

# Health risk assessment of heavy metals, BTEX and polycyclic aromatic hydrocarbons (PAHs) in the workplace in a secondary oil re-refining factory

Iman Molaei<sup>1</sup>, Sayed Mostafa Khezri<sup>1,✉</sup>, Mohammad Sadegh Sekhvatjou<sup>1,3</sup>, Abdolreza Karbassi<sup>1,4</sup>, Azamalsadat Hosseini Alhashemi<sup>1,5,6</sup>

1. Department of Environmental Engineering, Tehran West Branch, Islamic Azad University, Tehran, Iran
2. Environment and Energy Department, Science and Research Branch, Islamic Azad University, Tehran, Iran
3. Department of Environmental Engineering, Science and Research Campus, Islamic Azad University, Ahvaz, Iran
4. School of Environment, College of Engineering, University of Tehran, Tehran, Iran
5. Department of Earth and Environmental Science, Irving K. Barber School of Arts and Sciences, University of British Columbia, Okanagan Campus, 1177 Research Road, Kelowna, BC, V1V 1V7, Canada
6. Department of Environmental Pollution, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran

**Date of submission:** 23 Dec 2019, **Date of acceptance:** 27 Jan 2020

## ABSTRACT

The present study aimed to evaluate the health risk of heavy metals (iron, zinc, cadmium, arsenic, nickel, lead, and mercury), benzene, toluene, ethylbenzene and xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs) in the workplace in a secondary oil re-refining factory. In this descriptive, cross-sectional study, samples were collected and analyzed using the NIOSH 1501 method at eight sampling points with determined concentrations of BTEX, 16 $\Sigma$  PAHs, and heavy metals. The concentration of each pollutant was evaluated based on the type of workers (packaging/filtration). The risk assessment of the contaminants was carried out using the RAIS software, and the risk of non-carcinogenic compounds was estimated based on the reference respiratory concentration ( $\text{mg}/\text{m}^3$ ). The results showed that the lifetime cancer risk index (LCR) cumulative risk of the heavy metals was within the definitive risk range at all the sampling points. The highest carcinogenic risk of LCR belonged to arsenic at sampling point H (filtration chamber), and the highest cumulative carcinogenic risk of the total contaminants in the environmental sampling points belonged to sampling point H. At all the sampling points, the LCR carcinogenic risk accumulation for the hydrocarbon compounds was within the definitive range. The maximum cumulative lifetime cancer risk for the hydrocarbon compounds was evaluated in filtration (point B), and the most hazardous carcinogens were arsenic, benzo(a)pyrene, and naphthalene. The proposed risk assessment method was observed to be comprehensive, and its results could be used for corrective and controlling measures and the prioritization of risk reduction resources.

**Keywords:** Risk assessment, Heavy metals, BTEX, Polycyclic aromatic hydrocarbons, Volatile organic compounds

## Introduction

✉ Sayed Mostafa Khezri  
Khezri@Sharif.Edu

**Citation:** Molaei I, Khezri S M, Sekhvatjou M S, Karbassi A, Hosseini Alhashemi A. Health risk assessment of heavy metals, BTEX and polycyclic aromatic hydrocarbons (PAHs) in the workplace in a secondary oil re-refining factory. J Adv Environ Health Res 2020; 8(2): 79-94

Working with materials in various industries is an important stage of the chemical life cycle, which poses irreversible risks to the employees. Today, the health and safety of humans in the workplace have become a greater concern due to the presence of various hazardous chemicals.<sup>1, 2</sup> Workplace chemical

pollutants include gases, vapors, and particulates, each of which is associated with specific hazards, and their adverse effects depend on the type of chemical, entry route, duration of contact, and their concentration. Excessive exposure to these pollutants in workplaces and industries leads to severe diseases. In recent years, significant changes have occurred in chemicals, processes, and types of activities in industries, thereby increasing the number of high-risk workers for chemical contamination.<sup>3,4</sup>

Organic pollutants, especially volatile organic compounds (VOCs), are important pollutants, some of which have carcinogenic effects. VOCs have various generation resources and could easily be released into the environment and work environments.<sup>5</sup> The main pathways for exposure to these compounds are inhalation, swallowing, contact with the eyes, and absorption by the skin.<sup>6</sup> Aromatic compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX) have been identified as the most frequent and important volatile organic compounds in ambient and industrial environments, which may remarkably affect human health and air quality.<sup>7,8</sup> Based on the classification of the United States Environmental Protection Agency (USEPA), these compounds are known as priority pollutants.<sup>9</sup> Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbon compounds, which have observed an increasing trend in the air around industrial areas, such as petrochemicals, refineries, and oil industries. PAHs could disperse in all sectors of the environment through natural and anthropogenic resources,<sup>4</sup> intensely threatening human health<sup>10</sup> due to properties such as toxicity, high stability, aggregation, biotransformation, carcinogenesis, and mutagenesis.<sup>11</sup> Since these compounds are of a lipophilic nature, they have a high tendency to accumulating in living organisms, which in turn leads to toxicity.<sup>12</sup> Some human carcinogens among PAHs include benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene,

chrysene, dibenz(a,h) anthracene, and indeno(1,2,3-cd)pyrene.<sup>13</sup>

In addition to BTEX and PAHs, heavy metals are another group of pollutants, the annual contamination rate of which has been reported to be on the rise mainly due to industrialization at higher concentrations than their natural or background levels. Among various heavy metals, lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), and cobalt (Co) are considered particularly harmful. These elements have a long half-life and the ability to accumulate in the human body. Numerous health problems are associated with heavy metal contamination, and scientists have observed acute toxic effects on various organs of laboratory animals, such as the kidneys, liver, pancreas, and lungs (through respiration).<sup>14</sup>

To achieve the health goals regarding the protection of the workforce, it is essential to examine their exposure to chemicals and risks associated with harmful substances, such as heavy metals.<sup>15</sup> In order to decide on the control measures to protect employees against the adverse effects of chemicals, it is critical to assess the health risks of exposure to chemicals in particular. The risk assessment process is considered to be the key solution to the evaluation of the risks associated with occupational and environmental exposure to chemicals.<sup>16,17</sup> In assessing the health risk of exposure to chemicals and toxicants, the level of risk to the users is specified, and measures are taken to protect personnel against hazardous chemicals. According to the current national rules and regulations, industrial workers and personals must only be exposed to safe chemicals.<sup>18</sup>

The assessment of exposure to chemical compounds implies the identification and quantification of their sources, as well as the pathways for their entry to the human body and their adverse effects on human health.<sup>19</sup> Such health risks are particularly high in the workers involved in secondary oil re-refining factories due to the emissions of harmful pollutants, such as heavy metals, BTEX, and PAHs in the

workplace. Therefore, secondary oil re-refining factories regarded as important anthropogenic chemical compound emission sources.<sup>18</sup>

Regarding the estimation of lung cancer risk associated with PAH exposure through inhalation, the World Health Organization (WHO) has suggested the unit risk of  $8.7 \times 10^{-2}$  ( $\mu\text{g}/\text{m}^3$ ) for lifelong PAH exposure (70 years), assuming one is exposed to benzo[a]pyrene equivalent concentration of  $1 \mu\text{g}/\text{m}^3$ .<sup>20</sup> It is notable that the mentioned unit risk has been proposed for lifetime exposure and adopted for assessing the exposure of adults to ambient atmospheric PAHs.<sup>21</sup>

Today, many international organizations, including the WHO, USEPA, and United States Food and Drug Administration (USFDA) consider the application of quantitative risk assessment to be the basis for legislation on chemicals. The lifetime cancer risk index (LCR) is commonly used to estimate the risk of carcinogenic pollutants, which has been introduced as an indicator of the increased risk of cancer due to specific exposures. In addition, the hazard quotient (HQ) is employed to estimate the risk of exposure to non-carcinogenic pollutants, and the HQ equation represents the ratio of exposure to certain levels of a substance that do not have adverse effects.<sup>22</sup> In the present study, LCR was calculated for the compounds with approved inhalation unit risk factor (IUR)

values based on the USEPA risk assessment method, and the HQ was estimated for the compounds with approved RfC values.

Workers at secondary oil re-refining factories are constantly exposed to various materials, such as heavy metals, BTEX, and PAHs. However, no studies have been focused on the health risk assessment of these materials to date. Therefore, their examination through a risk assessment process to identify and calculate the risk of each chemical produced in these plants (BTEX and PAHs) is considered essential to prioritizing the implementation of control measures.

The present study aimed to evaluate the health risk of heavy metals, BTEX, and PAHs in a secondary oil re-refining factory.

## Materials and Methods

### Study area

This cross-sectional study was conducted in Garmsar Industrial Town, Iran. Garmsar is located in the west of Semnan province (coordinates:  $34^\circ 28' 30''\text{N}$  and  $51^\circ 52'$  to  $52^\circ 55'\text{E}$ ), covering an area of  $10,686 \text{ km}^2$ . Fajr Industrial Estate is located within 10 km from Garmsar-Tehran road in the western part of Garmsar city (coordinates:  $35^\circ 14' 56''\text{N}$   $52^\circ 14' 2''\text{E}$ ), covering an area of approximately 300 hectares per km (Fig. 1). The area of Fajr Industrial Estate is 210 hectares, which consists of 293 deployed units and 60 active units.

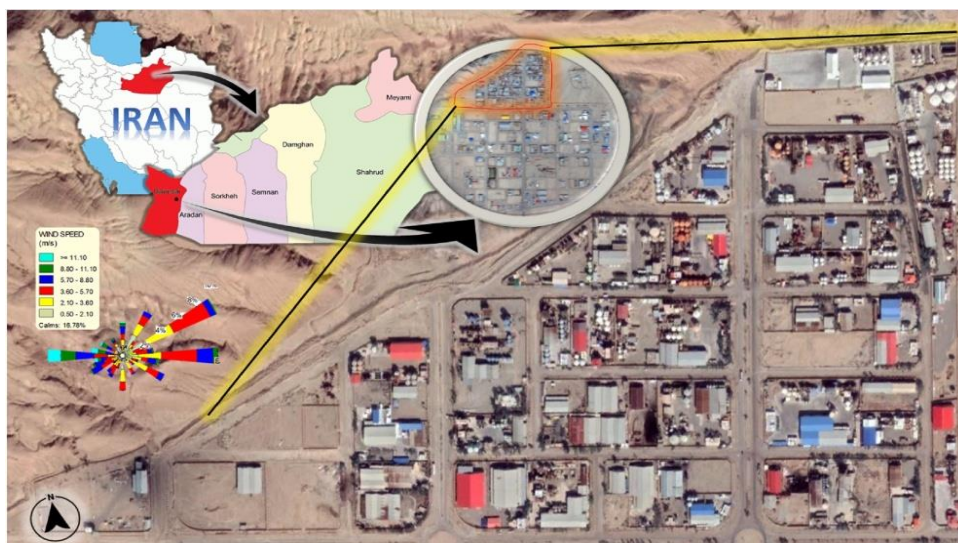


Fig. 1. Map of Garmsar city and location of secondary oil refineries factories

### ***Air sampling and analytical procedures***

Air samples were collected to estimate the concentrations of BTXS, PAHs, and heavy metals in the selected sites using the methodology 1501, proposed by the US National Occupational Health and Safety Research Center (NIOSH 1501).<sup>23</sup> Considering the similarity of the methods and materials employed in these factories to re-refine the used oils, eight sampling points were selected, including points A (staff management and administrative building), B (packing, labeling salons, and cans, barrels, and oil storerooms), C (used [burned] oil inlet units), D (first distillation and acidification units [heat: 300-400 °C]), E (second distillation unit [heat: 200 °C]), F (filtration and collection units of refined oils), G (open-area units for painting the barrels and metal cans of oil), and H (entrance of Tizro Grease Factory). The samples were collected at each sampling point (used oil re-refining plant) from ambient air during spring-winter 2018. Sampling was performed at 8:00 AM-2 PM at 6 h intervals (maximum factory production) using SKC Universal Pumps and SKC constant flow personal sampling pumps (models: PCXR4, PCXR8, and 44XR).

Sample collection was carried out at the height of 1.6 meters above the ground (human breathing height) using SKC personal sampling pumps (SKC, model: 224-44 MTX, USA) at the flow rate of 0.2 l/min. The sampling lasted 2-3 h, and the air was passed through a sorbent tube containing coconut shell charcoal (SKC; 226-01). At all the sampling sites, the field blanks were obtained as well. The tubes were preserved at the temperature of -18 °C for 48 h before the analysis. The absorbent in the two sectors of the tube (front and back) was poured into two separate vials, and one milliliter of solvent (CS<sub>2</sub>) was added to each vial. Following that, the vials were let stand for 30 min with occasional shaking. Afterwards, 2 µL of the extracted solution was injected into a gas chromatography device equipped with a flame ionization detector (GC/FID; Agilent GC, 7890 A, USA). The running time of GC for the

analysis of BTEX and PAHs was 4.66 min. The injector and detector temperatures were set at 160 and 300 °C, respectively. The temperature of the oven was initially maintained at 40 °C for 1 min, reaching 15 °C per minute and remaining constant at 80 °C for 1 min.

Active sampling methods were employed to estimate the concentration of heavy metals at the secondary oil re-refining plant. To this end, SKC pumps were used with low flow rates by employing a 37 mL fiberglass membrane filter; the filter had been previously weighed. After transferring the collected filters to the laboratory in special holders, the concentrations of the heavy metals (iron, zinc, cadmium, arsenic, nickel, lead, and mercury) were separately estimated using the acid digestion method and inductively coupled plasma spectroscopy (model: PQ9000, Elite, Germany).

### ***Health risk assessment***

In order to investigate the effects of the heavy metals on human health, the risk assessment methods developed by health and environmental authorities (EPA, Agency for Toxic Substances and Disease Registry (ASTDR) and Risk Assessment Information System (RAIS)) were used. After determining the concentration of each pollutant and heavy metal in the air of the study area, the guidelines of the USEPA, which were published during the integrated risk information system (IRIS) in 2005, were used to determine the exposure concentration of each individual in the study area with these substances through various ways (USEPA 2005). The amount of exposure through inhalation was calculated based on 8 h of working per day for the factory workers and 24 h per day for the residents.

To calculate the risk of the studied contaminants, the contaminants with the reported values of carcinogenic and non-carcinogenic risks reported by the EPA were initially determined. According to the information in Table 1, the EPA has approved the non-carcinogenic risk of the contaminants with reported reference respiratory concentration



(RfC) values and carcinogenic risks for the pollutants with IUP values. As for the contaminants for which the IUR and RfC values have not been reported, it was not possible to calculate the carcinogenic and non-carcinogenic risks. Therefore, these compounds were excluded from the risk assessment process in the final reports.

**Risk assessment of carcinogenic pollutants**

The calculation of carcinogenic risk required estimating the mean concentration of the pollutants and slope factor (SF) of these compounds. LCR was calculated by multiplying the SF by the amount of the chronic daily intake (CDI) of each compound by Eq. 1.

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

SF is an acceptable range that makes it possible to generate a response per unit of the consumed chemicals within a lifetime (mg/kg/day). In the present study, the CDI was calculated in mg/kg/day using Eq. 2:

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

where, *C* is the mean concentration of the contaminant (mg/m<sup>3</sup>), *IR* shows the inhalation rate (m<sup>3</sup>/h), *ED* represents the exposure duration (hour/week), *EF* is the exposure frequency (week/year), *LE* shows the work experience of the individual (year), *BW* is the body weight (kg), *ATL* is the mean lifetime, and *NY* represents the number of the days in the year. Data on the individual history, exposure duration, and frequency of exposure were collected from the available documents at the industrial site. The inhalation rate was determined to be 0.875 m<sup>3</sup>/h, and the mean body weight was 70 kg. The mean lifetime was 70 years, and the number of the days per year was 365 days. In addition, the concentrations of the compounds were determined using the mentioned methods, and their annual mean values were also calculated for the risk assessment. The SF was extracted from the recommended values by the USEPA and RAIS. The carcinogenic results were not calculated individually and were determined based on the assumption of a healthy adult with

the working characteristics obtained from the EPA website.

Table 1. Inhalation unit risk factor (IUR) and inhalation reference concentration (RfC) of studied pollutants

Chemical	VOCs	IUR (µg/m <sup>3</sup> )	RfC (mg/m <sup>3</sup> )
Acenaphthene	Yes	-	-
Acenaphthylene	Yes	-	-
Anthracene	Yes	-	-
Benz[a]anthracene	Yes	0.00006	-
Benzo[a]pyrene	No	0.0006	2E-06
Benzo[b]fluoranthene	No	0.00006	-
Benzo[g,h,i]perylene	No	-	-
Benzo[k]fluoranthene	No	0.000006	-
Chrysene	No	6E-07	-
Dibenz[a,h]anthracene	No	0.0006	-
Fluoranthene	No	-	-
Fluorene	Yes	-	-
Indeno[1,2,3-cd]pyrene	No	0.00006	-
Naphthalene	Yes	0.000034	0.003
Phenanthrene	Yes	-	-
Pyrene	Yes	-	-
Arsenic, Inorganic	No	0.0043	1.5E-05
Cadmium	No	-	-
Iron	No	-	-
Lead and Compounds	No	0.000012	-
Mercury (elemental)	Yes	-	0.0003
Nickel Refinery Dust	No	0.00024	1.4E-05
Zinc and Compounds	No	-	-
Benzene	Yes	7.8E-06	0.03
Ethylbenzene	Yes	2.5E-06	1
Toluene	Yes	-	5
Xylenes	Yes	-	0.1

**Acceptable risk range of carcinogenic compounds**

As recommended by the WHO, the LCR of 10<sup>-5</sup>-10<sup>-6</sup> and lower is considered an acceptable reference range. According to the WHO, the recommended risk for these compounds is within the range of 10<sup>-5</sup>-10<sup>-6</sup>, and the lower values are considered acceptable, with the higher values regarded unacceptable. Considering the ability of the utilized software to classify and display the outputs with specific color codes, the comparison was presented in more detail, and the risk intensity of the contaminants could be detected with four color codes (Table 2).

Table 2. LCR range and color codes for each range

Risk range	Color code
Risk > 0.01	Black
Risk > 0.0001	Red
Risk > 0.000001	Yellow
Risk < 0.000001	No color

### Risk assessment of the non-carcinogenic compounds

In the present study, the risk of the non-carcinogenic compounds was estimated based on the RfC and expressed in  $\text{mg}/\text{m}^3$ . Moreover, the HQ was calculated by dividing the concentration of the contaminant by the RfC of the same contaminant using Eq. 3:

$$HQ = CC/RfC \quad (3)$$

where, HQ shows the hazard quotient (health risk or non-carcinogenic effects), EC or CC represents the annual mean concentration of the pollutant ( $\text{mg}/\text{m}^3$ ), and RfC is the reference pollutant concentration ( $\text{mg}/\text{m}^3$ ) as the concentration of the pollutants without non-carcinogenic health effects during exposure. In addition, the CC values were obtained using Eq. 4:

$$CC = \frac{CA \times ET \times EF \times ED}{LT \times 365(\text{days/year}) \times 24(\text{hours/day})} \quad (4)$$

where, ED is the exposure per year (work experience), EF shows the exposure frequency per day, ET denotes the exposure duration (hour/day), and LT is the mean life expectancy (year). It is notable that the exposure rate was the annual mean concentration, and the daily intake dose for the non-carcinogenic materials was indicated by EC or CC, while the carcinogenic compounds were indicated by CDI.

### Acceptable risk of the non-carcinogenic compounds

According to the literature,  $HQ > 1$  indicates that the concentration of the volatile organic compounds VOCs is higher than the standard concentration levels, leading to concerns about the general health of populations, while  $HQ \leq 1$  indicates that the VOCs concentrations are below the RfC to exert adverse effects and expected to cause no harm to humans. As a result,  $HQ \leq 1$  has been recommended by the WHO and considered acceptable for non-carcinogenic pollutants. This classification was shown as the color code in the outputs of the software, which made it faster and easier to identify the high-risk pollutants (Table 3).

Table 3. RfC range and color codes for each range

Hazard Index or Quotient	
Danger range	Color code
HQ or HI < 0.1	Colorless
HQ or HI > 0.1	Purple
HQ or HI > 1	Blue

### Cumulative risk calculation

The cumulative risk for the carcinogenic compounds was determined by calculating the sum of the LCR of each pollutant using Eqs. 5 and 6.

$$R = \sum LCR \quad (5)$$

The risk index for the non-carcinogenic compounds, which represents the cumulative risk, was the sum of the hazard quotient of each non-carcinogenic pollutant, as shown in Eq. 6.

$$R = \sum HQ \quad (6)$$

## Results and Discussion

### BTEX concentrations

Table 4 shows the mean values of BTEX in all the sampling sites. As is observed, the highest and lowest mean concentrations of BTEX were observed at sampling points D ( $94.88 \mu\text{g}/\text{m}^3$ ) and F ( $85.30 \mu\text{g}/\text{m}^3$ ), respectively. Among the four BTEX compounds (benzene, toluene, ethylbenzene, and xylene), the highest value belonged to benzene at sampling point D ( $45.33 \mu\text{g}/\text{m}^3$ ). In addition, ethylbenzene had the lowest concentration with the maximum concentration of  $5.367 \mu\text{g}/\text{m}^3$  at sampling point D.

Table 4 shows the mean values of BTEX based on the type of occupation (packing [a] and filter cake [b]). Accordingly, the highest and lowest mean BTEX concentrations were observed in filter cake ( $108.24 \mu\text{g}/\text{m}^3$ ) and packing ( $88.33 \mu\text{g}/\text{m}^3$ ), respectively. Between the mentioned occupations, the highest concentration belonged to benzene in filter cake ( $50.33 \mu\text{g}/\text{m}^3$ ) and packing ( $42.0 \mu\text{g}/\text{m}^3$ ).

The risk assessment results regarding the LCR and HQ based on the sampling location and process outputs are presented in separate tables. In order to evaluate the results of the risk assessment, the final results based on the

pollutants were divided into three categories of heavy metals, BTEX compounds, and PAHs,

which were also presented in a separate table.

Table 4. Mean changes in concentrations of BTEX (benzene, toluene, ethylbenzene, and xylene) pollutants at Tizro grease oil re-refining plant of Garmsar ( $\mu\text{g}/\text{m}^3$ )

Study area		Parameters				
		Benzene	Toluene	Ethylbenzene	Xylenes	BTEX
A	Mean	36.5	32.17	4.41	20	93.08
	SD	7.05	7.69	1.1	2.35	17.43
B	Mean	36.41	30.5	4.42	19.33	90.67
	SD	7.56	7.52	0.5	2.89	17.51
C	Mean	36.31	31.35	4.33	18.83	90.8
	SD	8.72	9.13	1.19	2.59	20.44
D	Mean	36.5	32.25	4.83	20.5	94.08
	SD	8.15	8.161	0.79	3.31	19.48
E	Mean	34.32	29.75	4.5	18	86.58
	SD	7.07	6.62	0.43	3.91	17.46
F	Mean	33.92	30.92	4.41	15.75	85
	SD	5.37	4	0.42	3.18	14.51
G	Mean	35	29.58	4.5	18.33	87.41
	SD	6.31	7.36	0.79	2.68	16.28
H	Mean	35.08	30.58	4.66	19.25	89.58
	SD	6.22	7.78	0.60	1.95	16.12
a*	Mean	35.82	27.42	6.29	18.77	88.32
	SD	6.77	3.60	1.33	2.79	14.15
b**	Mean	45.42	33.37	8.80	20.65	108.24
	SD	6.34	5.15	1.84	6.97	20.12

\* (a) Packing; \*\* (b) Filter cake

### LCR, HQ, and non-carcinogenic risk of BTEX compounds

Tables 5 and 6 show the results of the LCR assessment of benzene, ethylbenzene, and their cumulative risk. The results of the long-term LCR of benzene indicated that the carcinogenic risk of benzene was within the possible risk range in all the sampling sites, while the maximum and minimum values were determined at sampling points B and F, respectively. Furthermore, the LCR results of ethylbenzene at sampling points A, B, C, D, E, F, G, and H were classified within the risk-free range. At sampling points A and B, the LCR results were higher and within the possible risk range, while the maximum and minimum LCR values of ethylbenzene were observed at sampling points B and C, respectively.

The LCR values of the BTEX compounds are presented in Tables 5 and 6 and were within the possible range in all the sampling sites. On the other hand, the maximum and minimum LCR of the BTEX compounds were observed

at sampling points B and F, respectively.

Tables 5 and 6 show the HQ values of the BTEX components (benzene, ethylbenzene, toluene, and xylene). The calculated non-carcinogenic HQ of benzene was within the acceptable range at all the sampling points, while close to the unacceptable range. Moreover, the HQ value of ethylbenzene was within the risk-free range in all sampling sites, and the maximum and minimum values were reported at sampling points B and C, respectively. In the case of toluene, the calculated values were also within the risk-free range, and the results were very close. The HQ and non-carcinogenic risk associated with xylene were also within the risk-free range.

According to the findings, the cumulative risk of the non-carcinogenic BTEX compounds was within the acceptable range, with the highest value calculated at sampling point B and the lowest value observed at sampling point F. Since benzene is a definitive human carcinogen and classified in Group I of

the International Agency for Research on Cancer (IARC), it is associated with a high-risk level, and exposure to benzene could have irreparable effects on human health. As such, the permissible exposure limit to this pollutant is extremely low (0.5 ppm).<sup>24</sup> In a study conducted by Colman Lerner *et al.* in Argentina, benzene risk in repair jobs was reported to be definitive, while the risk of

benzene was observed to be probable *in-vitro*.<sup>25</sup> Moreover, Rahimnejad *et al.* conducted a study in an oil-dependent chemical industry, claiming that the LCR of benzene was definitive in 13 complexes and probable in eight complexes, and in all the studied complexes, the risk of benzene was higher than the recommended limits by the WHO.<sup>22</sup>

Table 5. LCR and HQ of BTEX compounds

Chemical	A		B		C		D		E		F		G		H	
	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR
Benzene	0.278	2.32E-05	0.277	2.32E-05	0.277	2.31E-05	0.278	2.32E-05	0.261	2.18E-05	0.258	2.16E-05	0.266	2.23E-05	0.267	2.23E-05
Ethylbenzene	0.0011	9.85E-07	0.001	9E-07	0.00099	8.83E-07	0.001	9E-07	0.001	9.17E-07	0.001	9E-07	0.001	9.17E-07	0.0011	9.51E-07
Toluene	0.0015	-	0.0014	-	0.00143	-	0.0015	-	0.0014	-	0.0014	-	0.0014	-	0.0014	-
Xylenes	0.0468	-	0.0441	-	0.043	-	0.0457	-	0.0411	-	0.036	-	0.0419	-	0.0439	-
*Total Risk/Hi	0.327	2.42E-05	0.324	2.4E-05	0.322	2.4E-05	0.326	2.4E-05	0.305	2.3E-05	0.296	2.25E-05	0.311	2.3E-05	0.313	2.3E-05

Table 6. LCR and HQ of BTEX compounds based on type of occupation

Chemical	a*		b**	
	HQ	LCR	HQ	LCR
Benzene	0.273	2.28E-05	0.346	2.89E-05
Ethylbenzene	0.0014	1.28E-06	0.002	1.79E-06
Toluene	0.0013	-	0.0015	-
Xylenes	0.0406	-	0.0495	-
*Total Risk/Hi	0.316	2.4E-05	0.399	3.1E-05

\* (a) Packing and \*\* (b) Filter cake

### PAH concentrations

The mean concentrations of 16 target PAHs ( $\Sigma 16$ PAHs in the atmospheric ambient air samples obtained from the secondary oil re-refining plant in sampling sites A-G) were as follows: 43.5-2,586.1 ng/m<sup>3</sup> (mean: 411.7 ng/m<sup>3</sup>), 42.5-2,630 ng/m<sup>3</sup> (mean: 410.93 ng/m<sup>3</sup>), 40.5-2,432 ng/m<sup>3</sup> (mean: 398.20 ng/m<sup>3</sup>), 49-2,806.6 ng/m<sup>3</sup> (mean: 440.72 ng/m<sup>3</sup>), 48-2,638 ng/m<sup>3</sup> (mean: 436.83 ng/m<sup>3</sup>), 38.5-2,298 ng/m<sup>3</sup> (mean: 393.77  $\mu$ g/m<sup>3</sup>), 40.5-2,262  $\mu$ g/m<sup>3</sup> (mean: 390.93  $\mu$ g/m<sup>3</sup>), and 45-2,593.3  $\mu$ g/m<sup>3</sup> (mean: 417.65 ng/m<sup>3</sup>) (Table 7). According to the information in Table 7, the highest concentration of PAHs (mean:  $\Sigma 16$ PAHs = 440.72 ng/m<sup>3</sup>) was observed at sampling point D. Since the oil temperature increased to 400 °C in the first distillation section (sampling point D), the molecular bonds between the lighter materials in the oil were destroyed, and all the solvents and lighter materials were removed from the oil and transferred to cooling tanks or distillers, where

acidification was performed. In these conditions, the leakage and removal of the VOCs (e.g., PAHs from the furnaces, pipes, and oil transfer joints) may have increased. The lowest mean concentration of  $\Sigma 16$ PAHs (390.93 ng/m<sup>3</sup>) was observed at sampling point G, which is an open area for the coloring of oil barrels and metal cans (Table 7).

In the present study, it was expected that proximity to emission sources would significantly affect the PAH levels, and lower concentrations were observed in the air samples obtained from the open area for the painting of the oil barrels and metal cans (sampling point G). Furthermore, the highest and lowest mean concentrations of PAHs belonged to naphthalene (2,186.23  $\mu$ g/m<sup>3</sup>) and indeno[1,2,3-cd]pyrene (47.37  $\mu$ g/m<sup>3</sup>). This finding is in line with the results reported by Salaudeen *et al.*<sup>26</sup> and Liu *et al.*<sup>27</sup>

Table 7 shows the mean PAH values based on the type of occupation (a: packing, b) filter cake). Accordingly, the highest mean concentrations of PAHs were observed in filter cake (496.63 ng/m<sup>3</sup>), while the lowest mean concentrations of PAHs were observed in packing (468.58 ng/m<sup>3</sup>). Moreover, naphthalene concentration was highest among  $\Sigma 16$ PAHs in both occupations, so that the highest mean concentration in filter cake was 2,552.4 ng/m<sup>3</sup>, while it was 2,416.8 ng/m<sup>3</sup> in packing.



Table 7. Mean concentrations of PAHs in Tizro Grease Oil re-refining plant of Garmsar at various sampling points

Study area	Parameters	Parameters									
		A	B	C	D	E	F	G	H	a*	b**
Naphthalene	Mean	2183	2201	2118	2309.41	2286	2126.16	2098.	2168.3	2416.8	2552.4
	SD	311.51	325.9	341.5	465.08	397.3	201.14	190.76	320.1	395.64	405.73
Acenaphthylene	Mean	1095.1	1090	1059	1150.29	1142	1062.66	1047.8	1083	1230	1306.9
	SD	174.41	181.8	173.9	243.67	220.5	124.59	116.06	168.04	184.2	189.49
Acenaphthene	Mean	779.2	775.3	754	816.62	812.1	756.12	746.3	770.04	878.91	933.83
	SD	115.7	120	113.4	161.9	146.7	79.88	73.7	111.31	124.43	127.85
Fluorene	Mean	103.54	103.1	100.5	107.87	107.7	100.54	99.2	101.79	130.8	139.0
	SD	18.57	19.11	17.39	23.53	23.23	13.75	13.36	17.84	14.15	14.31
Phenanthrene	Mean	362.5	360.7	351	379.04	377.6	351.58	347.5	357.91	426.4	453.2
	SD	58.79	60.72	56.65	78.8	74.06	41.85	39.568	55.96	53.41	54.82
Anthracene	Mean	282.16	279.6	271.7	308.58	305.9	262.4	263.75	298.2	292.3	310.5
	SD	30.93	29.35	22.96	38.8	36.3	15.49	19.1	52.96	31.61	32.1
Fluoranthene	Mean	357	354.1	344.4	397.5	392.7	328.25	330.41	382.45	409.8	435.3
	SD	41.72	44.23	40.3	32.27	30.55	44.71	35.43	26.02	49.4	50.73
Pyrene	Mean	535.41	530.4	516.8	597.12	588.1	491.25	493.95	574.9	613.4	641.5
	SD	64.72	69.0	62.3	51.71	48.52	70.17	56.3	39.53	77.04	80.46
Benz[a]anthracene	Mean	285.54	283.1	275.3	317.83	314.1	262.9	264.8	305.41	334.2	355.3
	SD	32.56	35.35	31.10	24.52	23.78	35.12	27.36	20.83	37.93	38.95
Chrysene	Mean	111.62	110.1	107.3	123.58	122.5	102.75	103.91	118.21	137.1	146.1
	SD	11.54	12.86	10.91	7.51	7.81	12.19	9.12	7.764	13.45	14.01
Benzo[b]fluoranthene	Mean	86.75	85.95	83.5	95.67	95.45	80.42	80.66	91.92	109.5	116.3
	SD	8.62	9.36	8.26	5.83	5.77	9.07	7.22	5.9	10.13	10.34
Benzo[k]fluoranthene	Mean	100.5	99.5	96.79	111.37	110.4	92.95	93.79	106.7	126.1	134.2
	SD	10.92	11.26	9.51	6.88	6.74	10.81	8.33	7.32	12.00	12.05
Benzo[a]pyrene	Mean	120.75	120.1	116.4	133.75	132.8	112.12	112.79	128.95	150.6	160.1
	SD	12.97	13.74	11.9	8.88	9.18	12.94	10.43	8.89	14.58	14.94
Dibenz[ah]anthracene	Mean	51.08	50.58	49.2	56.42	56.25	47.45	47.62	53.67	69.7	74.1
	SD	4.81	5.25	4.51	2.87	2.75	4.74	3.78	3.49	5.87	6.03
Benzo[ghi]perylene	Mean	86.04	84.95	82.5	94.87	94.45	79.41	80.25	91	110.7	117.8
	SD	8.44	9.42	8.26	5.66	5.77	9.07	6.75	5.97	10.22	10.37
Indeno[1,2,3-cd]pyrene	Mean	47.04	46.54	44.87	51.75	51.33	43.375	44.21	49.83	65.41	69.62
	SD	4.14	4.58	4.09	2.5	2.82	4.82	3.31	3.38	5.377	5.693

(ng/m<sup>3</sup>; \*a: Packing, \*\*b: Filter cake)

### LCR, HQ, and non-carcinogenic risk of PAHs

PAHs are pollutants with similar properties and nature to BTEX. Among the studied hydrocarbon compounds, acenaphthene, acenaphthylene, anthracene, benzoyl(ghi)perylene, fluoranthene, fluorene, phenanthrene, and pyrene were excluded from the calculation table since no confirmed studies were available for the determination of IUR and RfC. On the other hand, benzene(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, indeno(1, 2, 3-cd)pyrene, and naphthalene had carcinogenicity and have been confirmed by validated studies. Tables 8 and 9 show the reported respiratory IUR values of these compounds, which were included in the risk assessment calculations in the present study. Accordingly, the LCR of benz(a)anthracene was within the definitive risk range at all the sampling points, with the maximum value

observed at sampling point B, and the minimum value observed at sampling point F. In addition, the LCR of benzo(a)pyrene was within the definitive risk range at all the sampling points, with the maximum and minimum values observed at sampling points B and F, respectively. The obtained results were similar in the case of benzo(b)fluoranthene, and the LCR at all the sampling points was within the definitive risk range. The maximum and minimum values were reported at sampling points B and F, respectively. Although the LCR values of benzo(k)fluoranthene and chrysene were lower than the other pollutants in this group, they were within the possible risk range at all the sampling points, with the highest values observed at sampling point B, and the minimum value reported at sampling point F.

According to the obtained results, the calculated LCR value for dibenz(a,h)anthracene at all the sampling points was within the definitive risk range,

with the maximum risk value observed at sampling point B, and the minimum value reported at sampling points F and G. Furthermore, the LCR of indeno(1, 2, 3-cd)pyrene at all the sampling points exceeded

the acceptable range and was within the definitive cancer risk range. The maximum and minimum values were observed at sampling points B and F, respectively.

Table 8. LCR and HQ of PAHs

Chemical	A		B		C		D		E		F		G		H			
	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR		
Benz[a]anthracene	-	0.0014	-	0.00138	-	0.00135	-	0.00134	-	0.00154	-	0.00155	-	0.00129	-	0.00132	-	0.00149
Benzo[a]pyrene	13800	0.00591	13700	0.00587	13300	0.00570	15200	0.00650	15300	0.00654	12800	0.00549	12900	0.00552	14700	0.00631		
Benzo[b]fluoranthene	-	0.000424	-	0.000421	-	0.000409	-	0.000467	-	0.000468	-	0.000493	-	0.000395	-	0.000455		
Benzo[k]fluoranthene	-	4.92E-05	-	4.87E-05	-	4.74E-05	-	0.000054	-	5.45E-05	-	4.55E-05	-	4.59E-05	-	5.22E-05		
Chrysene	-	5.46E-06	-	5.39E-06	-	5.25E-06	-	5.99E-06	-	6.05E-06	-	5.03E-06	-	5.08E-06	-	5.78E-06		
Dibenz[a,h]anthracene	-	0.00257	-	0.00247	-	0.00241	-	0.00275	-	0.00276	-	0.00236	-	0.00233	-	0.00263		
Indeno[1,2,3-cd]pyrene	-	0.00023	-	0.000228	-	0.00022	-	0.000251	-	0.000253	-	0.000212	-	0.000216	-	0.000244		
Naphthalene	166	0.00605	168	0.0061	161	0.00587	174	0.00634	176	0.0064	162	0.00589	160	0.00582	165	0.00601		
*Total Risk/HI	14000	0.0164	13900	0.0164	13500	0.0159	15300	0.0177	15400	0.0179	13000	0.0155	13000	0.0155	14900	0.017		

Table 9. LCR and HQ of PAHs based on type of occupation

Chemical	a*		b**	
	HQ	LCR	HQ	LCR
Benz[a]anthracene	-	0.00164	-	0.00174
Benzo[a]pyrene	17200	0.00737	18300	0.00784
Benzo[b]fluoranthene	-	0.000536	-	0.000569
Benzo[k]fluoranthene	-	6.17E-05	-	6.57E-05
Chrysene	-	6.7E-06	-	7.15E-06
Dibenz[a,h]anthracene	-	0.00341	-	0.00363
Indeno[1,2,3-cd]pyrene	-	0.00032	-	0.000341
Naphthalene	184	0.0067	194	0.00708
*Total Risk/HI	17400	0.0198	18500	0.021

\* (a) Packing and \*\* (b) Filter cake

Naphthalene was the final contaminant in this group, and the risk assessment results indicated that its LCR was within the definitive risk range in all the studied sites. Unlike the other hydrocarbons, the lowest estimated LCR value for naphthalene was at sampling point G, while the highest value was denoted at sampling point B. The cumulative LCR of the hydrocarbon compounds was represented by the black color code, demonstrating that at all the sampling points, the cumulative LCR of the hydrocarbon compounds was within the definitive range. The maximum cumulative LCR of the hydrocarbon compounds was evaluated at sampling point B, while the minimum value was reported at sampling points F and G.

Although all the studied hydrocarbon

compounds were carcinogenic compounds with previously reported IUR values, RfC was only available for benzo(a)pyrene and naphthalene. Consequently, the calculations of HQ, non-cancer risk, and cumulative risk were carried out only for these two compounds (Tables 8 and 9). According to the information in Tables 8 and 9, the color codes clearly indicated that the HQ and non-cancer risk associated with benzo(a)pyrene were unacceptable in all the studied sites, with the maximum and minimum values calculated at sampling points B and F, respectively. Furthermore, the HQ and non-cancer risk associated with naphthalene were unacceptable at all the sampling points, and the highest HQ values were calculated at sampling point B, while the lowest value was observed

at sampling point G. The cumulative non-cancer risk and cumulative HQ values resulting from the sum of the risks of the two compounds (benzo[a]pyrene and naphthalene) were predictable since both compounds were within the unacceptable range. Similarly, the cumulative non-cancer risk of the hydrocarbon compounds in all sampling sites was within the unacceptable range. The highest cumulative non-cancer risk was observed at sampling point B, and the lowest was denoted at sampling points F and G.

### Heavy metal concentrations

Table 10 shows the concentration of the heavy metals based on the sampling points and type of occupations. Among the studied heavy

metals, iron had the highest concentration. According to the information in Table 3, the mean concentration of the heavy metals (iron, zinc, lead, cadmium, arsenic, and nickel) was as follows: sampling point F (196.29 ng/m<sup>3</sup>), sampling point H (67.58 ng/m<sup>3</sup>), sampling point F (17.54 ng/m<sup>3</sup>), sampling point H (15.08 ng/m<sup>3</sup>), and sampling point H (5.45 ng/m<sup>3</sup>). Table 3 also shows that iron concentration was higher in filter cake (253.66 ng/m<sup>3</sup>), followed by zinc (1,717 ng/m<sup>3</sup>) and lead (60.33 ng/m<sup>3</sup>). In addition, the lowest concentrations of the studied heavy metals based on the type of occupation belonged to nickel and mercury, which is consistent with the results obtained by Hosseini *et al.*, which demonstrated iron to have the highest concentration.<sup>28</sup>

Table 10. Mean changes in concentrations of heavy metals in Tizro Grease Oil re-refining plant of Garmsar (ng/m<sup>3</sup>)

Study area	Parameters	Parameters					
		Fe	Zn	Cd	As	Ni	Pb
A	Mean	233.62	167.29	14.95	12.87	4.33	54.4
	SD	23.53	17.30	2.33	1.16	0.47	6.98
B	Mean	228.91	163.79	14.72	12.02	4.33	53.16
	SD	24.49	15.75	2.51	1.45	0.47	7.10
C	Mean	173.45	123	11.7	9.21	3.66	40.45
	SD	47.72	26.35	3.91	2.84	0.94	11.11
D	Mean	239.08	170.34	15.87	14.58	5.12	63
	SD	41.61	19.36	3.71	1.34	0.49	7.33
E	Mean	254.25	183.08	16.22	12.45	4.08	53.95
	SD	36.19	36.41	0.629	0.93	0.16	6.36
F	Mean	270.87	196.29	17.54	11.79	4.166	49.95
	SD	59.25	54.76	2.35	0.91	0.33	5.77
G	Mean	265.37	190.16	16.79	14.41	4.95	63.87
	SD	20.9	20.02	1.95	1.34	0.34	8.23
H	Mean	247.53	177.08	16.04	15.08	5.45	67.58
	SD	30.98	20.19	2.62	2.45	1.1	13.23
a*	Mean	218.12	155.11	14.48	11.94	5.09	52.34
	SD	32.55	15.2	3.83	1.198	0.27	6.84
b**	Mean	219.02	156.54	14.81	12.25	5.48	53.15
	SD	32.58	15.32	3.97	1.26	0.23	6.52

\* (a) Packing and \*\* (b) Filter cake

### LCR, HQ, and non-carcinogenic risk of heavy metals

According to the information in Tables 11 and 12, the calculated LCR for arsenic was within the definitive risk range at all the sampling points. Moreover, the calculated LCR for lead at all the sampling points was within the probable risk range, and the calculated LCR for nickel was within the

definitive risk range at sampling points D, H, and B, while it was within the probable risk range at the other points. Moreover, the cumulative LCR for all the heavy metals was within the definitive risk range at all the sampling points. Among the studied heavy metals, the highest LCR belonged to arsenic at sampling point G, and the highest LCR among the sampling points was observed in sampling

site H. It is also notable that cadmium, iron, and zinc were not involved in the LCR calculations.

According to the findings of the current research, the color codes in the tables corresponded to the risk values calculated in each table cell. The LCRs for white cells are known to be risk-free, while the yellow cells

were indicative of the probable risk, the red cells showed the definitive risk, and the black cells represented the highest risk (i.e., definitive risk). In the case of HQ, the white color indicated the lack of known risk, purple was interpreted as the acceptable limit, and blue demonstrated the unacceptable limit.

Table 11. LCR and HQ of heavy metals

Chemical	A		B		C		D		E		F		G		H	
	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR	HQ	LCR
Arsenic	196	0.00451	183	0.00422	140	0.00323	222	0.00511	190	0.00437	179	0.00413	219	0.00505	230	0.00529
Lead	-	5.32E-05	-	0.000052	-	3.96E-05	-	6.16E-05	-	5.28E-05	-	4.89E-05	-	6.25E-05	-	6.61E-05
Mercury	0.76	-	0.76	-	0.76	-	0.76	-	0.76	-	0.76	-	0.76	-	0.76	-
Nickel	70.7	8.48E-05	70.7	8.48E-05	59.8	7.18E-05	83.6	0.0001	66.6	7.99E-05	68	8.15E-05	80.9	0.00009	89	0.00010
*Total Risk/Hi	267	0.00465	255	0.00436	201	0.00334	306	0.00528	257	0.0045	248	0.00426	301	0.00521	319	0.00546

Table 12. LCR and HQ of heavy metals based on occupation

Chemical	a*		b**	
	HQ	LCR	HQ	LCR
Arsenic	182	0.00419	187	0.0043
Lead	-	5.12E-05	-	0.000052
Mercury	0.76	-	0.76	-
Nickel	83.1	9.97E-05	89.5	0.000107
*Total Risk/Hi	266	0.00434	277	0.00446

\* (a) Packing and \*\* (b) Filter cake

Since the RfC values were only available for arsenic, mercury, and nickel, the HQ results were calculated and presented for these elements only. Tables 11 and 12 show the results of the HQ for the studied heavy metals. The obtained results indicated the risk of chronic pathogenicity caused by these pollutants and their non-carcinogenic risk. At all the sampling points, the highest HQ and non-carcinogenic risk belonged to arsenic, the HQ values of which were significantly higher compared to the other heavy metals. Therefore, it could be inferred that the non-carcinogenic risk of arsenic at all the sampling points was within the unacceptable range. Moreover, the HQ of nickel was unacceptable at all the sampling points, while the HQ values and non-carcinogenic risk associated with mercury were within the acceptable range as demonstrated by the purple color in the table. The cumulative risk values for the non-

carcinogenic of the heavy metals were also within the unacceptable range. Among the evaluated heavy metals, the highest HQ and non-carcinogenic risk belonged to arsenic at sampling point H, and the highest HQ and non-carcinogenic risk among the sampling points were observed at sampling point H.

#### *Risk assessment of the studied pollutants based on carcinogenicity and Non-carcinogenicity*

To this end, the studied pollutants were presented in two separate tables (Tables 13 and 14). The contaminants with the reported numerical IUR values were categorized as the carcinogenic pollutants, and their cumulative risk was presented in Table 13 after calculation as shown by the color codes of their risk intensities. On the other hand, the pollutants for which the risk of exposure was expressed as RfC values were categorized as non-carcinogenic contaminants, and their cumulative risk was presented in Table 13 after calculation, with their risk intensity shown by the color codes.

#### *Risk assessment of the studied carcinogenic pollutants*

In the case of carcinogenic effects, even the least amount of exposure to the target contaminant increases the risk of cancer in



humans. IUR is considered to be the ultimate estimate (95% possibility) for the increased risk of cancer in the lifetime of an individual based on the relative inhalation of a substance. This factor is based on micrograms per cubic meter of the respiratory air that humans have been in contact with for a lifetime, which may lead to the relative increase in the risk of cancer due to continuous exposure to a substance in the air. According to the information in Table 13, ethylbenzene was the only contaminant for which the carcinogenic risk was in the white or

risk-free range at most of the sampling points, while it was within the probable risk range at sampling points A and B. Similarly, lead, nickel, benzene, benzo(k)fluoranthene, and chrysene were within the possible cancer risk range in almost all the sampling sites, and the most carcinogenic pollutants were arsenic, benzene(a)anthracene, benzo(a)pyrene, benzene(b)fluoranthene, dibenz(a,h)anthracene, indeno(1, 2, 3-cd)pyrene, and naphthalene.

Table 13. Single and cumulative risk of studied carcinogenic pollutants

Chemical	A	B	C	D	E	F	G	H	a	b
Arsenic	0.00451	0.00422	0.00323	0.00511	0.00437	0.00413	0.00505	0.00529	0.00419	0.0043
Lead	0.000053	0.00005	0.000039	0.00006	0.000052	0.00004	0.00006	0.00006	0.00005	0.00005
Nickel	0.000084	0.00008	0.000071	0.0001	0.000079	0.00008	0.00009	0.00010	0.00009	0.0001
Benzene	0.000023	0.00002	0.000023	0.00002	0.000021	0.00002	0.00002	0.00002	0.00002	0.00002
Ethylbenzene	9.85E-07	0.000009	8.83E-07	0.000009	9.17E-07	0.000009	9.17E-07	9.51E-07	1.28E-06	1.79E-06
Benz[a]anthracene	0.0014	0.00138	0.00135	0.00154	0.00155	0.00129	0.0013	0.00149	0.00164	0.00174
Benzo[a]pyrene	0.00591	0.00587	0.0057	0.0065	0.00654	0.00549	0.00552	0.00631	0.00737	0.00784
Benzo[b]fluoranthene	0.000424	0.00042	0.000409	0.00046	0.000468	0.00039	0.00039	0.00045	0.00053	0.00056
Benzo[k]fluoranthene	0.000049	0.00004	0.000047	0.00005	0.000054	0.00004	0.00004	0.00005	0.00006	0.00006
Chrysene	0.000005	5.39E-06	0.000005	5.99E-06	0.000006	5.03E-06	0.00000	0.00000	0.00000	7.15E-06
Dibenz[a,h]anthracene	0.0025	0.00247	0.00241	0.00275	0.00276	0.00232	0.00233	0.00263	0.00341	0.00363
Indeno[1,2,3-cd]pyrene	0.00023	0.00022	0.00022	0.00025	0.000253	0.00021	0.00021	0.00024	0.00032	0.00034
Naphthalene	0.00605	0.0061	0.00587	0.00634	0.0064	0.00589	0.00582	0.00601	0.0067	0.00708
*Total Risk/HI	0.0212408	0.0209	0.0193770	0.0232037	0.0225570	0.0199284	0.0208647	0.0226783	0.02440	0.02576

Table 14. Unit and cumulative risk of studied non-carcinogenic pollutants

Chemical	A	B	C	D	E	F	G	H	a	b
Arsenic	196	183	140	222	190	179	219	230	182	187
Mercury	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761
Nickel	70.7	70.7	59.8	83.6	66.6	68	80.9	89	83.1	89.5
Benzene	0.278	0.277	0.277	0.278	0.261	0.258	0.266	0.267	0.273	0.346
Ethylbenzene	0.0011	0.00101	0.000989	0.00101	0.00103	0.00101	0.00103	0.00107	0.00144	0.00201
Toluene	0.00147	0.00139	0.00143	0.00147	0.00136	0.00141	0.00135	0.0014	0.00125	0.00152
Xylenes	0.0468	0.0441	0.043	0.0457	0.0411	0.036	0.0419	0.0439	0.0406	0.0495
Benzo[a]pyrene	13800	13700	13300	15200	15300	12800	12900	14700	17200	18300
Naphthalene	166	168	161	174	176	162	160	165	184	194
*Total Risk/HI	14234	14123	13662	15681	15734	13210	13361	15185	17650	18772

In terms of the intensity of carcinogenicity, cumulative risk assessment results indicated the highest risk at sampling point B, while sampling point C had the lowest risk level. In addition, the black color code in all the cells related to the cumulative risk

assessment indicated high levels of carcinogenic risk at all the sampling sites. In other words, the cumulative LCR in all the sampling sites was within the definitive risk range. Due to the standard hazard limit (1-100 per one million), the risk of cancer was higher

in the workers exposed to benzene-1,3,5 and cadmium.

### ***Risk assessment of the studied non-carcinogenic pollutants***

In the non-carcinogenic group, the probability of human exposure is extremely low until the amount of human exposure to the contaminant reaches a certain level (i.e., threshold limit). In the case of air pollutants, the inhalation reference concentration is equivalent to the amount of the pollutants that must be inhaled through the respiratory tract to perceive the possible adverse effects on the human body; this value is reported in milligrams per cubic meter. If an individual is exposed to contaminants at higher levels than this threshold, the hazard index, which is obtained by dividing the amount of the contaminant (concentration of the inhaled air) by the inhalation reference concentration, the value is greater than one, which indicates that the exposed individuals are at the risk of non-carcinogenic health complications.

Table 14 shows the HQ values of the non-carcinogenic pollutants at the sampling points. Since all the studied non-carcinogenic pollutants are presented in Table 14, the calculated cumulative risk in the table more broadly indicates the extent of non-carcinogenic risks. According to the information in Table 14, the three pollutants (ethylbenzene, toluene, and xylene) were within the permissible limits as shown by the white color code at all the sampling points, while mercury and benzene were within the acceptable range.

According to the results of the present study, the non-carcinogenic pollutants associated with the highest risk included arsenic, nickel, benzo(a)pyrene, and naphthalene, and risk assessment results of all these elements were within unacceptable ranges at all the sampling points. On the other hand, benzo(a)pyrene was the compound with the maximum distance and acceptable levels. The highest cumulative non-carcinogenic risk was observed at sampling point B, and the lowest cumulative non-carcinogenic risk was

reported at sampling point F. To determine the level of non-carcinogenic risk due to the presence of heavy metals in the air, the daily exposure value was calculated ( $\text{mg}/\text{m}^3$ ), and the long-term and chronic HQ for the heavy metals was also determined to estimate the non-carcinogenic effects.

### **Conclusion**

According to the results, the highest concentrations of the organic compounds (BTEX and PAHs) were observed at sampling point D. Between BTEX and PAHs, the highest concentration belonged to benzene and naphthalene in all the sampling sites, respectively, the values of which were above the standard. Furthermore, the highest concentration of the pollutants (BTEX, PAHs, and heavy metals) was observed in the filter cake occupation. Among the studied heavy metals, iron had the highest concentration, followed by zinc ( $1,717 \mu\text{g}/\text{m}^3$ ) and lead ( $60.33 \mu\text{g}/\text{m}^3$ ).

The obtained results demonstrated that the cumulative LCR for the evaluated heavy metals at all the sampling points was within the definitive risk range, and the highest LCR of carcinogenic risk belonged to arsenic at sampling point H (filtration chamber). In addition, the highest cumulative carcinogenic risk among the environmental sampling sites was reported at sampling point H. At all the sampling points, the LCR carcinogenic risk belonged to the hydrocarbon compounds within the definitive risk range, and the maximum cumulative LCR carcinogenicity among the hydrocarbon compounds was observed in the filtration room (sampling point B). On the other hand, the risk assessment results demonstrated that the most hazardous carcinogens were arsenic, benzo(a)pyrene, and naphthalene. Risk assessment results could be used to prioritize resources for risk reduction, engineering, management, and control measures.

### **Acknowledgements**

This article was extracted from a Ph.D. thesis conducted by Iman Molaei and approved

by the Islamic Azad University, Research and Sciences Branch, Iran. Hereby, we extend our gratitude to the Islamic Azad University for the financial and instrumental support of this research project.

## References

- Dargahi A, Bagheri S, Poursadeghiyan M, Hosseini Ahagh MM, Farrokhi M. Knowledge and attitudes of students in Khalkhal medical sciences faculty on health actions in emergencies. *Health Emergen Disaster* 2017; 3(1): 51-6.
- Eslami F, Salari M, Dehghani MH, Dargahi A, Nazmara S, Beheshti A. Relationship of formaldehyde concentration in ambient air with CO, NO<sub>2</sub>, O<sub>3</sub>, temperature and humidity: modeling by response surface model. *Arch Hyg Sci* 2019; 8(1): 9-16.
- Bahrami A, Ghorbani Shanh F, Rahimpour R. Comparison of health risk assessment carcinogenic hydrocarbons in Workplace air in an oil-dependent industry by the Environmental Protection Agency (EPA) and the Department of Human Resources Malaysia. *Iran Occup Health* 2017; 14(5): 107-17.
- Ali N. Polycyclic aromatic hydrocarbons (PAHs) in indoor air and dust samples of different Saudi microenvironments; health and carcinogenic risk assessment for the general population. *Sci Total Environ* 2019; 696: 133995.
- Khamutian R, Najafi F, Soltanian M, Shokoohizadeh MJ, Poorhaghighat S, Dargahi A, *et al.* The association between air pollution and weather conditions with increase in the number of admissions of asthmatic patients in emergency wards: A case study in Kermanshah. *Med J Islam Repub Iran* 2015; 29(1): 558-65.
- Harb P, Locoge N, Thevenet F. Emissions and treatment of VOCs emitted from wood-based construction materials: Impact on indoor air quality. *Chem Eng J* 2018; 354: 641-52.
- Cerón Bretón JG, Cerón Bretón RM, Vivas Ucan F, Baeza CB, Fuentes MDLLE, Lara ER, *et al.* Characterization and sources of Aromatic Hydrocarbons (BTEX) in the atmosphere of two urban sites located in Yucatan Peninsula in Mexico. *Atmosphere* 2017; 8(6): 107.
- Davey NG, Bell RJ, Gill CG, Krogh ET. Mapping the geospatial distribution of atmospheric BTEX compounds using portable mass spectrometry and adaptive whole air sampling. *Atmos Pollut Res* 2019; 11(3): 545-53.
- USEPA (US). Environmental protection Agency. Integrated risk information system (IRIS). 2014b; Available from: <http://www.epa.gov/iris/index.html>.
- Mari M, Harrison RM, Schuhmacher M, Domingo JL, Pongpiachan S. Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data. *Sci Total Environ* 2010; 408(11): 2387-93.
- Dauner ALL, Lourenço RA, Martins CC. Effect of seasonal population fluctuation in the temporal and spatial distribution of polycyclic aromatic hydrocarbons in a subtropical estuary. *Environ Technol Innov* 2016; 5: 41-51.
- Ebrahimi-Seirizi Z, Riyahi-Bakhtiari A, Ghaffari S. Petroleum pollution risk assessment in sediment of Hara protected zone with determination of polycyclic aromatic hydrocarbons. *J Mazandaran Univ Med Sci* 2014; 23(2): 186-94.
- Kermani M, Asadgol Z, Arfaeinia H. A study of polycyclic aromatic hydrocarbons (PAHs) and Trace Elements in Ambient air PM<sub>2.5</sub> in an urban site of Tehran, Iran. *Iran J Health Safe Environ* 2018; 5(2): 947-56.
- Almasi A, Dargahi A, Ahagh M, Janjani H, Mohammadi M, Tabandeh L. Efficiency of a constructed wetland in controlling organic pollutants, nitrogen, and heavy metals from sewage. *J Chem Pharm Scie* 2016; 9(4): 2924-8.
- Jahangiri M, Jalali M, Saeidi C, Mohammadpour H, Mardi H, Mehr Alipour J. Health risk assessment of harmful chemicals in order to provide control guidelines: Case study in a polyurethane foam industry. *Occup Med Q J* 2014; 5(4): 33-41.
- Mustafa MF, Liu Y, Duan Z, Guo H, Xu S, Wang H, *et al.* Volatile compounds emission and health risk assessment during composting of organic fraction of municipal solid waste. *J Hazard Mater* 2017; 327: 35-43.
- Dehghani MH, Baghani AN, Fazlzadeh M, Ghaffari HR. Exposure and risk assessment of BTEX in indoor air of gyms in Tehran, Iran. *Microchem J* 2019; 150: 104135.
- Mousavian NA, Mansouri N, Nezhadkurki F. Estimation of heavy metal exposure in

- workplace and health risk exposure assessment in steel industries in Iran. *Meas* 2017; 102: 286-90.
19. Duruibe JO, Ogwuegbu M, Egwurugwu J. Heavy metal pollution and human biotoxic effects. *Int J Phys Sci* 2007; 2(5): 112-8.
  20. WHO. Air quality guideline for Europe. WHO European Series, WHO Regional Office for Europe, Copenhagen, 1987, 105–117. <http://www.euro.who.int/air>.
  21. Lin Y-C, Lee W-J, Chen S-J, Chang-Chien G-P, Tsai P-J. Characterization of PAHs exposure in workplace atmospheres of a sinter plant and health-risk assessment for sintering workers. *J Hazard Mater* 2008; 158(2-3): 636-43.
  22. Rahimnejad S, Bahrami A, Assari M, Sultanian A, Rahimpour R, Negahban A, *et al*. Quantitative risk assessment of occupational exposure to volatile organic compounds in the oil-dependent chemical industry. *J Sabzevar Univ Med Sci* 2014; 21(5): 829-41.
  23. Hydrocarbons A. Method 1501. NIOSH Manual of Analytical Methods (NMAM), Four Available from: <https://www.cdc.gov/niosh/docs/2003-154/pdfs/1501.pdf>.
  24. WHO (World Health Organization). Air quality guidelines for Europe. Regional Office for Europe, Copenhagen, Copenhagen. 2th ed; 2111. [updated Accessed February 20, 2100]; Available from: [http://www.euro.who.int/data/assets/pdf\\_file/70732/1110/E70222.pdf](http://www.euro.who.int/data/assets/pdf_file/70732/1110/E70222.pdf).
  25. Colman Lerner JE, Sanchez EY, Sambeth JE, Porta AA. Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina. *Atmos Environ* 2012; 55: 440-7.
  26. Salaudeen I, Sonibare O, Sojinu S, Ekundayo O. Polycyclic aromatic hydrocarbons in air from industrial areas in Lagos and Ogun states, Nigeria. *Pollut* 2017; 3(4): 561-73.
  27. Liu Y, Zhu L, Shen X. Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China. *Environ Sci Technol* 2001; 35(5): 840-4.
  28. Hosseini G, Teymouri P, Giahi O, Maleki A. Health risk assessment of heavy metals in atmospheric PM10 in Kurdistan University of Medical Sciences campus. *J Mazandaran Univ Med Sci* 2016; 25(132): 136-46.