Research Article

Characteristics and health risk of BTEX and ground-level ozone in an important industrial-residential-ecological area in southern Iran

Ahmad Tarassoli, Abbas Esmaili Sari[*], Nader Bahramifar
Department of Environment, Faculty of Natural Resources and Marine Science, Tarbiat Modares University, Imam Reza Street, Noor, Mazandaran, Iran
[*]Email: esmaili@modares.ac.ir

Abstract

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are categorized as hazardous air pollutants (HAPs) due to their role in ground-level ozone formation and cancer and non-cancer risk in humans. This study aimed to determine BTEX concentration and their seasonal variations, spatial mapping, and ozone formation potential (OFP) in four locations and assess health risks in workers and populations living near Southern Iran's largest petrochemical complexes and gas refineries. The analytical method was based on NIOSH method 1501. Ambient air sampling was collected by activated charcoal tubes and was analyzed using a gas chromatograph with a flame ionization detector. Results indicated that the ΣBTEX concentrations ranged from 2.3 ± 0.9 to 61.7 ± 9.8 μg m^{-3}. The highest concentrations of benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene were found in the petrochemical zone at the wastewater treatment unit with 27.8, 14.2, 12.7, 6.7, 6.9, and 6.2 μg m^{-3}, respectively. The high levels of BTEX were detected during the winter season. The m-xylene was the largest contributor to the OFP at the industrial sampling points, with 34.5 and 36.7 μg m^{-3}, respectively. Toluene has the maximum contribution to ozone formation in the residential areas and Nayband National Park with 24.2 and 5.6 μg m^{-3}, respectively. The cancer risk for benzene in all sampling points at the industrial areas was 1.0E-06, which is higher than the limits recommended by the US EPA.
Keywords: BTEX, spatial mapping, seasonal distribution, lifetime cancer risk, South Pars

Introduction

Petroleum, gas refineries, and related industries are recognized as the major emission sources of VHAPs, such as VOCs, into the atmosphere(Zhang et al.,.Several VOCs not only play an

important role in atmospheric chemistry (i.e., tropospheric photochemical ozone formation, PAN, and SOA) but also have a carcinogenic impact on the general population(Hoque et al., 2008; Yilmaz Civan et al., 2015). Inhalation exposure to VOCs like BTEX may cause damage to the central nervous system, respiratory system, brain, liver, reproductive system, lung cancer, anemia, and leukemia(Ramirez et al., 2012; Ren et al. 2017). According to the classification of the IRAC, benzene and ethylbenzene are categorized as group 1 (human carcinogen) and group 2 (probable human carcinogen), respectively. Xylenes and toluene are classified as group 3 (non-carcinogen for humans) (Garg & Gupta 2019).

In Iran, several studies have reported the BTEX concentration of ambient air in urban (Hazrati et al. 2016; Miri et al. 2016; Dehghani et al. 2018; Hajizadeh et al. 2018; Tohid et al. 2018). However, to the author's knowledge, research on atmospheric BTEX concentrations in Iran's energy capital, including large industrial-residential and ecological areas, has not been reported in detail. One of the world's largest gas condensate fields is in the Persian Gulf, shared between Iran and Qatar. According to the IEA report, the volumes of in-situ natural gas and natural gas condensates of this field is estimated at 51 trillion cubic meters and 7.9 billion cubic meters, respectively. The Iranian section of this field, called South Pars, contains approximately 48% of the Iranian total gas reservoirs and 7.5% of the world's gas reservoirs.(Tofigh and Abedian 2016; Mirimoghadam and Ghazinoory 2017). The South Pars region is one of the most important energy-producing poles in the Middle East, and it includes eight gas refineries, twelve petrochemical plants, and two power plants. After sour gas sweetening in the refineries, it is sent to petrochemical complexes as feedstock. Petrochemical complexes in the region produce various products such as ethane, butane, propane, ethylene, propylene, styrene, benzene, ethyl benzene, xylene isomers, urea, and ammonia.

As regards South Pars is recognized as one of the air pollution hot spots; therefore, the purpose of the present study was (1) to determine of the ambient levels and spatiotemporal characteristics of BTEX compounds in four different zones (PC, GR, RA, and NNP),(2) to investigate the OFP of these compounds in ambient air of South Pars and (3) to assess the potential non-cancer and cancer risks via inhalation of BTEX (US.EPA method) on health of the worker and people vicinity the these industrial.

Material and methods

Study area and sampling sites description

The South Pars is located in the southeastern of Bushehr Province in Asaluyeh County with 52º 31′ to 52º 42′ longitude and 27º 29′ to 27º 38′ latitude. In this area, gas refining and petrochemical facilities are adjacent to residential areas and National Park. About 16,130 people

work in these industries, and residents around Asaloyeh City reach up to 25,500 people, according to the last census(Statistical Center of Iran, 2016). In this area, Nayband National Park was designated as a primary protected marine area in 2004. The main plant species in this area are mangrove forests. This National Park is located about 2.3 and 1.5 kilometers from the industrial and residential areas, respectively.

In order to determine the exact coordinates of the sampling locations, a field study was conducted first, and the parameters like emission sources (industrial facilities, traffic, and gas stations), settlements, distance from emission sources, and wind direction were taken into consideration. Accordingly, sampling sites were selected in PC (n = 6), GR (n = 7), RA (n = 7), and NNR (n = 3), as shown in Fig.1.Flow diagram of the study stages is shown in Fig.2.

Data collection and analysis

The ambient concentration of BTEX were sampled during winter (January to February 2019), spring (April to May 2020), summer (July to August 2020), and autumn (October to November 2020) at 23 sampling locations. A total of276 samples were collected from all locations. BTEX samples were taken based on the NIOSH manual of analytical method no 1501(Masih et al. 2016). BTEX pollutants were sampled with sorbent tubes (Coconut shell charcoal, 100 mg/50 mg, SKC Inc.) and a sampling pump (Model 222-3, SKC Inc.), at a flow rate of 200 ml min^{-1} for 1 h at 1.5 m above the ground level which is the average human breathing height. Field and duplicate blanks were also collected at the all-sampling sites. After sampling was complete, the samples were covered with plastic caps, stored at 4ºC and transported to the laboratory. The charcoal beds containing BTEX samples were transferred into 2.0 ml vials and extracted by adding 1.0 ml of benzene free carbon disulfide, agitating 30 min in an ultrasonic bath. After extraction and separation, it was analyzed by GC-FID (Agilent technologies 7890B).The capillary column was 30 m × 32 mm. Pure helium with the flow rate of 2.6 ml min^{-1} and a volume of 1.0 μl with a 5:1 ratio was used as the carrier gas. The injector and detector temperatures were kept at 250 and 300 °C, respectively. The initial oven temperature was set at 40 °C for 10 min and then 10 °C min^{-1} to 230 °C(Dehghani and Ghaffari 2019).
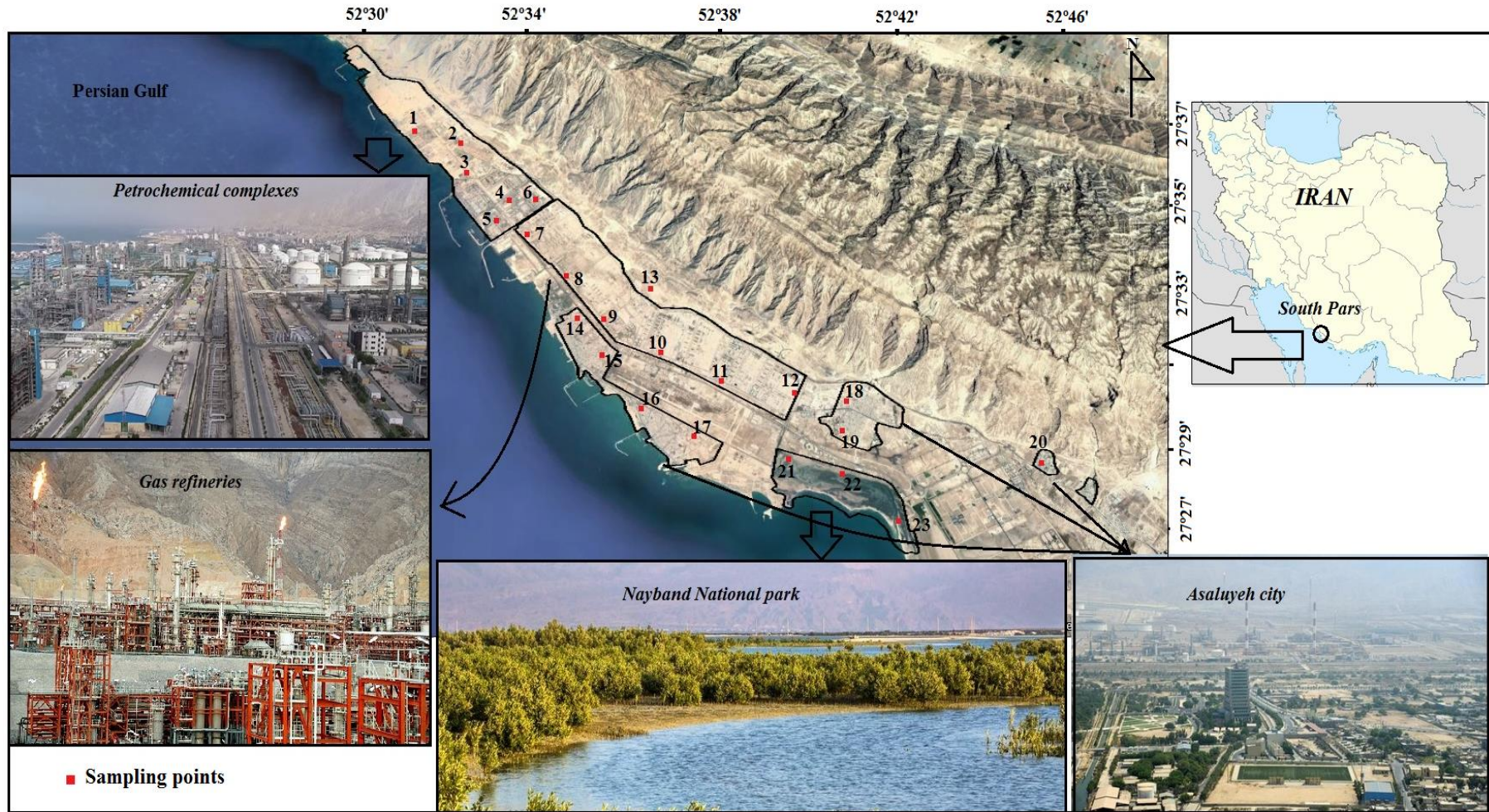
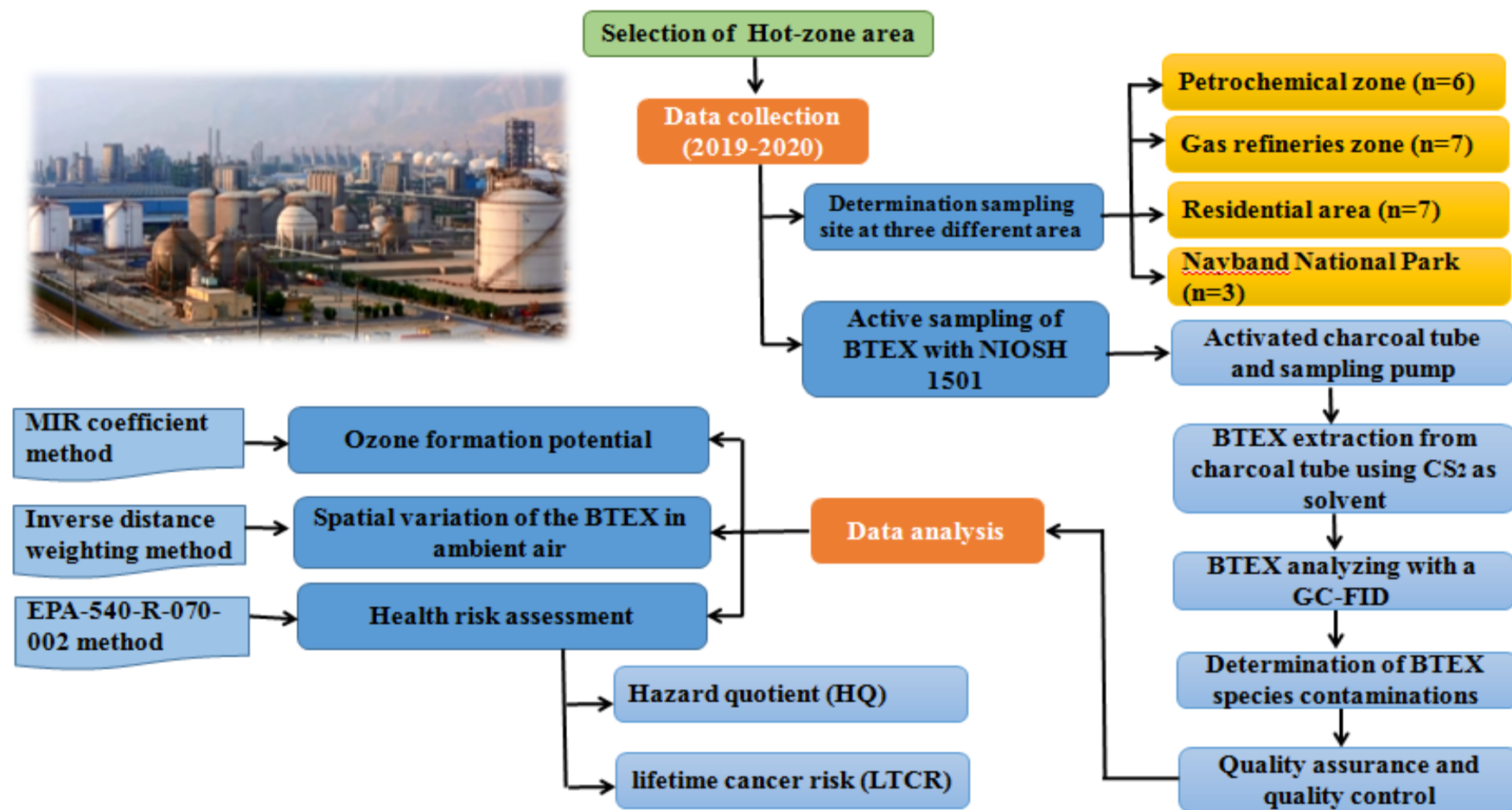**Figure 1.** Geographical locations and sampling points

Figure 2. Flow diagram of study stages

Quality assurance/Quality control (QA/QC)

Calibration curves were created using eight points from 0.5 to 100 ppm that R^2 value for all BTEX compounds obtained 0.999. To check the breakthrough of all sorbent tubes, back and front of the tubes were analyzed separately. For 96% of the samples, none of the target compounds were detected in the back section. For 4% remaining, the amount of target combinations detected in the back section was less than 2% of the front section. The recovery values for BTEX were between 95 and 105%.

Statistical analysis

Statistical analysis was carried out using SPSS analytical software (Version 22.00). The Kolmogorov-Smirnov test was used to test the normality of measured pollutants. Since the data distribution was non-normal, the Kruskal-Wallis nonparametric method was used to analyze the effect of season and sampling locations on BTEX pollution. The significance level of the analyses was set at 5%.

Ozone formation potential

Generally, OFP estimates the potential amount of ozone formation from ambient VOCs. The ranking of BTEX can be done about OFP using Carter's MIR. OFP is calculated as follows (Eq.1):

$$OFP = BTEX\ concentrations\ (\mu gm^{-3}) \times MIR\ (g\ O_3\ g\ VOCs^{-1}) \tag{1}$$

MIR is the amount (g) of ozone formed per gram of VOCs compounds. MIR coefficients are unit less and their values for benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene were 0.81, 3.97, 2.79, 10.61, 4.25, and 7.49, respectively (Tiwari et al., 2010; Masih et al., 2016).

Spatial distribution

The ArcGIS 10.2 software (developed by ESRI company) was used to spatial distribution of BTEX pollutants. There are various techniques for estimating variables that have spatial and temporal variations. The difference of these technique relates to the calculation of the weight that is given to the points of observation around the unknown point. The IDW technique is usually used in the environmental studies to predict the pollutants concentration in unmeasured locations by the optimal spatial prediction method(Whitworth et al. 2011; Dehghani et al. 2018). The IDW algorithm is described as follows (Eq. 2):

$$Z(x) = \frac{-\sum_{i=1}^{n} WiZi}{\sum_{i=1}^{n} Wi} \tag{2}$$

$$Wi = d_i^{-u}$$

where Z(x) is the predicted value at an interpolated point, Z_i is a known point, n is the total number of known points is equal to 23 points in this study, d_i is the distance between station i and the prediction point, Wi is the weight assigned to point i, and u is the weighting power that decides how the weight decreases with increasing distance(Xie et al. 2011).

Health risk assessment

Inhalation is the most important pathway of exposure with the BTEX hydrocarbons. In the present study, the US.EPA methodology was used to assess the cancer and non-cancer risk of workers and eleven age groups of people living near industrial areas (US.EPA 2014; Heibati et al. 2017)To estimate health risks from exposure to BTEX, the inhalation LTCR and the HQ were calculated using the data acquired in this study. The LTCR was calculated using Eq.3.

$$LTCR = CDI \times CSF \tag{3}$$

The inhalation CSF values for benzene and ethylbenzene are 2.73×10^{-2} and 3.85×10^{-3} (mg kg^{-1} day^{-1}), respectively, derived from the IRIS database (IRIS, 2019). CDI is the chronic daily intake (mg kg^{-1} day^{-1}) which will be determined as follows(Eq.4):

$$CDI = (C \times IR \times CF \times ET \times ED \times EF)/(AT \times BW) \tag{4}$$

where C is the concentration of BTEX species in the ambient air (μg m^{-3}); IR is inhalation rate (m^3 day^{-1}); CF is a conversion factor (mg μg^{-1}), ED and EF are exposure duration (year) and exposure frequency (days year^{-1}); and AT and BW are average lifetime (years) and body weight (kg), respectively.

Non-carcinogenic risk was determined using the HQ. The cumulative non-carcinogenic HI is the sum of the HQs of the various pollutants. HQ and HI will be calculated using Eqs.(5) and (7), respectively(US.EPA 2014)

$$HQ = \frac{EC}{RfC \times 1000} \tag{5}$$

where EC is the exposure concentration (mg m^{-3}) and will be calculated by Eq.6

$$EC = \frac{(C \times ET \times ED \times EF)}{(AT)} \tag{6}$$

$$HI = \sum_{i=1}^{n} (HQ_i) \tag{7}$$

The HQ $\leq$1 illustrates that the adverse health impacts are not likely to occur, and thus the risk can be considered to have negligible hazards, even to a sensitive individual. On the other hand, the

HQ >1 shows that there may be some possible risks for the sensitive individuals as a result of exposure. The RfC means an amount of chemical concentration with no observable carcinogenic impacts during a definite exposure time. The RfC for benzene, toluene, ethylbenzene andxyleneare3 $\times$ 10^{-3}, 5, 1 and1 $\times$ 10^{-1} mg m^{-3}, respectively(Zhang et al. 2012; US.EPA 2014). A set of the different variables applied in the calculation of chronic exposure rate are tabulated in Table S1 of the Supplementary material.

Results and discussion

BTEX concentration

Table1 presents the average value and standard deviations ($\pm$SD) for BTEX compounds in the ambient air of the PC, GR, RA and NNP. Comparison of analysis between sites sampled using Kruskal-Wallis showed a significant difference in the levels of BTXE in the four selected sites ($P<0.05$). The results showed that the average of the ΣBTEX levels during the study period in PC (S1 – S6), GR (S7 – S13), RA(S14– S20),and NNP (S21– S23) were 37.5 $\pm$ 16.3, 24.3 $\pm$9.3, 14.0 $\pm$ 5.2, and 4.0$\pm$1.5µg m^{-3},respectively.The annual average concentrations of benzene, toluene, ethylbenzene, p-xylene, m-xylene and o-xylene compounds was obtained in the PC and GR as an industrial zone at the levels of 14.4 $\pm$ 8.3 (8.6 $\pm$ 3.5), 6.6 $\pm$ 2.3 (3.9 $\pm$ 1.5), 7.2 $\pm$ 4.2 (4.0 $\pm$ 2.1), 3.1 $\pm$ 0.9 (2.1 $\pm$1.1), 3.3 $\pm$ 0.9 (3.5 $\pm$1.8), and 3.1 $\pm$1.1 (2.3 $\pm$1.1)µg m^{-3}, respectively. It is clear that benzene had the maximum average concentration in these two regions. These results are in line with those obtained by Zhang et al. (2017b) and Yilmaz Civan et al. (2015), which reported that benzene had the highest levels of BTEX in industrial areas. Although, studies at a heavily industrialized region in Aliaga Turkey showed the concentrations of benzene, toluene, ethylbenzene, and xylenes to be 2.7, 7.7, 0.6, and 3.5 µg m^{-3}, respectively, which contradicts the above findings (Dumanoglu et al. 2014).

On the other hand, in the studied at the urban areas of Canada (Windsor, Ontario), Iran (Ahvaz), China (the suburban area of Beijing), and Turkey (Düzce) which toluene were dominance pollutant among to the BTEX species in air ambient at urban area (Miller et al. 2012; Rad et al. 2014; Wang et al. 2016; Bozkurt et al. 2018). The results of the present study also showed that toluene is dominant among BTEX compounds in residential areas. The annual average concentration of toluene in the RA was 6.1 $\pm$ 2.8 µg m^{-3}, which is approximately one a half times the average concentration recorded in the GR (3.9 $\pm$ 1.5 µg m^{-3}). A comparison of measured BTEX values with the results of previous studies in large industrial - urban areas is shown in Table 2. In many cases, the various factors in each study that can be effective in determining the

concentration of BTEX compounds include sampling time, sampling period of time, the distance between the sampling points, type of sampler, atmospheric conditions, topography, number and variety of industries and the sources of VOCs emissions (Yilmaz Civan et al. 2015; Hajizadeh et al.2018).

Table 1. Average concentration (± standard deviation) of annual BTEX compounds ($\mu g\ m^{-3}$)

Locations	Sampling sites	Benzene	Toluene	Ethylbenzene	p-xylene	m-xylene	o-xylene	ΣBTEX
Petrochemical complexes	S1	9.1±2.1	3.3±1.1	4.2±0.2	3.1±0.3	1.5±0.5	1.1±0.5	22.3±2.9
	S2	6.1±1.2	3.1±0.8	2.9±0.2	1.7±0.2	0.7±0.2	0.6±0.1	15.1±2.0
	S3	27.8±5.7	14.2±3.6	10.8±3.8	2.4±0.4	2.8±0.2	3.7±1.5	61.7±9.8
	S4	18.3±6.2	4.1±0.6	12.7±8.8	1.9±0.1	4.2±1.2	6.2±2.8	47.4±6.3
	S5	17.3±3.9	9.7±3.8	9.2±2.7	6.7±2.5	6.9±2.2	4.3±1.3	54.1±4.5
	S6	7.5±2.1	4.9±1.7	3.3±1.4	2.7±0.2	3.4±0.2	2.6±0.2	24.4±3.1
Gas refineries	S7	8.2±2.2	3.2±1.0	7.2±3.5	4.2±1.1	5.1±2.8	2.7±0.2	31.1±2.2
	S8	6.1±1.3	3.3±0.9	4.5±1.2	1.4±0.1	4.5±1.2	3.1±0.1	22.9±3.1
	S9	4.2±1.2	2.1±0.6	1.2±0.2	1.1±0.1	1.3±0.2	1.1±0.8	11±1.2
	S10	14.2±3.4	5.6±1.3	3.2±0.9	2.1±0.1	3.5±0.9	1.4±0.2	30±4.7
	S11	6.5±1.3	3.6±0.2	6.1±1.3	2.4±0.3	5.2±0.7	3.5±0.3	27.3±3.6
	S12	16.7±4.3	6.2±2.1	3.6±0.1	2.4±0.2	3.2±0.5	3.2±0.7	35.3±5.5
	S13	4.1±1.5	3.3±0.6	2.2±1.1	1.1±0.5	0.9±0.1	1.1±0.3	12.7±1.3
Residential area	S14	3.8±0.2	4.7±0.9	1.7±0.1	1.3±0.2	3.1±0.7	1.3±0.3	15.9±1.4
	S15	3.1±0.1	8.1±2.4	1.9±0.2	1.7±0.3	2.1±0.6	1.6±0.2	18.5±2.5
	S16	2.2±0.2	9.3±3.8	1.6±0.1	1.3±0.1	2.1±0.2	1.1±0.1	17.6±3.1
	S17	1.9±0.1	6.5±1.2	0.9±0.3	1.0±0.1	1.8±0.1	1.4±0.2	13.5±2.1
	S18	2.6±0.1	6.1±2.5	1.1±0.1	1.2±0.2	2.1±0.3	0.9±0.1	14±2.1
	S19	2.6±0.1	7.2±1.2	1.6±0.2	1.6±0.2	1.8±0.1	1.5±0.4	16.3±2.2
	S20	0.5±0.1	0.7±0.1	0.3±0.1	0.1±0.1	0.1±0.4	0.1±0.2	2.1±0.2
Nayband National Park	S21	1.2±0.4	1.6±0.1	0.3±0.0	0.6±0.2	0.4±0.1	0.3±0.1	4.4±0.6
	S22	1.3±0.1	1.1±0.1	0.3±0.1	0.5±0.2	0.4±0.2	0.4±0.0	4.1±0.5
	S23	0.6±0.2	1.0±0.1	0.2±0.1	0.3±0.1	0.1±0.0	0.1±0.1	2.3±0.4

Table 2. Comparison of BTEX levels in South Pars with those reported for other industrial - residential areas(μg m^{-3})

Locations	Land use type	Pollutants (μg m^{-3})				The potential sources of BTEX emission	Reference
		Benzene	Toluene	Ethybenzene	Xylenes		
Ulsan, Korea	Urban	2.2	8.4	3.2	5.7	Petrochemical activities, automobile, and ship building industries	(Kim et al. 2019)
Mažeikiai, Lithuania	Rural, urban and Industrial	1.2 - 2.4	1.3 - 3.5	0.3 - 0.7	0.1 - 2.4	The crude oil refinery and motorway	(Marciulaitiene et al. 2017)
Aliaga, Turkey	Petrochemical plant	4.7	3.9	0.9	2.7	Petrochemical complex and petroleum refinery activities, vehicular and traffic	(Yilmaz Civan et al. 2015)
	Residential	0.6	1.6	0.2	0.4		
	Roadsides	0.5	1.1	0.3	2.06		
	Rural	1.9	3.9	0.6	0.9		
Jinan, China	Suburban	1.9	0.8	0.08	0.2	Petroleum Refinery, vehicle-natural gas station, and traffic	(Zhang et al. 2017b)
Gdansk , Poland	Urban	0.66	1.63	0.67	2.9	Shipbuilding industry, the petrochemical and energy industry	(Marc et al. 2015)
Tabriz, Iran	Urban	8.1	14.6		14.6	The machinery factories, petrochemical plant, traffic and CNG stations	(Tohid et al. 2018)
Tehran, Iran	Urban	3.4	16.2	3.6	17.1	Vehicle, traffic, gasoline evaporation and industrial plants	(Miri et al. 2016)
South Pars, Iran	Petrochemical complexes	14.4	6.6	7.2	9.5	Petrochemical complexes, Gas refineries, traffic and gasoline stations	The current study
	Gas refineries	8.6	3.9	4.0	7.9		
	Residential	2.4	6.1	1.3	4.3		
	National Park	1.0	1.4	0.3	1.1		

Spatial analysis

The spatial variations of the concentrations of BTEX species are shown in Fig3. It clearly shows that the highest concentration of ΣBTEX were observed in PC followed by GR > RA > NNP. The highest annual average concentration of ΣBTEX in PC were recorded at S2 (61.7 ± 9.8 μg m^{-3}), S5 (54.1 ± 4.5 μg m^{-3}) and S4 (47.4 ± 6.3 μg m^{-3}) points that located to near the aeration basin of the centralized industrial wastewater treatment unit, the olefin production plant and the aromatic production complex, respectively. One the other hands, the maximum concentration of ΣBTEX in GR were detected in S12 (35.3 ± 5.5 μg m^{-3}) and S7 (31.1 ± 2.2μg m^{-3}) dealing with vapor emitted from condensate storage tanks and industrial wastewater treatment unit, respectively. Wastewater treatment facilities in these industries are recognized as the most important emissions sources of VOCs into the atmosphere. However leakage of equipment (valves, flanges, compressor seals, pressure relief valves, and other piping components) and evaporation from condensate storage tanks can also occur (Pandya et al. 2006; Zhang et al. 2018).

Based on results the highest average of ΣBTEX at the RA were found S15 (18.5 ± 2.5μg m^{-3})and S16(17.6 ± 3.1μg m^{-3}) points which affected by daily traffic volume and gasoline station, respectively. It is also noteworthy that the average concentrations of these compounds at S18 and S14 points were 16.3 ± 2.2 and 15.9 ± 1.4 μg m^{-3}, respectively, which could be due to the low distance to industrial areas. The findings of the previous study show that fuel quality, traffic volume, and vicinity to industrial sites were responsible for the increasing ambient BTEX in residential areas (Zhang et al. 2008). In this study, wind direction is from the northwest to the southeast, therefore can affect in air quality of S14 and S18 points due to petrochemical complexes and gas refineries activities. The lowest average concentrations of BTEX species detected was at the NNP. This fact is probably related to the influence of the distance of source emission, dilution, and photochemical reactions (Masih et al. 2016).

In present study, the relative abundance for BTEX species in PC and GR were in following order: benzene > ethylbenzane > toluene > m-xylene > p,o-xylene. The average concentration of benzene in ambient air at the PC and GR and all seasonal sampling sites exceeded the annual average threshold limit of 5 μg m^{-3} proposed by the European Union directive 2000/69/EC for 2010 (EEA 2017). The highest level of benzene was found in S3, S4, S5, S12 and S14 at the PC and GR with 27.8, 18.3, 17.3, 16.7 and 16.7 μg m^{-3}, respectively. The average concentrations of benzene reported in studies conducted with petroleum, gas and petrochemical industrials at the Greece, the US, Italy, and Taiwan were 5.3, 3, 9, and 8.2 μg m^{-3}, respectively (Kalabokas et al.

2001; Reiss2006; Fustinoni et al. 2012; Chen et al.2016). These different results can probably in relation to the number of plants, volume of product and using of new technology.

To the best of the author's knowledge, data about the concentrations of ambient air BTEX in national protected areas and national parks near to the industrial - urban areas are scant. In a study conducted by Villanueva et al. (2014)at Cabañeros National Park border, Spain to investigate the effects of road transport, concentrations of benzene and toluene were reported 0.05 and 0.06 $\mu g\ m^{-3}$, respectively. The present study, annual average concentrations of benzene, ethylbenzene , p-xylene, m-xylene and o-xylene in the NNP atmosphere were detected 1.0 ± 0.4, 1.4 ± 0.1, 0.3 ± 0.2, 0.5 ± 0.2, 0.3 ± 0.2 and 0.3 ± 0.2 $\mu g\ m^{-3}$, respectively. Generally, the ratio of benzene-to-toluene (B/T) has been proposed as an indicator for determining the emission sources of BTEX compounds. A ratio exceeding 0.5 indicate that the source of benzene is not only related to motor vehicle exhausts, but also industrial activities(Miri et al. 2016; Dehghani et al. 2018).The B/T ratios for S21, S22 and S23 points at NNP area at all seasonal sampling sites were 0.7, 0.8 and 0.6, respectively. These results can be attributed the BTEX emissions related to vehicle and industrial activities on the NNP atmosphere.
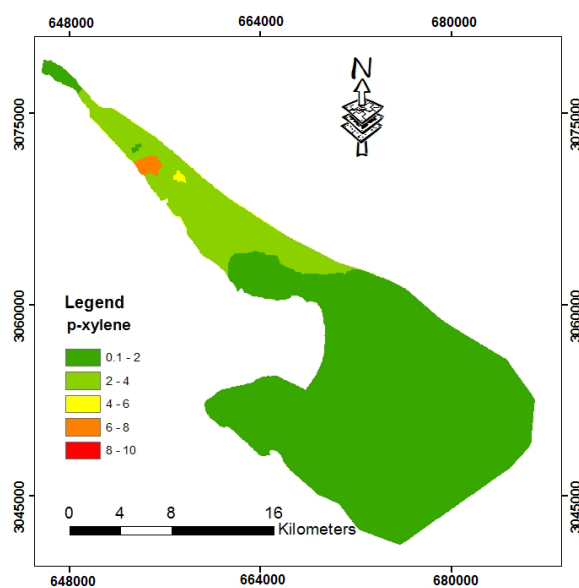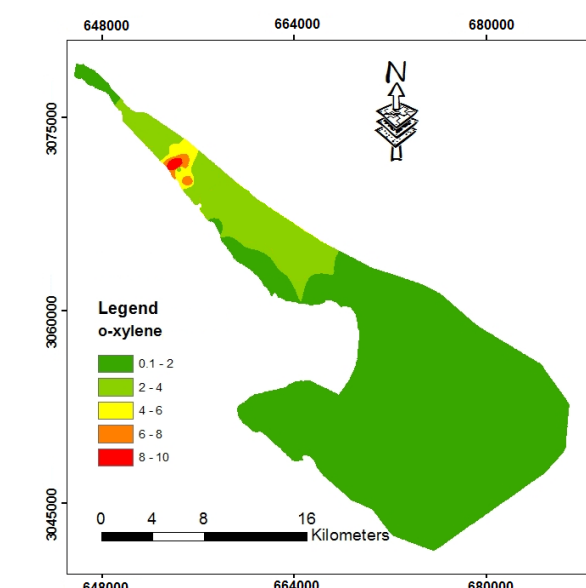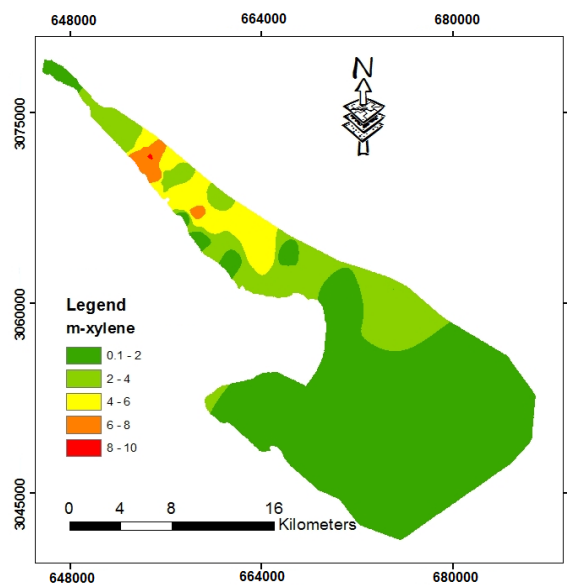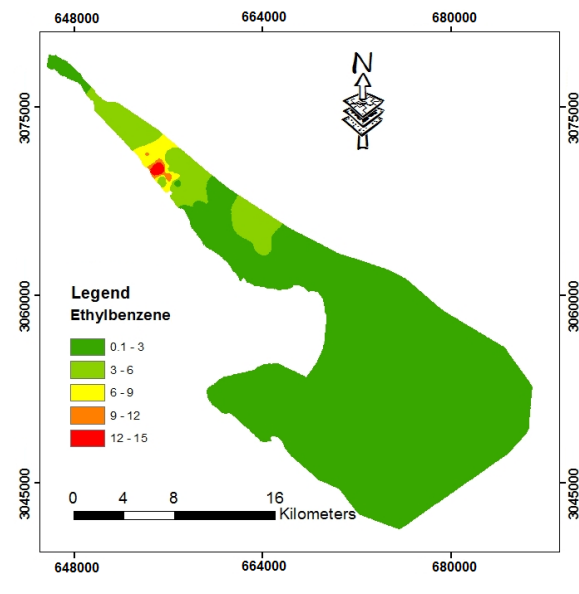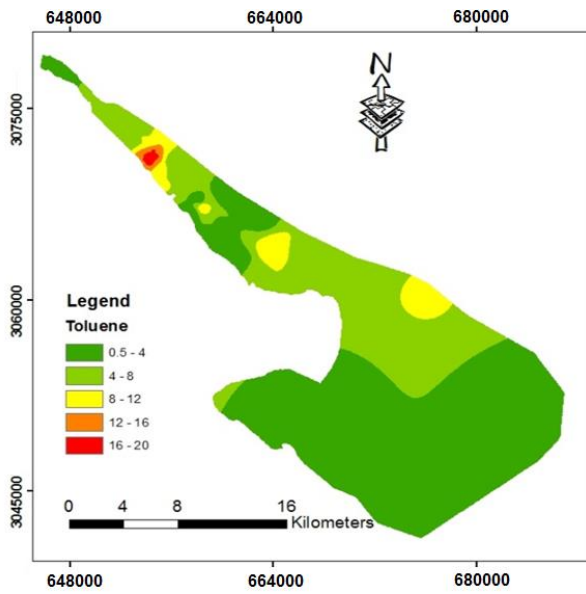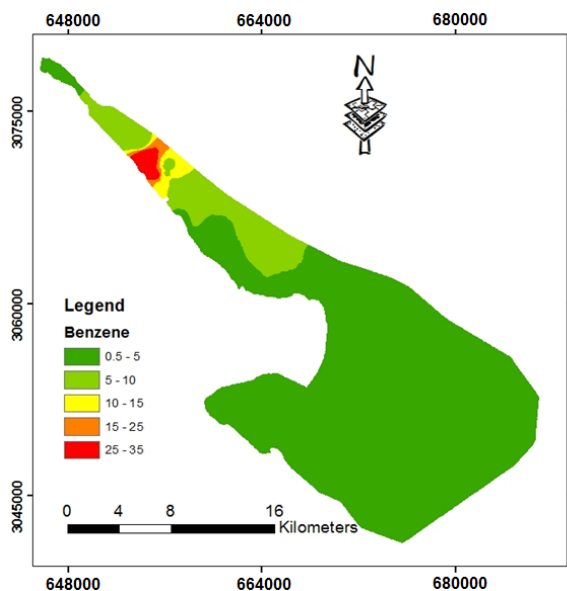
Figure 3. Spatial mapping of annual average concentrations ($\mu g\ m^{-3}$) of BTEX species.

Seasonal variations

The results of the Kruskal-Walli's test indicated that significant differences existed between the BTEX concentration in different seasons ($P < 0.05$). Seasonal variations of the BTEX compounds' concentrations showed that the highest average concentrations of benzene, toluene, ethylbenzene, and ΣBTEX were observed in winter. At the same time, xylenes it was found in autumn at all sampling sites. The highest concentration of BTEX in winter was recorded at the PC site, followed by GR > RA > NNP. The maximum concentrations of benzene, toluene, ethylbenzene, p-xylene, m-xylene and o-xylenein winter at S3 point were $38.5 \pm 10.1, 15.4 \pm 3.1$, $19.8 \pm 5.6, 7.1 \pm 2.9, 6.2 \pm 1.9$, and $8.8 \pm 2.4 \mu g\ m^{-3}$, respectively. The minimum concentrations of BTEX species were detected in the summer. The similar results were demonstrated by Hoque et al. (2008), Mullaugh et al. (2015), Sharma and Giri (2016) and Marciulaitiene et al. (2017). The occurrence of higher concentrations of air pollution in different seasons is associated with the atmospheric conditions and the volume of anthropogenic activity. During summer, high thermal turbulence and unstable atmospheric conditions play an important role in the distribution of pollutants. Furthermore, in this season, the removal of BTEX by OH radicals leads to dilution of those compounds, whereas in winter, with calm conditions and high atmospheric stability, less dispersion and accumulation of pollutants occur(Rad et al. 2014; Singh et al.2016).However, in the Seoul, Korea (Shin et al. 2013), Tehran, Iran(Miri et al. 2016) and Yazd, Iran(Hajizadeh et al. 2018)the lowest concentration of ΣBTEX was recorded in winter, which is in contrast to the present study. Those major reasons are mentioned due to the atmospheric precipitation in the winter season.

Ozone formation potential

Knowing the qualitative and quantitative characterization of VOCs in an area can help in comprehending the ground-level ozone formation process and evaluating the best strategy for management and control of VOCs. The present study, based on the MIR values m-xylene at PC (OFP = $34.5 \mu g\ m^{-3}$) and GR (OFP = $36.7 \mu g\ m^{-3}$) were the most dominant contributor to ozone formation among BTEX compounds. This result was in agreement with the several studies (Hoque et al. 2008; Tiwari et al.2010; Hajizadeh et al.2018). The second most dominant compounds were toluene, followed by o-xylene> ethylbenzene> p-xylene > benzene (Table3).While, toluene has the maximum contribution in ozone formation at RA (OFP = $24.2 \mu g\ m^{-3}$) and NNP (OFP = $5.6 \mu g\ m^{-3}$). The results obtained are found to be in agreement with the observations of Masih et al. (2016) at north India and Wang et al. (2016) at Beijing China. In additional the ΣOFP levels predicted in PC was higher than the threshold value of 120 $\mu g\ m^{-3}$ proposed by WHO. Previous studies have shown that exposure to the high levels of OFP could

result in throat irritation, lung dysfunction, wheezing, and upper respiratory tract infections (Bell et al., 2004; Ebi and McGregor, 2008).

Table 3. Ozone formation potential with respect to MIR coefficient at different sites (μg m^{-3})

locations	Benzene	Toluene	Ethylbenzene	p-xylene	m-xylene	o-xylene	ΣBTEX
PA	11.6	26	20	23.1	34.5	13.1	128.3
GR	6.9	15.5	11.2	14.7	36.7	9.8	94.8
RA	1.9	24.2	3.6	8.8	20	4.9	63.4
NNP	0.8	5.6	0.7	3.7	3.2	1.1	15.2
Average	5.3	17.8	8.9	12.8	23.6	7.2	75.7

Health risk assessment

In this study, health risk was calculated for eleven age groups in the RA area and worker group age (21-61 years) in the PC and GR areas. Estimation of health risk for exposures to BTEX compounds revealed that non-cancer risk (HQ) was lower than 1.0 for all groups in the RA areas. As well, the HQ calculated at the PC and GR indicated no likelihood of adverse health effect occurring at this level of exposure for workers (HQ<1.0). The HI calculated for all these pollutants at all study areas were lower than 1, which showed no harmful health effects.

The acceptable range of LTCR for humans set by WHO is 1×10^{-5} to 1×10^{-6}, however other standards such as US.EPA recommend the amounts less than 1×10^{-6}(Miri et al. 2016). In the current study, the LTCR values for benzene at the PC and GR industrial areas were higher than the threshold value (Fig.4).Similar findings have been reported by Fustinoni et al. (2012) at the Mediterranean industrial site (3.3×10^{-4}),Ramirez et al. (2012) at neighboring regions of two petrochemical complexes located in the city of Tarragona, Spain (3.4×10^{-4}),Chen et al. (2016) at a petrochemical industrial zone in southern Taiwan (6.4×10^{-5}), Hajizadeh et al. (2018) in the ambient residential air in Yazd, Iran (1.6×10^{-4}), and Dehghani et al. (2018) in the ambient residential atmosphere of Shiraz, Iran (1.9×10^{-4}). The LTCR for ethylbenzene just in S3, S5 and S8 points were higher than the threshold value (Fig 3).

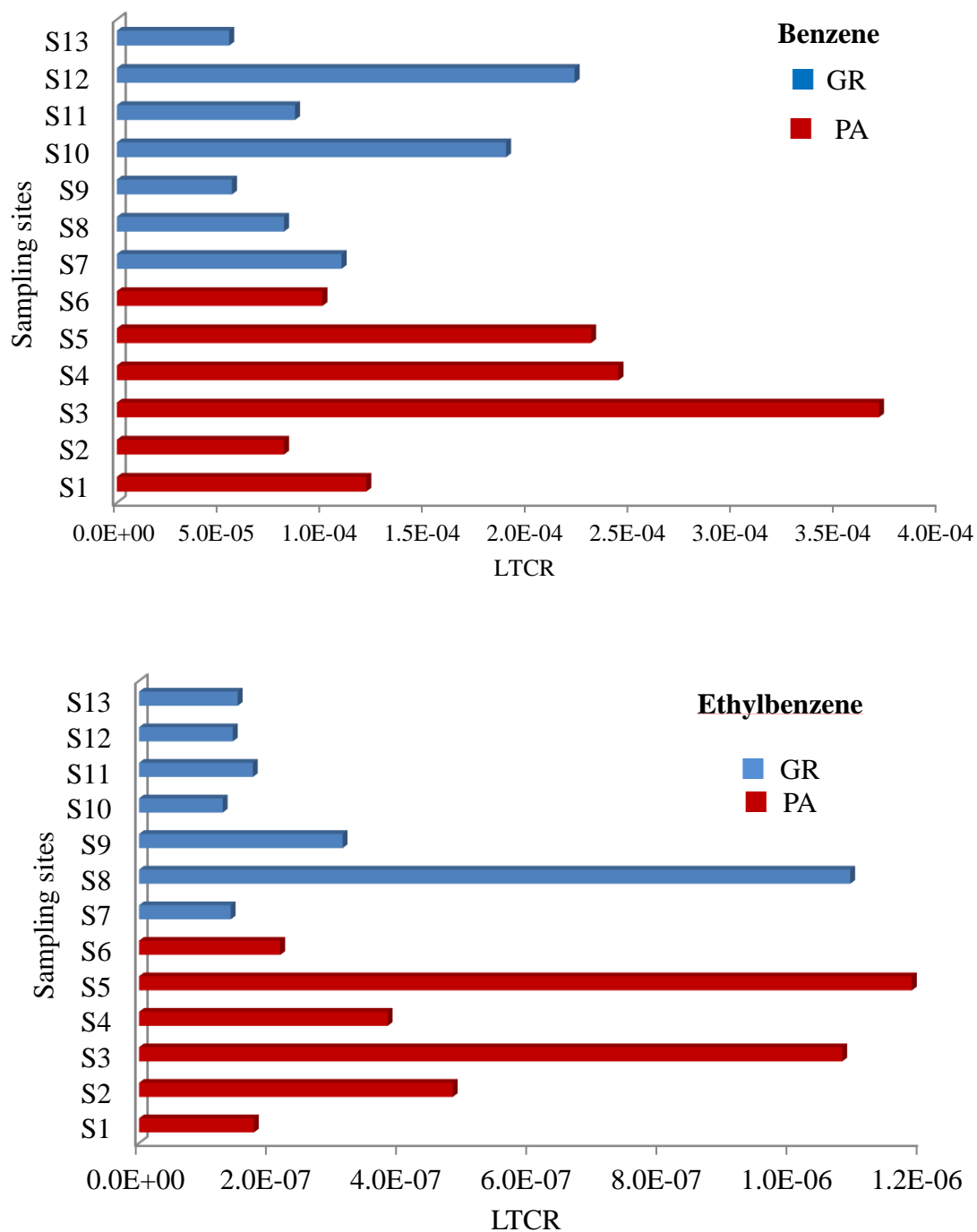**Figure 4.** LTCR for personal exposure to benzene and ethylbenzene at PA and GR areas (based on an acceptable risk level of 1×10^{-6}).

On the other hand, the predicted LTCR for benzene was higher than the threshold value 1×10^{-6} at the S24 points for all age groups, in the sampling points S25 to S29 and from the age groups of 1–2 to >81 years, and S30 from 6-11 to >81 years (Table 4).

Table 4. The LTCR calculated for benzene and ethylbenzene at RA area according to CSF proposed by IRIS

LTCR for benzene

Age groups (year)

Locations	Birth to <1	1-2	2-3	3-6	6-11	11-16	16-21	21-61	61-71	71-81	> 81
S24	1.3E-06	1.2E-06	2.2E-06	5.7E-06	2.1E-05	1.7E-05	1.6E-05	2.2E-04	1.0E-04	4.7E-05	2.2E-05
S25	1.1E-07	9.4E-07	1.8E-06	4.7E-06	1.7E-05	1.4E-05	1.3E-05	1.8E-04	8.4E-05	3.8E-05	1.8E-05
S26	7.5E-07	6.7E-07	1.3E-06	3.3E-06	1.2E-05	9.8E-06	9.4E-06	1.3E-04	6.0E-05	2.7E-05	1.3E-05
S27	6.4E-07	5.8E-07	1.1E-06	2.9E-06	1.1E-05	8.5E-06	8.1E-06	1.1E-04	5.2E-05	2.3E-05	1.1E-05
S28	8.8E-07	7.9E-07	1.5E-06	3.9E-06	1.5E-05	1.2E-05	1.1E-05	1.5E-04	7.1E-05	3.2E-05	1.5E-05
S29	8.8E-07	7.9E-07	1.5E-06	3.9E-06	1.5E-05	1.2E-05	1.1E-05	1.5E-04	7.1E-05	3.2E-05	1.5E-05
S30	1.7E-07	1.5E-07	2.9E-07	7.5E-07	2.8E-06	2.2E-06	2.1E-06	2.9E-05	1.4E-05	6.2E-06	2.9E-06
LTCR for ethylbenzene											
S24	9.6E-10	8.6E-10	1.6E-09	4.3E-09	1.6E-08	1.3E-08	1.2E-08	2.9E-08	7.7E-08	3.5E-08	1.6E-08
S25	9.6E-10	8.6E-10	1.6E-09	4.3E-09	1.6E-08	1.3E-08	1.2E-08	2.9E-08	7.7E-08	3.5E-08	1.6E-08
S26	9.6E-10	8.6E-10	1.6E-09	4.3E-09	1.6E-08	1.3E-08	1.2E-08	2.9E-08	7.7E-08	3.5E-08	1.6E-08
S27	9.6E-10	8.6E-10	1.6E-09	4.3E-09	1.6E-08	1.3E-08	1.2E-08	2.9E-08	7.7E-08	3.5E-08	1.6E-08
S28	9.6E-10	8.6E-10	1.6E-09	4.3E-09	1.6E-08	1.3E-08	1.2E-08	2.9E-08	7.7E-08	3.5E-08	1.6E-08
S29	9.6E-10	8.6E-10	1.6E-09	4.3E-09	1.6E-08	1.3E-08	1.2E-08	2.9E-08	7.7E-08	3.5E-08	1.6E-08
S30	9.6E-10	8.6E-10	1.6E-09	4.3E-09	1.6E-08	1.3E-08	1.2E-08	2.9E-08	7.7E-08	3.5E-08	1.6E-08

Conclusions

This study aimed to determine the concentrations, the spatial and seasonal variation of BTEX, OFP, and carcinogenic risks due to inhalation exposure to these compounds in the ambient air of South Pars, Iran. The main findings of this study are summarized as follows: Spatial analysis indicated that maximum levels of ΣBTEX were located in the PC zone, followed by GR> RA > NNP. The highest level of the ΣBTEX was observed in the atmosphere near the industrial wastewater treatment unit. The PC and GR found the highest average benzene concentrations, while toluene was the dominant pollutant in RA and NNP. The annual benzene concentrations in all industrial zone sampling points exceeded European legislation recommendations. The seasonal variation indicated that the maximum average concentration of BTEX compounds was observed in winter due to high atmospheric stability. The maximum ozone formation capacity calculated from BTEX compounds demonstrated that m-xylene in the PC and GR areas and toluene in the RA and NNP areas were the most important compounds. According to the results, the values of the non-cancer risk of BTEX in all sampling points were under the permissible recommended level. However, LTCR for benzene in PC and GR and some of the sampling points of the RA were higher than the threshold values established by the USEPA. These findings can help develop control-based strategies for BTEX compound emissions and GLO formation, improving air quality and reducing health risks. Policymakers should enforce the limits on releasing pollutants into the atmosphere in the study area by strengthening existing legislation.

References

Bozkurt Z, Uzmez OO, Dogeroglu T, et al. (2018). Atmospheric concentrations of SO_2, NO_2, ozone and VOCs in Düzce, Turkey using passive air samplers: Sources, spatial and seasonal variations and health risk estimation. Atmos Pollut Res 1–10. Doi: 10.1016/j.apr.2018.05.001

Chen MJ, Lin CH, Lai CH, et al (2016). Excess lifetime cancer risk assessment of volatile organic compounds emitted from a petrochemical industrial complex. Aerosol Air Qual Res 16:1954–1966. doi: 10.4209/aaqr.2015.05.0372

Dehghani M, Fazlzadeh M, Sorooshian A, et al. (2018). Characteristics and health effects of BTEX in a hot spot for urban pollution. Ecotox and Environ Safety 155:133–143. doi: 10.1016/j.ecoenv.2018.02.065.

Dehghani M, Norouzian Baghani A, Fazlzadeh M, et al. (2019). Exposure and risk assessment of BTEX in indoor air of gyms in Tehran, Iran. Microchemical Journal. 150:104-135. https://doi.org/10.1016/j.microc.

Dumanoglu Y, Kara M, Altiok H, et al. (2014). Spatial and seasonal variation and source apportionment of volatile organic compounds (VOCs) in a heavily industrialized region. Atmos. Environ. 98, 168–178; doi.org/10.1016/j.atmosenv.2014.08.048.

Ebi K, Mcgregor G. (2008). Climate Change, Tropospheric Ozone and Particulate Matter, and Health Impacts. Environmental health perspectives. 116. doi:1449-55. 10.1289/ehp.11463.

EEA (2017) Air Quality in Europe 2017 report

Fustinoni S, Campo L, Satta G, et al. (2012). Environmental and lifestyle factors affect benzene

uptake biomonitoring of residents near a petrochemical plant. Environ Int 39:2–7 . doi: 10.1016/j.envint.2011.09.001

Garg A, Gupta NC (2019). A comprehensive study on spatio-temporal distribution, health risk assessment and ozone formation potential of BTEX emissions in ambient air of Delhi, India. Sci Total Environ 659:1090–1099. doi: 10.1016/j.scitotenv.2018.12.426

Hajizadeh Y, Mokhtari M, Faraji M, et al. (2018). Trends of BTEX in the central urban area of Iran: A preliminary study of photochemical ozone pollution and health risk assessment. Atmos Pollut Res 9:220–229. Doi: 10.1016/j.apr.2017.09.005

Hazrati S, Rostami R, Farjaminezhad M, Fazlzadeh M (2016). Preliminary assessment of BTEX concentrations in indoor air of residential buildings and atmospheric ambient air in Ardabil, Iran. Atmos Environ 132:91–97. doi: 10.1016/j.atmosenv.2016.02.042

Heibati B, Godri KJ, Karimi A, Yazdani J (2017). Ecotoxicology and Environmental Safety BTEX exposure assessment and quantitative risk assessment among petroleum product distributors. Ecoto and Environ Safety 144:445–449. doi: 10.1016/j.ecoenv.2017.06.055

Hoque RR, Khillare PS, Agarwal T, et al. (2008). Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India. Sci Total Environ 392:30–40 . doi: 10.1016/j.scitotenv.2007.08.036

Hsu C, Chiang H, Shie R, et al. (2018). Ambient VOCs in residential areas near a large-scale petrochemical complex : Spatiotemporal variation, source apportionment and health. Environ Pollut 240:95–104. doi: 10.1016/j.envpol.2018.04.076

Kalabokas PD, Hatzianestis J, Bartzis JG, Papagiannakopoulos P (2001). Atmospheric concentrations of saturated and aromatic hydrocarbons around a Creek oil refinery. Atmos Environ 35:2545–2555. doi: 10.1016/s1352-2310(00)00423-4

Kim SJ, Kwon H, Lee M et al. (2019). Spatial and temporal variations of volatile organic compounds using passive air samplers in the multi-industrial city of Ulsan, Korea. Environ Sci Pollut Res 26, 5831–5841. doi.org/10.1007/s11356-018-4032-5

Marć M, Namieśnik J, & Zabiegała B (2015). BTEX concentration levels in urban air in the area of the Tri-City agglomeration (Gdansk, Gdynia, Sopot), Poland. Air Quality, Atmosphere & Health. 7. doi:10.1007/s11869-014-0247-x.

Marciulaitiene E, Sereviciene V, Baltrenas P, Baltrenaite E (2017). The characteristics of BTEX concentration in various types of environment in the Baltic Sea Region, Lithuania. Environ Sci Pollut Res 24:4162–4173 . doi: 10.1007/s11356-016-8204-x

Masih A, Lall AS, Taneja A, Singhvi R. (2016). Inhalation exposure and related health risks of BTEX in ambient air at different microenvironments of a terai zone in north India. Atmos Environ 147:55–66 . doi: 10.1016/j.atmosenv.2016.09.067

Miller L, Xu X, Grgicak-Mannion A, et al (2012). Multi-season, multi-year concentrations and correlations amongst the BTEX group of VOCs in an urbanized industrial city. Atmos Environ 61:305–315 . doi: 10.1016/j.atmosenv.2012.07.041

Miri M, Rostami Aghdam Shendi M, Ghaffari HR, et al. (2016). Investigation of outdoor BTEX: Concentration, variations, sources, spatial distribution, and risk assessment. Chemosphere 163:601–609 . doi: 10.1016/j.chemosphere.2016.07.088

Mullaugh KM, Hamilton JM, Avery GB, et al. (2015). Temporal and spatial variability of trace volatile organic compounds in rainwater. Chemosphere 134:203–209 . doi: 10.1016/j.chemosphere.2015.04.027

Pandya GH, Gavane AG, Bhanarkar AD, Kondawar VK (2006). Concentrations of volatile organic compounds (VOCs) at an oil refinery. Int J Environ Stud 63:337–351. doi: 10.1080/00207230500241918

Rad HD, Babaei AA, Goudarzi G, et al. (2014). Levels and sources of BTEX in ambient air of Ahvaz metropolitan city. Air Qual Atmos Health 7:515–524. doi: 10.1007/s11869-014-0254-y

Ramirez N, Cuadras A, Rovira E, et al. (2012). Chronic risk assessment of exposure to volatile organic compounds in the atmosphere near the largest Mediterranean industrial site. Environ Int 39:200–209. doi: 10.1016/j.envint.2011.11.002

Reiss R (2006). Temporal trends and weekend-weekday differences for benzene and 1,3-butadiene in Houston, Texas. Atmos Environ 40:4711–4724. doi: 10.1016/j.atmosenv.2006.04.023

Ren M, Li N, Wang Z, et al. (2017). The short-term effects of air pollutants on respiratory disease mortality in Wuhan, China: Comparison of time-series and case-crossover analyses. Scientific Rep 7:1–9 . doi: 10.1038/srep40482

Singh R, Gaur M, Shukla A (2016). Seasonal and spatial variation of BTEX in ambient air of Delhi. J Environ Prot 670–688.

Shin J, Chung K, Oh J, et al (2013). The effect of site quality on repurchase intention in Internet shopping through mediating variables: The case of university students in South Korea. Inter Journal of Information Management. 33. doi: 453–463. 10.1016/j.ijinfomgt.2013.02.003.

Statistical Centre of Iran. Iran Population and Housing Census (2016).

Tiwari V, Hanai Y, Masunaga S (2010). Ambient levels of volatile organic compounds in the vicinity of petrochemical industrial area of Yokohama, Japan. Air Qual Atmos Health 3:65–75 . doi: 10.1007/s11869-009-0052-0

Tofigh A and Abedian M (2016). Analysis of energy status in Iran for designing sustainable energy roadmap. Renewable and Sustainable Energy Reviews, 57C, 1296–1306. doi: 10.1016/j.rser.2015.12.209

Tohid L, Sabeti Z, Sarbakhsh P, et al (2018). Spatiotemporal variation, ozone formation potential and health risk assessment of ambient air VOCs in an industrialized city in Iran. Atmos Pollut Res 1–15. doi: 10.1016/j.apr.2018.10.007

US.EPA (2014) Framework for Human Health Risk Assessment to Inform Decision Making. 1–76

Villanueva F, Tapia A, Notario A, Albaladejo J (2014). Ambient levels and temporal trends of VOCs , including carbonyl compounds and ozone at Cabañeros National Park border, Spain. Atmos Environ 85:256–265

Wang G, Cheng S, Wei W, et al. (2016). Characteristics and source apportionment of VOCs in the suburban area of Beijing, China. Atmos Pollut Res 7:711–724. doi: 10.1016/j.apr.2016.03.006

Whitworth KW, Symanski E, Lai D, Coker AL (2011). Kriged and modeled ambient air levels of benzene in an urban environment : an exposure assessment study. Environ Health 10:1–10

Xie Y, Chen T, Lei M, et al. (2011). Chemosphere Spatial distribution of soil heavy metal pollution estimated by different interpolation methods : Accuracy and uncertainty analysis. Chemosphere 82:468–476. doi: 10.1016/j.chemosphere.2010.09.053

Yilmaz Civan M, Elbir T, Seyfioglu R, et al (2015). Spatial and temporal variations in atmospheric VOCs , NO2 , SO2 , and O3 concentrations at a heavily industrialized region in

Western Turkey, and assessment of the carcinogenic risk levels of benzene. Atmos Environ 103:102–113. doi: 10.1016/j.atmosenv.2014.12.031

Zhang G, Wang N, Jiang X, Zhao Y (2017a). Characterization of Ambient Volatile Organic Compounds (VOCs) in the Area Adjacent to a Petroleum Refinery in Jinan, China. Aerosol Air Qual Res 944–950. doi: 10.4209/aaqr.2016.07.0303

Zhang G, Wang N, Jiang X, Zhao Y (2017b). Characterization of ambient volatile organic compounds (VOCs) in the area adjacent to a petroleum refinery in Jinan, China. Aerosol Air Qual Res 17:944–950. doi: 10.4209/aaqr.2016.07.0303

Zhang J, Wang T, Chameides WL, et al. (2008). Source characteristics of volatile organic compounds during high ozone episodes in Hong Kong, Southern China. Atmos Chem Phys 8:4983–4996 . doi: 10.5194/acp-8-4983-2008

Zhang Y, Mu Y, Liu J, Mellouki A (2012). Levels, sources, and health risks of carbonyls and BTEX in the ambient air. J Environ Sci 24:124–130 . doi: 10.1016/S1001-0742(11)60735-3