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Carcinogenic and Health Risk Assessment of Respiratory Exposure to BTEX Compounds in Gasoline Refueling Stations in Karaj – Iran

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ABSTRACT

BTEX is one of the common compounds in the breathing air of gas station workers, which can cause high carcinogenic and health risks. The present study was conducted to assess the carcinogenic and health risks of occupational exposure to BTEX compounds in gasoline fuel distribution stations in Karaj. This descriptive and cross-sectional study was conducted to assess the carcinogenic and health risks caused by exposure to BTEX compounds in 2021 during the summer and winter in six fuel distribution stations in Karaj. Occupational exposure to BTEX was measured according to the NIOSH 1501 method. Cancer and non-cancer risk assessment were performed according to the United States Environmental Protection Agency (USEPA) method. Data were analyzed in SPSS software version 26. The average occupational exposure to benzene, toluene, ethyl benzene, and xylene during a work shift among all participants in summer and winter were 83.33 - 89.33, 202 - 210.66, 126.55 - 136.83, and 168.81 - 174.83 µg.m-3, respectively. The highest concentration of BTEX compounds was observed in Gas station in the center of the city. The mean carcinogenic risk value of benzene and ethylbenzene were 139×10-2 and 27×10-2, respectively. The highest carcinogenic risk value due to exposure to benzene and ethyl benzene was observed in Gas station in the center of the city. The mean non-carcinogenic and health risks of occupational exposure to benzene, toluene, ethyl benzene, and xylene were 173.79, 14.19, 3.61, and 12.87, respectively.
The findings demonstrated the values of carcinogenic and non-carcinogenic risk in the majority of participants were within the definitive and unacceptable risk levels. Therefore, corrective measures are necessary to protect the employees from the non-cancer and cancer risks.

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INTRODUCTION

Air pollution is the most critical environmental factor that causes many deaths worldwide every year. Cities are generally areas of air pollution and the cause of diseases caused by industrial pollutants. However, the exact extent of the health effects of air pollution in the city is still unknown (Khomenko et al., 2021; Soltanzadeh, Yarandi, Jazari, & Mahdinia, 2022; Yarandi, Mahdinia, Barazandeh, & Soltanzadeh, 2021). According to the World Health Organization, 7 million people die each year from air pollution. Air pollution is the sixth leading cause of death and the second leading cause of death from non-communicable diseases worldwide. Perhaps one of the leading causes of air pollution is incomplete combustion, which is caused by a lack of complete oxygen supply or improper air-fuel ratio after combustion and leads to the release of pollutants such as carbon monoxide, sulfur oxides, Nitrogen oxides, particulate matter, ash and soot, and unburned or unmodified hydrocarbons (Ma et al., 2017; Moshiran et al., 2021; Soltanzadeh, Mahdinia, et al., 2022). One of the most important compounds in air pollution is volatile organic compounds. Volatile Organic Compounds (VOCs) contain many hydrocarbons that can evaporate under atmospheric temperature and pressure due to their high vapor pressure. As a result, due to the volatility of these compounds, many people in industrial and non-industrial environments are exposed to these compounds. In this regard, exposure through respiration is the most important way of human contact with this group of chemical compounds (Sadeghi-Yarandi, Golbabaei, & Karimi, 2020; Sadeghi-Yarandi, Karimi, et al., 2020).

VOCs are divided into low-risk to high-risk types. Low-risk types of these compounds can cause minor allergies, such as runny nose, redness, or itchy eyes. While high-risk types of VOCs cause lung, cell, and other cancers. Emissions of VOCs come from various sources, such as moving and stationary sources, as well as plants (Moshiran et al., 2021). The most important sources of emissions of VOCs are human activities. VOCs compounds are released by various activities such as industrial activities, intentional or unintentional combustion, transportation, etc. (Sadeghi-Yarandi, Karimi, et al., 2020)

The most important VOCs include BTEX, which is an indicator of volatile organic compounds. These compounds enter the air in large quantities through vehicles, gasoline combustion, and the petrochemical industry (Cruz et al., 2020; Yarandi, Karimi, Sajedian, & Ahmadi, 2019). BTEX includes benzene, toluene, ethylbenzene, and xylene isomers. Benzene is a definite carcinogen of these compounds, and ethylbenzene is suspected of carcinogenicity (Alsbou & Omari, 2020; Cruz et al., 2020). Thus, exposure to BTEX leads to severe consequences such as neurological diseases and cancer (Alsbou & Omari, 2020). Recently, benzene has been used as an anti-spark agent in gasoline due to the removal of lead in car gasoline. Therefore, approximately 10% of the total consumption of benzene is used in car fuel, so that today, the use of benzene as a means of improving gasoline in car engines has increased. As a result, the most common way of contact for people with benzene is cars and fuel stations in cities (Capíková, Tesařová, Hlavaty, Ekielski, & Mishra, 2019).

According to the above, the release of BTEX compounds and the subsequent exposure to these compounds have adverse effects on the environment and human health. One of the sources of emissions of these compounds is fuel distribution stations in cities, which can emit high concentrations of these compounds and lead to respiratory exposure for employees in this sector. Since, according to various documents, evidence, and studies, the adverse effects of these compounds on human health have been proven, controlling and reducing the release of these compounds to prevent the negative impact on employees' health in these work environments is necessary.

Karaj is considered as one of the metropolises of Iran. The rapid increase in population and expansion of the city over the past few decades has led to the rise in vehicles and fuel distribution stations. According to the statistics, the number of gas stations in the city is more than 50. As various studies show, one of the main sources of BTEX compounds is fuel distribution stations, which adversely affect human health. Therefore, periodic or regular monitoring of the release of these compounds and determining the amount of carcinogenic and health risks due to occupational exposure to these compounds is of great importance.

All of those mentioned above connecting to BTEX compounds, particularly in the fuel distribution stations, due to the high volume of occupational exposure to this compound, demonstrate the importance of setting comprehensive monitoring and risk assessment strategy to decrease exposure to hazardous chemical compounds such as BTEX compounds. Generally, the procedure of carcinogenic and non-carcinogenic risk assessment is multi-stage. In the first stage, existing hazards are determined, then the exposure status is estimated. Ultimately, after determining the appropriate aspects, measuring the worker's exposure to a specific substance, employing different risk assessment techniques, graphs, and dose-response weights, the likelihood of causing adverse effects in the studied population will be calculated. Among all risk assessment techniques, quantitative risk assessment methods have notable importance. Today, many international organizations, such as the World Health Organization (WHO) and US Environmental Protection Agency (USEPA), utilize quantitative risk assessment techniques for chemical legislation (Sadeghi-Yarandi, Karimi, et al., 2020). Previous studies have demonstrated that BTEX compounds are one of the hazardous compounds in the respiratory region of fuel distribution station workers and have a high risk of causing occupational cancers.

Therefore, considering the importance of this issue and lack of similar studies in carcinogenic and health risk assessment of occupational exposure to BTEX compounds in various gas stations in Karaj as one of the metropolises of Iran, the present study was conducted to assess the carcinogenic and health risks of occupational exposure to BTEX compounds in gasoline fuel distribution stations in Karaj. In this study, the amounts of respiratory exposure to BTEX compounds were measured and evaluated, and in the next step, the carcinogenic and health risk values were evaluated using the Environmental Protection Agency (EPA) quantitative evaluation method as one of the most important and widely used tools.

MATERIALS AND METHOD

Study design

This descriptive and cross-sectional study was conducted to assess the carcinogenic and health risks caused by occupational exposure to BTEX compounds in 2021 during the summer and winter in 6 fuel distribution stations in Karaj. As one of the metropolises of the country, Karaj has more than 50 gasoline fuel stations, which can be a significant source of BTEX emissions. In this study, using software provided by the National Iranian Petroleum Products Distribution Company, single-purpose fuel stations in Karaj were identified, and the location of these stations is specified in Figure 1. The study stations were the center, north, south, east, west, and suburbs of Karaj. Considering the changes in weather conditions as well as the variability of daily traffic and population density in different parts of Karaj city, the investigated stations were selected in different parts of Karaj city. In choosing different stations, we tried to take into account the effect of the variety of climatic parameters as well as the population density and stations usage rate values.

These stations include conventional fuel, Euro 4, and super gasoline. In this study, 6 points of Karaj city were selected for sampling by examining the existing conditions. The reason for choosing these points was to determine the effect of geographical conditions such as altitude, urban density, traffic and type of vehicle, temperature and humidity, and the speed and direction of the wind on the concentration values of the studied compounds. The chemical structure of the studied compounds is presented in Figure 2.

The inclusion criteria were at least 12 months of work experience, having respiratory exposure to BTEX vapors according to the results of preliminary survey, non-smoking and enough consent

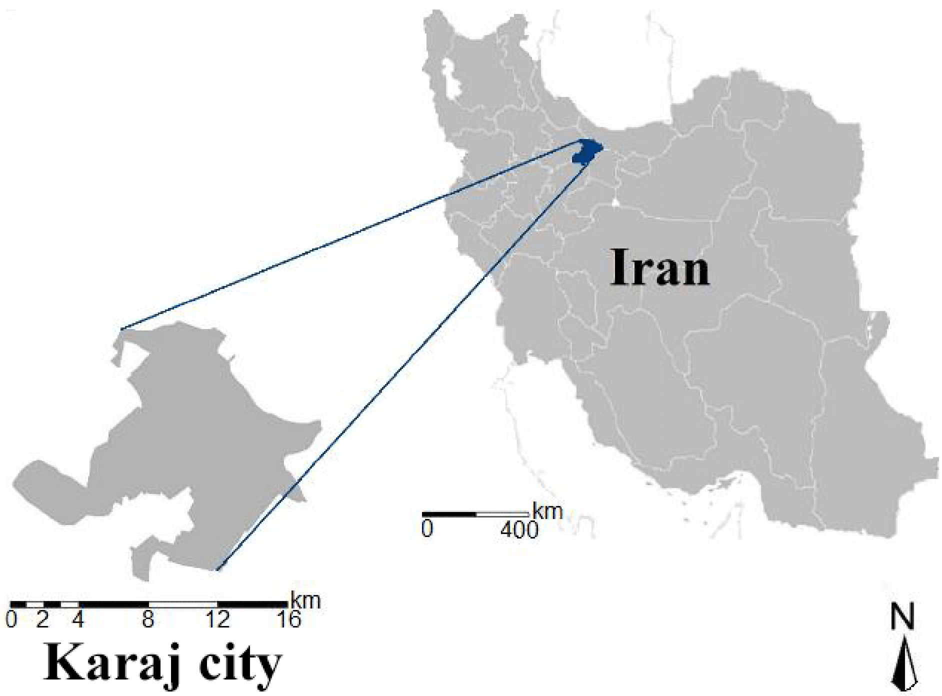

Fig 1. Location of Karaj city

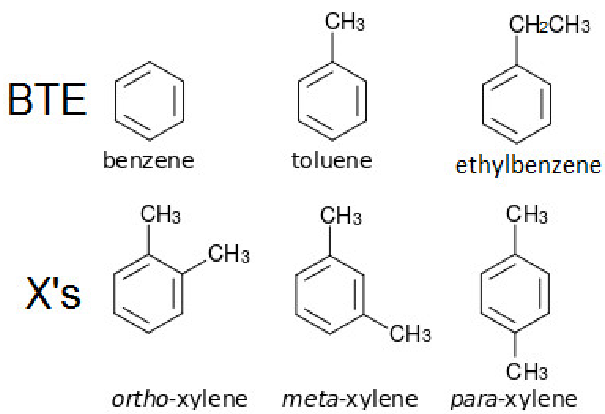

Fig 2. Chemical formula of BTEX compounds

to participate in the study. All participants in the present study completed the consent form for participation in the study before conducting the relevant air sampling. The stages of the study represent as follows.

Sampling, preparation and analysis

Information on the sampling method, preparation, and analysis is provided in Tables 1-3.

At the sampling stations, both sides of the adsorbent tubes were broken and connected to a personal sampling pump manufactured by SKC and calibrated by using a soap bubble flowmeter based on the sampling method (NIOSH 1501) (Sakhvidi, Zarei, Hachesu, & Zolfaghari, 2022). Then, the activated charcoal adsorbent tube was connected vertically to the worker's collar. To

Table 1. Sampling method information

Substance	Sampling Method No.	Sampling Method	Sample Size (ml)	Flow Rate	Calibration
Benzene	NIOSH 1501	Adsorption	5-30	≤ 0.2	Soap bubble flowmeter
Toluene	NIOSH 1501	Adsorption	1-8	≤ 0.2	Soap bubble flowmeter
Ethyl Benzene	NIOSH 1501	Adsorption	1-24	≤ 0.2	Soap bubble flowmeter
Xylene	NIOSH 1501	Adsorption	2-23	≤ 0.2	Soap bubble flowmeter

Table 2. Sampling preparation information

Substance	Recovery method	Extraction solvent	Solvent volume	Recovery time
Benzene	Chemical Recovery	Carbon disulfide	1 ml	30 min
Toluene	Chemical Recovery	Carbon disulfide	1 ml	30 min
Ethyl Benzene	Chemical Recovery	Carbon disulfide	1 ml	30 min
Xylene	Chemical Recovery	Carbon disulfide	1 ml	30 min

Table 3. Analysis information

Substance	Analysis Method No.	Analysis Method	Column	Detector - Temperature (°C)	Carrier gas - Flow rate (ml/min)	Injection Temperature (°C)	Initial Column Temperature (°C)	Final Column Temperature (°C)
Benzene	NIOSH 1501	GAS CHROMATOGRAPHY, FID	Capillary, fused silica	300 °C	He @ 2.6 mL/min	250 °C	40 °C	230°C
Toluene	NIOSH 1501	GAS CHROMATOGRAPHY, FID	Capillary, fused silica	300 °C	He @ 2.6 mL/min	250 °C	40 °C	230°C
Ethyl Benzene	NIOSH 1501	GAS CHROMATOGRAPHY, FID	Capillary, fused silica	300 °C	He @ 2.6 mL/min	250 °C	40 °C	230°C
Xylene	NIOSH 1501	GAS CHROMATOGRAPHY, FID	Capillary, fused silica	300 °C	He @ 2.6 mL/min	250 °C	40 °C	230°C

reduce possible errors and accurately assess the level of occupational exposure of each person, in this study, all employees of the stations were surveyed to 30 workers (5 workers per station) in the two seasons of summer and winter. Respiratory exposure of each person was measured with three samples during the work shift. A total of 180 samples were collected.

During the present study, each person's respiratory exposure was measured by three samples so that indicates the actual exposure of personnel during work shift (one sample at the beginning of the shift, one sample in the middle of the shift, and one sample at the end of the shift). The sampling time was 90 minutes at each sample, based on the preliminary studies and allowable air volume in the NIOSH 1501 method. Environmental samples were also used to determine the values of BTEX concentration in the rest room of each of the studied stations The number of environmental samples in this section was 6 absorbing tubes (one sample per room). After the sampling, to prevent the sample loss, both sides of the adsorbent tubes were instantly protected with plastic caps and kept in a cool box with a temperature below −3 °C and transferred to the laboratory for analysis and determining the amount of analytics.

This study collected blank samples in field sampling and laboratory analysis to specify contamination levels and possible errors during sampling, transferring, and analysis. All samples were corrected for the blank levels. In addition, spike samples were utilized to determine the accuracy of the measurements. The finding showed that the percentage of recovery was 91.44%. Finally, the calibration curve was plotted by using an external standard method. R^2 value of the calibration curve was 0.988. Also, the limit of detection (LOD) in the present study was 2 $\mu g.m^{-3}$. Duplicate samples were analyzed and it was found within 5% of variation.

The content of activated charcoal in both front and rear sections of the tubes was transferred to separate vials. Then, by employing the optimal NIOSH 1501 method, the extraction of the analyte was carried out by a chemical recovery strategy and using an extraction solvent produced by the German Merck Company (Carbon disulfide with purity of 99.5%). For complete extraction of BTEX compounds, at least 30 seconds were considered. Ultimately, 1μl of each sample with a 10μl gas-tight syringe manufactured by Hamilton Company was injected into the Gas Chromatography-Flame Ionization Detector (GC-FID) (model CP-3800 gas chromatography and FID detector, Varian Technologies, Japan). The split ratio was 1:5. Helium gas was also utilized as carrier gas. The standard solution of benzene, toluene, ethylbenzene, and xylene was used to draw the calibration curve. The area under the chromatographic peak was determined by employing Varian workstation software version 6.41.

The Dwyer instrument manufactured by Dwyer company (Michigan, USA) measured temperature and humidity at the sampling points, which has a separate sensor for measuring temperature and relative humidity.

Carcinogenic risk assessment

In the present examination, for cancer and non-cancer risk assessment, the USEPA risk assessment method and the Integrated Risk Information System (IRIS), provided by USEPA, were employed. The lifetime cancer risk (LCR) index counted the carcinogenicity risk of occupational exposure to BTEX compounds. The LCR index was calculated utilizing the following equation (Equation 1) (Sun et al., 2019):

$$LCR = CDI \times SF \tag{1}$$

Where CDI is chronic daily intake (mg.kg -1.day -1) and SF is the cancer slope factor (kg.day. mg -1) of an exact carcinogen substance. The slope factor describes an acceptable probability range of any chemical exposure-response. The weight of SF was acquired from the IRIS developed by USEPA. CDI demonstrates exposure to a mass of matter per unit of body weight and time over a relatively long period. CDI was calculated utilizing the following equation (Equation 2) (Zhang et al., 2018):

$$CDI = \frac{Ca \times IR \times ET \times EF \times ED}{BW \times ATL \times NY} \tag{2}$$

Where Ca is the concentration of compounds ($mg.m^{-3}$) in the sampling area. IR denotes the mean inhalation rate ($m^3.h^{-1}$), ET represents the exposure time ($h.\ week^{-1}$), EF is the exposure frequency ($week.\ year^{-1}$), ED implies exposure duration (years), BW is the body weight (kg), ATL is the average lifetime (years), and NY is the exposure time in one year (day) (Yarandi et al., 2019). Using a questionnaire, the present study collected information like exposure time, body weight, exposure time, and exposure frequency. The average inhalation rate ranged from 15.7 to 16 $m^3.day^{-1}$ based on the age of the participants, according to the values shown in the EPA exposure factors handbook, and the average lifetime was 70 years (Table 4). The average concentration of the studied compounds was estimated by sampling the respiratory air of the subjects. Regarding the classification of risk levels in this method, based on prior studies, the LCR value of more than 10^{-4} is considered as "Definite Risk," the LCR value between 10^{-4} and 10^{-5} as "Probable Risk," LCR values between 10^{-5} and 10^{-6} are classified as "Possible Risk," and LCR values below 10^{-6} are categorized as "Negligible Risk." (Yarandi et al., 2019).

Also, the coefficient values utilized to calculate the carcinogenicity and health risk indices of the BREX are given in Table 5.

Non- Carcinogenic and health risk assessment

The hazard quotient (HQ) for BTEX compounds was calculated employing the following equation (Equation 3) (Kumar et al., 2020):

$$HQ = \frac{EC}{RFC} \tag{3}$$

Where RFC is the inhalation reference concentration ($mg.m^{-3}$) and EC is the concentration by inhalation ($mg.m^{-3}$) calculated utilizing the subsequent equation (Equation 4) (Kumar et al., 2020):

Table 4. The parameters values for calculating chronic daily intake (CDI)

Parameter	Unit	Minimum – Maximum (Mean)	Source
Age	Year	28 – 59 (33.75)	Questionnaire
Work experience	Year	2 – 13 (9.78)	Questionnaire
Exposure duration (ED)	Year	(30)	Questionnaire
Exposure time (ET)	Hour / Day	5 – 14 (7.39)	Questionnaire
Exposure frequency (EF)	Day / Year	(285)	Questionnaire
Inhalation rate (IR)	m^3/day	15.7 – 16	EPA Exposure Factors Handbook: 2011 Edition
Body weight (BW)	Kg	66 – 108 (81.37)	Questionnaire
Average lifetime (ATL)	Year	(70)	WHO, ACGIH

Table 5. The reference exposure level and carcinogenic unit risk values

Parameter	Value/Group				Unit	Source
	Benzene	Toluene	Ethyl Benzene	Xylene		
Weight of evidence	A	-	-	-	-	IRIS. USEPA
	1	-	2B	-	-	IARC
Inhalation slope factor (SF)	0.029	-			kg.day.mg $^{-1}$	Cal/EPA, OEHHA
Inhalation reference concentration (RFC)	0.03	5	1	0.1	mg.m^{-3}	IRIS. USEPA, OEHHA
Inhalation unit risk (IUR)	2.9×10^{-5}	-	2.5×10^{-6}	-	µg.m^{-3}	IRIS. USEPA
					µg.m^{-3}	Cal/EPA, OEHHA
Reference Exposure Level (REL)	27	830	2000	700	µg.m^{-3}	IRIS. USEPA
Occupational exposure limit (OEL) The threshold limit value (TLV)	0.1	50	100	100	ppm	ACGIH

Note: Group 1, A = Carcinogenic to humans, IRIS. USEPA = US EPA, Integrated Risk Information System,
IARC = International Agency for Research on Cancer, Cal/EPA = California Environmental Protection Agency, OEHHA = California Office of Environmental Health Hazard Assessment,
ACGIH= American Conference of Governmental Industrial Hygienists

Table 6. Climatic information of the surveyed stations

Station		Dry Temperature (C)	Relative Humidity (%)	Wind Speed (m/s)	Wind Direction	Height From Sea (m)
Station 1 (North)	Summer	33	38	8	West to East	1600
	Winter	12	14	11		
Station 2 (South)	Summer	33	38	8	West to East	1410
	Winter	17	12	11		
Station 3 (East)	Summer	32	29	8	West to East	1480
	Winter	18	13	11		
Station 4 (West)	Summer	32	29	9	West to East	1490
	Winter	18	11	11		
Station 5 (Center)	Summer	33	31	8	West to East	1450
	Winter	17	16	12		
Station 6 (Suburbs)	Summer	33	28	9	West to East	1510
	Winter	18	13	11		

$$EC = \frac{C \times ET \times ED \times EF}{ATL} \quad (4)$$

According to the World Health Organization, if the HQ risk index value is less than one, there is no significant threat of negative health effects. If the value is more than one, the probability of creating adverse effects is high (sadeghi yarandi, karimi, sajedian, ahmadi, & golbabaei, 2020).

Data analysis

Finally, the analysis of the obtained data was performed using descriptive statistics (such as mean, standard deviation, and frequency percentage), statistical tests such as the non-parametric Kruskal-Wallis test, U man Whitney and Spearman correlation coefficient at a significant level of 0.05 in SPSS software Version 26. Kolmogorov-Smirnov test was employed to evaluate the normality / non-normality of data distribution.

RESULTS AND DISCUSSION

Climatic information of all six studied stations is presented in Table 6.

Occupational exposure to BTEX compounds

The average occupational exposure to benzene, toluene, ethyl benzene, and xylene during a work shift among all participants in all studied stations in summer and winter were 83.33 - 89.33, 202 - 210.66, 126.55 - 136.83, and 168.81 - 174.83 $\mu g.m^{-3}$, respectively. In all studied stations, the levels of respiratory exposure to BTEX compounds were below the occupational exposure limit (OEL) based on occupational features. Table 7 summarizes the average concentration of BTEX in the breathing zone of the exposed workers according to the occupational units.

The highest concentration of BTEX compounds was observed in station 5, located in the center of the Karaj metropolis. After Karaj central station, the most occupational exposure to BTEX compounds was observed in the southern station of the city. Other information on the concentrations of BTEX compounds in the respiratory zone of participants is presented in Table 7. The highest benzene, toluene, ethyl benzene, and xylene concentrations were 195, 491, 354, and 431 $\mu g.m^{-3}$, respectively. The results indicated that the concentration of BTEX compounds in the respiratory zone of employees in winter was much higher, and there was a significant difference between the concentration values in summer and winter (P-Value < 0.05). There was a significant difference between the concentrations of BTEX compounds and the studied stations (P-Value < 0.05) (Table 7).

The present study was conducted to assess the carcinogenic and health risks of occupational exposure to BTEX compounds in gasoline fuel distribution stations in Karaj. Causes of diseases such as cancer have been attributed to compounds of benzene, ethylbenzene, and PAHs. Also, toluene is a compound that is suspected of causing cancer. Knowing this, regular or periodic monitoring of the release of volatile organic compounds such as BTEX from emission sources seems necessary to prevent environmental pollution and protect human health. One of the constant emission sources of mentioned compounds is fuel distribution stations. Fuel stations have increased with the number of vehicles over the past few decades. The average occupational exposure to benzene, toluene, ethyl benzene, and xylene during a work shift among all participants in all studied stations in summer and winter were 83.33 - 89.33, 202 - 210.66, 126.55 - 136.83, and 168.81 - 174.83 $\mu g.m^{-3}$, respectively, and the levels of respiratory exposure to BTEX were below the occupational exposure limit (OEL).

Previous studies show that BTEX is one of the most important compounds in the breathing air of gas station employees, which can have many adverse effects on the body. Tunsaringkarn et

Table 7. Concentrations of BTEX compounds in the breathing zone of exposed workers

Stations		N	Benzene		Toluene		Ethyl Benzene		Xylene	
			Mean Concentration ($\mu g.m^{-3}$)	Maximum Concentration ($\mu g.m^{-3}$)	Mean Concentration ($\mu g.m^{-3}$)	Maximum Concentration ($\mu g.m^{-3}$)	Mean Concentration ($\mu g.m^{-3}$)	Maximum Concentration ($\mu g.m^{-3}$)	Mean Concentration ($\mu g.m^{-3}$)	Maximum Concentration ($\mu g.m^{-3}$)
Station 1 (North)	Summer	5	28	36	85	139	51	112	79	158
	Winter	5	25	39	82	128	48	97	72	137
Station 2 (South)	Summer	5	114	141	276	399	182	267	240	406
	Winter	5	120	163	285	436	185	279	234	369
Station 3 (East)	Summer	5	95	119	232	312	115	197	185	257
	Winter	5	112	131	254	349	163	301	200	437
Station 4 (West)	Summer	5	93	144	215	341	138	257	168	249
	Winter	5	98	158	220	364	142	241	185	308
Station 5 (Center)	Summer	5	128	171	302	477	200	354	253	431
	Winter	5	133	195	311	491	207	344	266	404
Station 6 (Suburbs)	Summer	5	42	88	102	182	73	167	88	155
	Winter	5	48	93	112	206	76	194	92	158
All Stations	Summer	30	83.33	171	202	477	126.55	354	168.81	431
	Winter	30	89.33	195	210.66	491	136.83	344	174.83	437

Note: N = Number of studied workers

al.; reported that the mean BTEX concentration in gas stations was slightly higher than that of the roadside; there was no significant difference in the concentration between inner and outer areas. The mean lifetime cancer risks for workers exposed to benzene and ethylbenzene for 30 years were estimated at 1.75×10^{-4} and 9.55×10^{-7}. The estimated hazard quotients for BTEX compounds were 0.600, 0.008, 0.007, and 0.002, respectively. The most prevalent symptoms of workers were headache (61%), fatigue (29%), and throat irritation (11%), respectively (Tunsaringkarn, Siriwong, Rungsiyothin, & Nopparatbundit, 2012). Vaporization of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds pollutes the air and causes health hazards at gasoline stations; these exposures can be affected by many parameters such as seasons, air temperature, population density, etc.

In the present study the highest concentration of BTEX compounds was observed in station 5, located in the center of the city. After central station, the most occupational exposure to BTEX compounds was observed in the southern station of the city. The highest benzene, toluene, ethyl benzene, and xylene concentrations were 195, 491, 354, and 431 $\mu g.m^{-3}$, respectively. The results indicated that the concentration of BTEX compounds in the respiratory zone of employees in winter was much higher, and there was a significant difference between the concentration values in summer and winter. Among the reasons for exposure to vapors of organic compounds, we can point out that the places under study are surrounded by tall buildings, the inappropriate and indirect passage of airflow inside the site, and the continuous lack of air layers. Other reasons can be mentioned, such as improper distribution of stations in the city. In addition to the above, it seems that the most crucial factor is the service level of the stations throughout the day and night. Among the reasons for higher exposure in the station located in the center of the city, we can mention the high volume of service and higher population density. Previous studies have made it clear that the highest concentrations of volatile organic compounds are in the winter season. Lee et al. revealed that the concentration of BTEX compounds constitutes about 60% of the total concentration of volatile organic compounds. Also, their findings demonstrated that the concentration of volatile organic compounds in winter was much higher than in summer, which is in line with the results of the present study (Lee, Chiu, Ho, Zou, & Wang, 2002). In 2019, Haji Adineh et al. showed that the average concentration of volatile organic compounds in the cold season is more than in the warm season, which is due to the pollution of domestic and commercial centers combined with the creation of inversion in the city of Tehran in the cold seasons of the year. The amount of these compounds in the high traffic parts and the city center is more than in other places. By moving away from these high traffic points, the concentration of these compounds gradually decreases, which is consistent with the results of the present study (Haji Adineh, Mohammadi Rouzbehani, Payandeh, & Ghanavati, 2020). Qin et al. also showed in their research that the peak concentration of hydrocarbons is during morning traffic, which is consistent with the current study (Qin, Walk, Gary, Yao, & Elles, 2007).

The results of Barros et al.'s study on the concentrations of BTEX and its biomarkers among residents near gas stations showed that exposure to these volatile organic compounds among people who are near stations is much higher than compared to other population. Their findings indicate the potential impact on air quality of BTEX emissions from gas stations, which confirms the importance of these findings in urban planning in order to minimize the impact on health and well-being of surrounding populations (Barros et al., 2019).

Environmental concentration of 1,3-Butadiene

The results of the study of the values of the environmental concentration of BTEX in the rest rooms of the personnel are given in Table 8.

Carcinogenic risk assessment

Examining carcinogenic risk values due to occupational exposure to benzene and ethylbenzene

Table 8. Environmental concentration of BTEX in rest rooms of studied sites

Stations		**Benzene**	**Toluene**	**Ethyl Benzene**	**Xylene**
		Mean Concentration ($\mu g.m^{-3}$)	Mean Concentration ($\mu g.m^{-3}$)	Mean Concentration ($\mu g.m^{-3}$)	Mean Concentration ($\mu g.m^{-3}$)
Station 1	Summer	9	ND	12	ND
(North)	Winter	7	ND	10	ND
Station 2	Summer	11	10	16	19
(South)	Winter	13	13	19	11
Station 3	Summer	8	ND	8	15
(East)	Winter	11	ND	15	17
Station 4	Summer	5	9	9	11
(West)	Winter	9	14	14	16
Station 5	Summer	12	10	13	20
(Center)	Winter	15	13	17	23
Station 6	Summer	4	10	11	10
(Suburbs)	Winter	7	15	14	15

ND = Non-detectable

demonstrated that the mean carcinogenic risk value of benzene and ethylbenzene were 139×10^{-2} and 27×10^{-2}, respectively. The highest carcinogenic risk value due to exposure to benzene and ethyl benzene was observed in station 5, located in the center of Karaj, and the values were calculated to be 199×10^{-2} ,and 48×10^{-2}, respectively.

The results showed that 88.3% of the risk of carcinogenicity due to respiratory exposure to benzene was in the definitive range (LCR> 10^{-4}), and 11.7% was in the probable carcinogenic risk level (10^{-4}> LCR> 10^{-5}). It was also found that 50.48% of the risk of carcinogenicity due to respiratory exposure to ethylbenzene was in the definite region and 49.2% was in the probable region. 100% of the calculated carcinogenic risk levels due to respiratory exposure to benzene at stations located in the south and center of Karaj were in the definite carcinogenic area. There was a significant difference between the carcinogenic risk of BTEX compounds and the studied stations (P-Value < 0.05) (Table 9 and 10).

The mean carcinogenic risk value of benzene and ethylbenzene were 139×10^{-2} and 27×10^{-2}, respectively. The highest carcinogenic risk value due to exposure to benzene and ethyl benzene was observed in station 5, located in the center of city, and the values were calculated to be 199×10^{-2} ,and 48×10^{-2}, respectively.

Table 9. Chronic daily intake (CDI) and Life cancer risk (LCR) results in different units

Stations	Benzene	Toluene	Ethyl Benzene	Xylene
	Mean (LCR) without unit	Mean (LCR) without unit	Mean (LCR) without unit	Mean (LCR) without unit
Station 1 (North)	46×10^{-2}	-	19×10^{-2}	-
Station 2 (South)	187×10^{-2}	-	37×10^{-2}	-
Station 3 (East)	165×10^{-2}	-	31×10^{-2}	-
Station 4 (West)	138×10^{-2}	-	28×10^{-2}	-
Station 5 (Center)	199×10^{-2}	-	48×10^{-2}	-
Station 6 (Suburbs)	99×10^{-2}	-	21×10^{-2}	-
All Stations	139×10^{-2}	-	27×10^{-2}	-

Table 10. Percentage of carcinogenic risk levels for respiratory exposure to BTEX compounds

Stations	Carcinogenic Risk Level (Percent)							
	Benzene		Toluene		Ethyl Benzene		Xylene	
	Definite	Probable	Definite	Probable	Definite	Probable	Definite	Probable
Station 1 (North)	65.0	35.0	-	-	35.0	65.0	-	-
Station 2 (South)	100.0	0.0	-	-	60.0	40.0	-	-
Station 3 (East)	90.0	10.0	-	-	50.0	50.0	-	-
Station 4 (West)	95.0	5.0	-	-	45.0	55.0	-	-
Station 5 (Center)	100.0	0.0	-	-	70.0	30.0	-	-
Station 6 (Suburbs)	80.0	20.0	-	-	45.0	55.0	-	-
All Stations	88.3	11.7	-	-	50.8	49.2	-	-

The results showed that 88.3% of the risk of carcinogenicity due to respiratory exposure to benzene was in the definitive range (LCR> 10^{-4}), and 11.7% was in the probable carcinogenic risk level (10^{-4}> LCR> 10^{-5}). It was also found that 50.48% of the risk of carcinogenicity due to respiratory exposure to ethylbenzene was in the definite region and 49.2% was in the probable region. 100% of the calculated carcinogenic risk levels due to respiratory exposure to benzene at stations located in the south and center of Karaj were in the definite carcinogenic area. Moreover, the mean non-carcinogenic and health risks of occupational exposure to benzene, toluene, ethylbenzene, and xylene were 173.79, 14.19, 3.61, and 12.87, respectively. The highest non-carcinogenic risk due to respiratory exposure to benzene, toluene, ethylbenzene, and xylene was observed at Station 5 in the center of city. One of the reasons for this is the higher volume of exposure in the center and south stations. Previous studies have also shown that respiratory exposure to volatile organic compounds, even in trace amounts, can lead to the risk of carcinogenesis (Moshiran et al., 2021; Sadeghi-Yarandi, Karimi, et al., 2020). Since International Agency for Research on Cancer (IARC) has categorized benzene and ethyl benzene as carcinogenic to humans by inhalation. Because of the high slope factor of these compounds, exposure at low levels to these compounds in occupational and non-occupational environments can affect people's health. Al-Harbi et al. reported that according to a deterministic health assessment of gasoline station workers to BTEX compounds, there was a high cancer risk for workers due to exposure to benzene (4.2×10^{-4} to 1.4×10^{-3}) and ethyl benzene (1.1×10^{-4} and 3.5×10^{-4}), which were higher than the acceptable limit of 1×10^{-6}. Stochastic exposure assessment with a Monte Carlo simulation demonstrated severe carcinogenic risks to all gasoline station employees, regardless of whether they were operating the gasoline pumps or doing other tasks, like collecting money, which is in line with the present study's findings (Al-Harbi, Alhajri, AlAwadhi, & Whalen, 2020). Soltanpour et al. showed in their systematic review that exposure to benzene, toluene, ethylbenzene, and xylene (BTEX) had been reported in gas stations. Exposure to BTEX can result in adverse health outcomes in employees, such as cancer and neurological effects. The health risk assessments of exposure to BTEX could help choose appropriate control actions. The health risk assessments demonstrated that employees at the gas station are at cancer and non-cancer risk, which is in line with the present study's findings (Soltanpour, Mohammadian, & Fakhri, 2021). The study conducted by Dacherngkhao et al. also revealed that the health risk of exposure to BTEX in the vicinity of fuel tanks is higher than the allowable limit and can lead to adverse health effects (Dacherngkhao & Chaiklieng, 2019). Ultimately, the carcinogenicity risk assessment results revealed that the parameters of respiratory exposure during the work shift, exposure frequency, and working hours per week were among the participants' most critical risk factors specifying the LCR index.

Non-carcinogenic risk assessment

The mean non-carcinogenic and health risks of occupational exposure to benzene, toluene, ethylbenzene, and xylene were 173.79, 14.19, 3.61, and 12.87, respectively. The highest non-carcinogenic risk due to respiratory exposure to benzene, toluene, ethylbenzene, and xylene was observed at Station 5 in the center of Karaj. Examination of non-carcinogenic risk levels due to respiratory exposure to BTEX compounds revealed that the not acceptable risk levels due to respiratory exposure to benzene, toluene, ethylbenzene, and xylene compounds were 78.29, 61.17, 47.17, and 62.34 percent, respectively (HQ is > 1.0). There was a significant difference between the non-carcinogenic risk of BTEX compounds and the studied stations (P-Value < 0.05) (Table 11).

Also the results of the systematic review study performed by Soltanpour et al. showed that exposure to BTEX in some cities of Iran was greater than the occupational exposure limits. However, results of health risk assessments demonstrated that neurological toxicity from exposure to BTEX was significant in different cities of Iran. The health risk assessments indicated

Table 11. Non-carcinogenic risk assessment results in different units

Stations	Mean non-Carcinogenic Risk value (Hazard Quotient) (without unit)				Non-Carcinogenic Risk Level (Percent)							
	Benzene	Toluene	Ethyl Benzene	Xylene	Benzene		Toluene		Ethyl Benzene		Xylene	
					A*	NA**	A*	NA**	A*	NA**	A*	NA**
Station 1 (North)	59.45	5.18	1.46	6.96	40	60	50	50	59	41	55	45
Station 2 (South)	239.30	18.18	4.81	17.07	5	95	35	65	50	50	25	75
Station 3 (East)	211.72	15.30	3.94	12.60	20	80	41	59	55	45	36	64
Station 4 (West)	176.80	16.50	3.31	11.74	30.3	69.7	39	61	60	40	30	70
Station 5 (Center)	270.80	23.24	5.99	22.50	0	100	22	78	41	59	19	81
Station 6 (Suburbs)	84.69	6.75	2.15	6.39	35	65	46	54	52	48	61	39
All Stations	173.79	14.19	3.61	12.87	21.71	78.29	38.83	61.17	52.83	47.17	37.66	62.34

Note: * Acceptable (HQ < 1.0), ** Not Acceptable (HQ > 1.0) that workers at gas station are at health risk, which is consistent with the results of the present study (Soltanpour et al., 2021).

It should be noted that the present study was conducted cross-sectionally, and the generalization of the outcomes for the annual exposures should be made with caution. In this study, the sampling phase took 20 days to cover a complete work cycle, reduce the day-to-day deviation, and measure the actual exposure of each employee.

Finally, the results of the present study showed that BTEX concentration values and carcinogenic and health risk values are influenced by psychometric parameters and the variables of population density, location of the site, distance from the emission site, and the period in the day and night are among the effective parameters in the exposure rate. Therefore, by controlling the above variables and proper planning, a practical step can be taken to plan control measures and reduce the emission of the said pollutant. Also, the present study's findings can help predict changes in the concentration and carcinogenic and non-carcinogenic risk of these compounds in different parts of the city and determine the points and times with a high probability of exposure.

Among the strengths of the present study, we can determine the BTEX concentration values and the carcinogenic and health risks caused by exposure to the mentioned compounds at different distances from the emission source, in different parts of the city, and in hot and cold seasons of the year and for the first time in the city. He mentioned Karaj as a metropolis. Among the limitations of the present study, we can mention the impossibility of conducting interventional studies, implementing control measures, and checking the effectiveness of preventive measures due to time and economic limitations. Therefore, it is suggested that researchers conduct interventional studies in the future and present the effectiveness of the mentioned cases.

CONCLUSION

Ultimately, the results of this study revealed that according to the amount of respiratory exposure to BTEX during the work shift as the most crucial predictor of LCR and HQ indices, the values of carcinogenic and non-carcinogenic risk in the majority of participants were within the definitive and unacceptable risk levels. The mean carcinogenic risk value of benzene and ethylbenzene were 139×10^{-2} and 27×10^{-2}, respectively. The highest carcinogenic risk value due to exposure to benzene and ethyl benzene was observed in Gas station in the center of the city. One of the reasons for this issue is the high traffic of vehicles and the high population density compared to other studied stations. Therefore, some management and engineering control measures such as reducing worker's working time, making restrooms with suitable sealing for staff, providing proper personal protective equipment, and using quantitative cancer and non-cancer risk assessment method as a complementary tool in monitoring programs for respiratory exposure in the various working environment should be taken to protect the workers from the non-cancer and cancer risks.

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CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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