitation. Precipitation could transfer BTEX compounds from the air to the earth's surface, into the water or soil (Mullaugh et al., 2015).

As indicated in Fig. 3, BTEX levels in the evening are obviously higher than the morning. The reasons for lower concentrations of BTEX in the morning than evening could be related to the atmospheric instability with sunny atmosphere, increasing temperature, photochemical reaction intensity, breaking the inversion, and vertical motion of air that can dilute BTEX.

In addition, the mean values of BTEX in three samples from S6, S8, and S14 sites at off-peak times at noon were obtained $121 \pm 34 \mu\text{g}/\text{m}^3$ in summer and $67 \pm 5 \mu\text{g}/\text{m}^3$ in winter, which are clearly less than the evening and morning values.

Therefore, there were peak loadings of BTEX in the evening. The evening rush hour in this city may be the reason for it. In addition,

BTEX is not easily diluted in the evening because of decreasing temperature, nighttime inversion, low-speed winds, and atmospheric stability.

In Beijing and Detroit, the diurnal trend of BTEX was correlated to traffic, emission sources, and meteorological factors, such as inversion, photochemical reactions, and the direction and speed of wind (Batterman et al., 2002; Li et al., 2014).

3.3. Spatial analysis of BTEX

Spatial mapping of the BTEX concentrations in the ambient air of Yazd is illustrated in Fig. 4. The % RMSE for the ordinary Kriging in the morning and evening, summer and winter, was calculated 32, 35, 42, and 38%, respectively. These values were located in the acceptance range and showed certainty between the predicted and measured values. Several studies in Iran and the United States have reported that the Kriging model with % RMSE of less than 50% has good performance in air pollution mapping compared to other interpolation models (Miri et al., 2016a, 2016b; Berman et al., 2015; Miri et al., 2016b; Mohammadi et al., 2016).

Based on Fig. 4, significant spatial variations existed in the various parts of city. The maps show that the maximum levels of BTEX were detected at the S7, S8, and S15 sites located in the urban areas. Notice that S7 and S15 were located in the high-density traffic area and S8 was located in the intermediate-density traffic area. In addition, these sites were situated to near fuel stations (gasoline and CNG). The odor of VOCs from gasoline was detectable several hundred meters away from the stations, and this phenomenon was more tangible in the summer because of the high

environmental temperature. Furthermore, as shown in Table 2, high levels of BTEX were recorded at sites S6, S9, S17, and S20 located in the urban areas. Obviously, the maximum concentration of benzene species was observed near highways and heavy traffic areas. Another reason was the direction of prevailing winds, blowing from the northwest to the southeast (based on Fig. 1), which can transfer BTEX compounds from the northwest to the center and then southeast. In a study conducted in the urban area of Gothenburg, an inverse relation was reported between the distance from the emission source (heavy traffic) and concentration of VOCs, which is consistent with our results (Thorsson and Eliasson, 2006).

The average concentration of total BTEX at sites with high traffic density (S3, S6, S7, S9, S15, and S17 located in the urban areas) was three times more than it was at sites with low traffic density (S1, S5, S10, S11, S14, S16, and S18 located in the sub-urban areas). These values are more than the levels of BTEX reported from European and Asian cities (Hansen and Palmgren, 1996; Miri et al., 2016b; Rad et al., 2014).

In the present study, comparing the effects of land use on the BTEX levels indicated that the regions located in the urban areas (S3, S6, S9, S15, and S17) and close to the industrial areas (S2, S7, and S13) had more pollution than the sub-urban areas (S1, S5, S10, S11, S14, S16, and S18). However, areas with maximum BTEX levels were found close to the fuel stations (gasoline and CNG).

3.4. Source identification and interspecies correlation

The Spearman correlation matrix between BTEX compounds in both seasons is given in Table 3. A strong positive correlation was

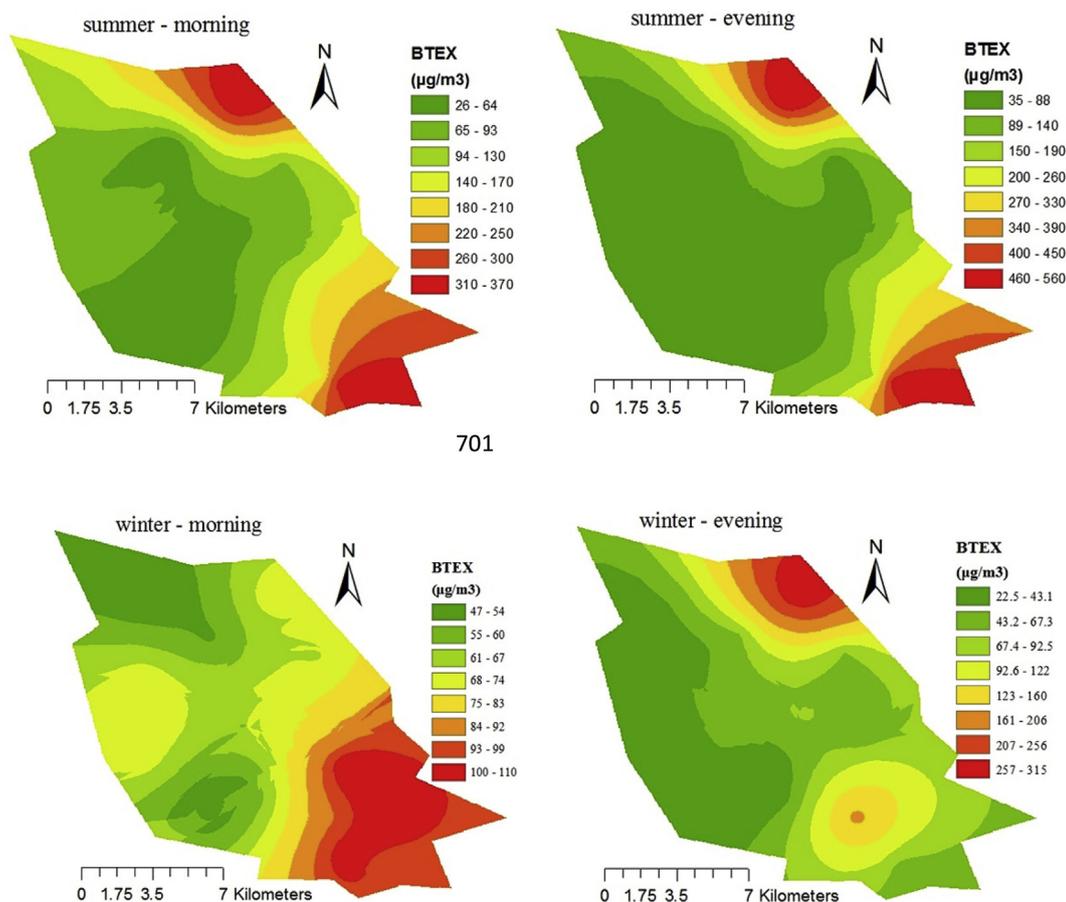


Fig. 4. Spatial mapping of the BTEX concentration.

observed between benzene and other BTEX compounds ($r > 0.86$). This high correlation indicated that the released BTEX compounds could be mainly attributed to the vehicles and gas stations. This is compatible with previous studies that showed a good correlation among BTEX compounds in the United States (Pankow et al., 2003), Canada (Miller et al., 2012), and India (Hoque et al., 2008). Since benzene is mostly released from the urban traffic, it is possible to use it as an indicator for BTEX compounds in the urban areas (Parra et al., 2006; Su et al., 2010). Moreover, a strong correlation between ethylbenzene and xylene showed that these compounds could be emitted from the gasoline vehicles and stations (Baldasano et al., 1998).

The interspecies ratio of BTEX has been proposed as another indicator of emission source by several researchers (Kerbach et al., 2006; Khoder, 2007). BTEX ratios with different photochemical reactivity can give information about the nature of BTEX influencing the different urban areas. The ratios of toluene/benzene (T/B), xylene/benzene (X/B), and xylene/ethylbenzene (X/EB) are presented in Table 4. The T/B ratio is a well-known and important indicator of the traffic emissions. Benzene and toluene are components of gasoline and may be released into the atmosphere through automobile exhausts (Mokhtari et al., 2015). A T/B ratio of 1.5–4.3 can reveal traffic-originated emission sources (Rad et al., 2014; Miri et al., 2016b). In this study, the mean T/B ratio was 1.8 and 1.4 in the summer and winter, respectively. These results are similar to those in previous studies, which reported a higher T/B ratio in summer (Chattopadhyay et al., 1997; Miller et al., 2012). Photochemistry, meteorology and emissions are the major factors affecting T/B ratio.

The ranges of the obtained X/EB and X/B ratios were 0.8–9 and 0.8–3.6, respectively. In the capital of Iran, Tehran, the annual average of X/EB and X/B ratios was reported as 7.9 and 3.5, respectively, which was in range of those in this study, due to the existence of VOCs with early photochemical and fresh emission sources in Tehran (Miri et al., 2016b). These ratios are less than those observed in Ahvaz, which were related to the high photochemical reactivity or high rate of photochemical OFP (Rad et al., 2014).

3.5. Ozone formation potential calculation

Each species of benzene has a unique role in the photochemical ozone formation. OFP is commonly used to predict the maximum capacity of ozone formation in the urban areas (Carter, 1990, 1994; Hung-lung et al., 2007).

In the present study, the estimation of OFP in the urban air was performed for the first time in Iran. The values of OFP obtained during the summer and winter are shown in Table 5. Based on the MIR scale, toluene and xylene were the most important factors for ozone formation. Benzene contributed the least in the summer and

Table 4

Average BTEX interspecies concentration ratios for the sampling sites.

Sampling site	T/B	X/B	X/EB
S1	2	2	5
S2	2	2	4
S3	2	2	6
S4	2	2	5
S5	2	2	3
S6	2	2	6
S7	2	2	6
S8	2	2	4
S9	2	2	6
S10	1	1	3
S11	2	3	5
S12	1	1	3
S13	2	2	5
S14	1	2	5
S15	2	2	5
S16	1	2	4
S17	2	2	3
S18	1	2	4
S19	2	1	3
S20	2	2	6
Mean \pm SD	1.6 \pm 0.5	1.8 \pm 0.6	4.6 \pm 1.8
Range	0.6–3.8	0.8–3.6	0.8–9
summer	1.8	2.0	5
winter	1.4	1.7	4.1

winter, which is consistent with results of studies in India, Korea, and Saudi Arabia (Alghamdi et al., 2014; Hoque et al., 2008; Na et al., 2005). In addition, the OFP ranked as follow: xylene > toluene > ethylbenzene > benzene in the summer and winter, which was similar to that seen in the previous studies (Grosjean et al., 1998; Na et al., 2005). Moreover, mean OFP values of 720 ± 724 and $375 \pm 319 \mu\text{g}/\text{m}^3$ in the summer and winter, respectively, were over the WHO air quality guidelines (recommended level is less than $120 \mu\text{g}/\text{m}^3$) (Organization, 2006). High OFP could induce the respiratory symptoms including coughing; deep breathing; wheezing; throat irritation; shortness of breath; pain, burning, or discomfort in the chest; lung dysfunction; and airway inflammation (USEPA, 2017).

The high values of ozone are related to increased asthma attacks, hospital admissions, mortality, and morbidity (Tunsaringkarn et al., 2014).

3.6. Health risk assessment

Risk assessment can determine the chronic effect of compounds that lead to cancer or other adverse effects. Inhalation exposure evaluation is usually derived in form of a chronic, daily “air intake” ($\text{mg}/(\text{kg}\cdot\text{day})$) using the method of the EPA's Risk Assessment Guidance for Superfund (RAGS) part A (USEPA, 2017) and a second update to the Superfund program of the USEPA (USEPA, 1992).

The estimated factors for non-cancer and cancer risk assessment of the benzene species are shown in Table 6. Exposure concentration changes were in the range of $21\text{--}41 \mu\text{g}/\text{m}^3$. HQ found as 4×10^{-2} to 7×10^{-1} and HI as 7.6×10^{-1} . The highest values of HQ belonged to benzene and xylene, which means the non-cancer risk of benzene and xylene are higher than toluene and ethylbenzene in the urban air of Yazd. According to the EPA guideline, pollutants with $\text{HQ} \leq 1$ have non-cancerous health effects on humans. The life cycle cancer risk of benzene was calculated as 1.64×10^{-4} . Based on the cancer risk of benzene recommended by the EPA (less than 10^{-6}), there is a potential cancer risk for people who have long-term exposure to benzene.

Table 3

Correlation coefficients (r) of the BTEX compounds in the summer and winter ($P < 0.01$).

	Benzene	Toluene	Ethylbenzene	Xylene
In summer (Spearman's correlation)				
Benzene	1			
Toluene	0.95	1		
Ethylbenzene	0.92	0.91	1	
Xylene	0.91	0.90	0.95	1
In winter (Pearson correlation)				
Benzene	1			
Toluene	0.97	1		
Ethylbenzene	0.87	0.86	1	
Xylene	0.96	0.97	0.86	1

Table 5
Ozone formation potential according to the MIR coefficient in Yazd.

BTEX species	MIR coefficient (g O ₃ /g VOCs)	Ozone formation potential (OFP) = (BTEX) × (MIR) (μg/m ³)					
		Summer			Winter		
		Mean	SD*	Range	Mean	SD	Range
Benzene	0.72	17	11	5–45	13	11	4–46
Toluene	4.8	238	226	51–850	127	115	25–430
Ethylbenzene	3.04	32	30	9–112	21	9	11–43
Xylene	7.8	416	409	90–1463	237	189	43–3688
Total formation		720	724	155–2470	375	319	87–1208

* SD: Standard Deviation.

Table 6
EC, HQ, HI, and life cycle cancer risk of BTEX species.

BTEX species	EC (μg/m ³) mean of seasons	RfC (mg/m ³)	IUR (m ³ /μg)	HQ	HI	Risk
Benzene	21	3 × 10 ⁻²	7.8 × 10 ⁻⁶	7 × 10 ⁻¹	7.631 × 10 ⁻¹	1.64 × 10 ⁻⁴
Toluene	38	5	–	7.6 × 10 ⁻³	–	–
Ethylbenzene	14	1	–	14 × 10 ⁻³	–	–
Xylene	41.5	1	–	4.15 × 10 ⁻²	–	–
EPA recommendation				<1	–	<1 × 10 ⁻⁶

EC: Exposure concentration, RfC: Reference concentration, IUR: Inhalation unit risk, HQ: Hazard quotient, HI: Hazard index.

4. Conclusion

This study aimed to assess the spatiotemporal variations of BTEX compounds, OFP, and health risk assessment of BTEX and determine the sources of these compounds in the ambient air of Yazd.

The average concentration of BTEX was 114 ± 119 μg/m³. The highest values belonged to toluene and xylene, with 38 ± 42 and 41 ± 45 μg/m³, respectively. Seasonal variation of the benzene species showed a downward trend from the summer to winter. This reduction can be attributed to the atmospheric precipitation. The peak hours for BTEX emission were in the evening, due to the rush hour and meteorological factors. Spatial analysis indicated that the areas with maximum levels of BTEX were located in the high-density traffic areas or near the gas stations and in the direction of prevailing winds. Good correlation coefficients between benzene and other BTEX compounds indicated that the BTEX compounds had been emitted from the main sources including gasoline vehicles and gas stations. The mean ratio of T/B detected in the summer was more than winter. Photochemistry, meteorology, and emissions were the major seasonal factors for the trend in T/B ratio. The higher X/EB and X/B ratios were associated with high photochemical reactivity or high rate of photochemical OFP.

In the present study, OFP calculations in the urban air were accomplished and OFP ranked as follows: xylene > toluene > ethylbenzene > benzene. The obtained OFP values were 720 ± 729 and 375 ± 319 μg/m³ in the summer and winter, respectively, which were higher than the WHO air quality guidelines (recommended level is less than 120 μg/m³). The values of the non-cancer risk of BTEX achieved in the study were under permissible recommended level.

However, there is potential cancer risk due to the high values of benzene in the air.

The OFP calculation, identification of sources, and health risk assessment of the benzene series were primarily considered in this study because of the limitation of the temporal and spatial sampling; thus, we suggest that further research will be done in the future.

The obtained knowledge from this study shows that in the urban air, monitoring and modeling of BTEX can be resulted to

identifying emission sources, determination of OFP, and assessment of health risks and can be useful for reduction of exhaust benzene homologues.

Finally, the result of this study, as a case report and the database, could be used to provide a basis for the improvement of air quality in Yazd and other different cities located in the middle-eastern countries.

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