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Original Article

Health Risk Assessment of Occupational Exposure to Chemical Materials in a Combined-Cycle Power Plant

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Abstract

Background: This study aimed to evaluate the occupational exposure of workers at a combined-cycle power plant located in the southwestern region of Iran. The assessment focuses on the inhalation exposure route to workplace emissions.

Methods: The primary locations for potential pollutant emissions were identified in close proximity to the areas where chemicals were introduced and utilized within the production process. Sulfuric acid, sodium hydroxide, ammonia, oil mist, toluene, hydrogen sulfide, hydrazine, and tetrachloromethane were measured and analyzed using the NIOSH standard. Dose-response assessment was estimated using inhalation unit risk (IUR) for cancer risks and reference concentration (RFC) and reference exposure levels (REL) for non-cancer risks. Risk assessment was performed based on the Environmental Health Hazard Assessment guideline.

Results: The results showed that ammonia and toluene had the highest and lowest concentration of pollutants emitted in workplace, respectively. The inhalation of ammonia and sulfuric acid and their daily absorption were at high risk level (HQ > 1). Other noncancerous compounds had HQ < 1. While the hazard index (HI) for total non-cancer risks was 5.34E + 01 (HI > 1), it was likely to have non-cancerous risks. For carcinogenic risks, they were calculated to be 9.58E-03 and 5.47E-04 for hydrazine and tetrachloromethane, respectively. The total carcinogenic risk of the emissions was calculated at 1.01E-02, which was in the significant range (more than 10-4) (i.e. in the range of hazardous cancer effects).

Conclusion: This study confirmed the presence of non-carcinogenic risks, while the quantity of cancer risks fell within the Significant range, indicating a potential for carcinogenic risks.

Keywords: Health risk assessment, Emissions, Cancer and non-cancer risk, Combined-cycle power plants, Inhalation route

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Introduction

Rapid industrial development over the past decades has led to continued growth in energy consumption. Easy access and control as well as high efficiency of the fossil fuels have made this type of energy popular among consumers. Fossil fuels supply a large part of the energy needs, as 80% of the world's energy needs are met by the fossil fuels.[1] After the generation of energy from fossil fuels, the release of toxic and chemical substances in workplaces and the environment becomes inevitable. In order to facilitate decision-making and management of chemical risks, a risk assessment of chemical emissions is of great importance.

Human health risk assessment is the process of estimating the likelihood and potential negative health effects on humans resulting from exposure to chemicals in contaminated environments, both in the present and future.[2] Exposure assessment detects the potential routes of human exposure to toxic substances and estimates the magnitude, frequency, and continuity of actual and/or potential exposures.[3] Exposure to contaminated materials can result from inhalation, ingestion of water or food or skin absorption.[4]

Due to the increasing growth of technology and industry, the incidence of occupational diseases is on the rise.[5] An increase of 8% in fatal occupational accidents was reported between 2010 and 2014. There are more than 7500 job-related deaths per day, of which 1000 are due to occupational accidents and 6500 people die of work-related illness. The main causes of death due to occupational diseases are 31% of circulation diseases, 26% of work-related cancers, 17% of respiratory diseases and 14% of occupational injuries, accounting for 90% of total work-related deaths.[6]

Power plants, being one of the methods for electricity generation, are not an exception. Power plants are places to generate electrical energy for consumption in domestic and industrial sectors. For example, Lee et al[7] conducted a study on management of the health risks of a combined-cycle power plant in order to prevent cardiovascular and musculoskeletal disorders among workers. They evaluated the particular attempts associated with the onsite health of the workers as well as the expected results.

Rohr et al[8] assessed the potential occupational hazards of biomass-based power generation in a power plant and three stages of pre-combustion exposure to combustibles, combustion products, and post-exposure to residual ash. Their results indicated that the concentration of dust in the biomass-fueled power plant varied greatly. In some places, the concentration of wood dust and general inhalable dust exceeded the occupational permissible limits. However, the risks categorized under the combustion and post-combustion classes were as the same as the fossil-fuel in the power plant. Mokhtar et al[9] assessed the health risks of a coal-fueled power plant in Malaysia. To do so, they measured the concentration of SO_2 and Hg, which are categorized as emissions with non-carcinogenic risks according to Malaysian Clean Air Regulations, and Cr as a heavy metal emission with carcinogenic risks. They recommended conducting further studies based on meteorological indices as the most important parameter affecting the emissions levels to detect short- and long-term health outcomes from the exposure to the power plant emissions.

The studied power plant is one of the combined cycle power plants in southwest of Iran. It has four gas turbine units, each with a capacity of 123.4 MW (total of 493.6 MW) and two steam turbine units, each with a capacity of 160 MW (total of 320 MW) as a supplementary firing of the cycles. Its main fuel is gas; however, in the absence of gas or in emergencies, the power plant can fire gasoline. The maximum capacity of the power plant including both gas and steam units is 820 MW.

In order to reduce or prevent possible occupational diseases, the following objectives were pursued: (1) identification of potential sources of gases and steam emissions in the workplace; (2) determining the frequency and concentration of exposures that in the short- or long-term would lead to non-carcinogenic or carcinogenic outcomes on the personnel; and (3) characterization and assessment of health risks. In this study, only exposure through the inhalation route was investigated, which was identified based on accurate field studies conducted due to the power plant's processes and personnel's working conditions.

Materials and Methods

Potential Exposure Routs and Locations

In order to implement the risk assessment, it was necessary in the first step to identify the routs and places that have the greatest impact on the health of the power plant personnel. The main potential sources of emissions are basically in the vicinity of the sites where chemicals are used and injected into the process. Contaminants emitted from the emission site can be transmitted to the receiver through the three routes of oral, inhalation, and skin contact. In this study, only the inhalation exposure route was investigated. Since the areas where chemicals are "injected or used in the process" within power plants are primarily enclosed within sheds and closed environments, the highest concentration of pollutant emissions occurs in these locations. An examination of the medical records of personnel from various units revealed that employees working in these areas were experiencing respiratory problems and had been referred to the power plant's clinic. To achieve this and conduct a more detailed examination to identify units with the highest pollution levels, exclusive interviews were conducted with experts and personnel from various units of the power plant. A comprehensive questionnaire was then developed based on the Health, Safety, and Environment (HSE) questionnaire provided by the Health and Safety Laboratory (HSL) of the United States.[10]

In the next step, the validity and reliability of the questionnaire were examined. First, the face validity of the questionnaire was tested, qualitatively. Then, the content validity was investigated. The questionnaires were analyzed in terms of both the content validity ratio (CVR) and the content validity index (CVI).

In order to determine the reliability of the questionnaire, the Cronbach's test was used and Cronbach's alpha coefficient was determined using SPSS v20.0 software. After testing the reliability of the questionnaire, the number of questionnaires was determined based on the statistical population (the personnel of the power plant) using the Cochran equation (see Cochran).[11] The questionnaires were distributed by the "random sampling" method among the personnel of all the units in the power plant. The questionnaires were analyzed by SPSS v20.0 software and using ANOVA at 95% confidence interval (CI). To verify and improve the accuracy of the data from the questionnaires, field visits were also conducted.

To identify the primary pollutants released in the most polluted units, an extensive process study, multiple field visits, and interviews with process experts were conducted. This comprehensive examination allowed for the identification of the types of chemicals used in various units and pinpointed the main materials consumed, which had adverse effects on human health according to the guidelines from the Agency for Toxic Substances and Disease Registry (ATSDR). These substances were subsequently measured.

Human Health Risk Assessment

Risk assessment includes four main steps namely hazard identification, exposure assessment, dose–response assessment, and risk characterization.[12] Figure 1 shows the stages of health risk assessment.

1) Hazard Identification

The process of identifying potential risks and pathways of emissions, along with the characterization of pollutants in each unit of the power plant, was described.

2) Exposure Assessment

To assess exposure, it was necessary to determine the concentration of the emissions which leads to biological effects. Therefore, the sampling was performed at the designated points as the places with highest emission of pollutants.

The samples were taken to measure the concentration of the gases and vapors in the air through the inhalation route. The sampling was conducted seasonally (in the middle of each season), over a period of one year from October 2017 to September 2018. It was done actively by a SKC sampling pump (A060068 model), after the onsite calibration of the pump. The sampling method and the applied equipment were based on National Institute for Occupational Safety and Health (NIOSH). Based on the investigations carried out, the main gases and vapors released in the highly-polluting units included sulfuric acid, sodium hydroxide vapors, ammonia (in the Unit of Industrial Water Treatment Plant), oil mist (at the site of Gas Unit), hydrazine vapors (during repair and maintenance at the site of Steam Unit), toluene, hydrogen sulfide and tetrachloromethane (carbon tetrachloride) (at Repair and Maintenance Unit). The personnel's health risks were assessed for both short- and long-term exposures to gases and vapors.

The Department of Health and Human Services (DHHS), the International Agency for Research on Cancer (IARC), and the Environmental Protection Agency (EPA) do not classify sodium hydroxide (caustic soda) as a carcinogen for human beings.[13] Based on the ATSDR, its chronic effects can only lead to the ulceration of nasal duct. Accordingly, acute respiratory health outcomes of sodium hydroxide (including respiratory irritation, spasm of the larynx, congestion of respiratory tracts, inflammation of lungs, and accumulation of fluids within them in high inhalation) are more important.[14] According to the Air Toxics Hot Spots Program (ATHSP) Risk Assessment Guidelines,[15] the maximum concentration of sodium hydroxide was measured in the short term to assess its potential impact on acute respiratory health outcomes. Therefore, to determine the non-cancerous risks of sodium hydroxide, reference exposure level (REL) were considered as a reference.

IARC states that exposure to strong sulfuric acid mists is a carcinogen for humans.[16] Since many chronic inflammations and chronic stimuli can lead to cancer,[17] according to the ATHSP risk assessment guidelines, the annual average (long-term) exposure to sulfuric acid vapors was considered to determine the chronic health outcomes.

The sampling method of sulfuric acid vapors in air was based on the NIOSH 7908, sodium hydroxide 7401 and oil mist 5026. Hydrazine with the chemical formula of N_2H_4 is a highly toxic substance used in boilers for the deoxygenation and corrosion protection purposes. In addition, for descaling the boiler during repair and maintenance, it is transported by the worker in high volumes (20-L gallons) in a traditional and manual way, in which the worker is in directly contacted with it.

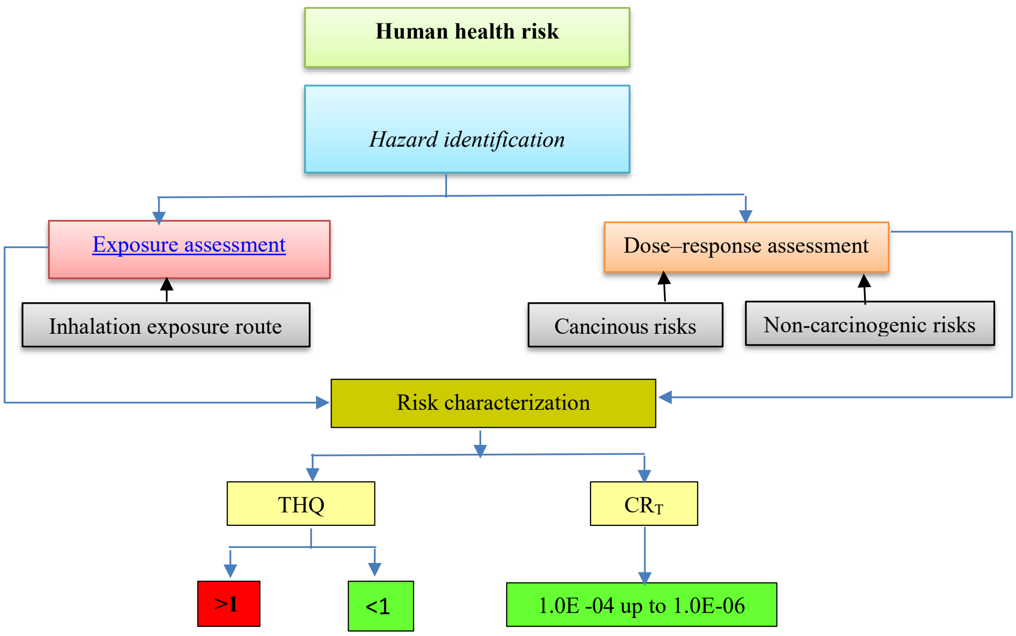

Figure 1. The Steps of Human Health Risk Assessment Process

Accordingly, the measurement of hydrazine concentration was important during transport and storage of hydrazine in the sampling unit and the direct contact with hydrazine under the repair and maintenance conditions of the boilers. The hydrazine sampling method was based on the 3503 NIOSH method. The sampling method of ammonia was based on the 6016 NIOSH method, tetrachloromethane (carbon tetrachloride (1003), hydrogen sulfide (6013) and toluene (1501). Table 1 shows the sampling and analysis methods of the chemical pollutants.

After measuring and determining the concentration of major gases and vapors released into the workplace, the personal monitoring of inhalation exposures was required for each of the emissions. In accordance with Exposure Factors Handbook provided by the US EPA, the exposure to toxic substances was estimated by the average daily intake (ADI) of a toxic substance, which is a function of concentration, inhalation rate, body weight, and exposure duration.[22] The ADI of the pollutants was calculated using Eq. 1.[23]

$$ADI = \frac{E_i \times EF \times ED}{BW \times AT} \tag{1}$$

Where:
ADI = Average daily intake (mg/kg/d)
EF = Exposure frequency (day/year)
ED = Exposure Duration) year)
BW = Average body weight (70 kg)
AT = Average time (days) (AT = 30 years × 365 days/years)

In which, the level of exposure to the pollutant i (Ei) was determined using Eq. 2.

$$E_i = C \times IR \times t \tag{2}$$

Where:
E_i = Personal exposure to pollutant i (mg/d)
C = Concentration of the pollutant (mg/m³)
IR = Inhalation rate (m³/h)
t = Exposure time (h/d)

According to the ATHSP Risk Assessment Guidelines, the exposure duration factor is considered for three periods of 9 years, 30 years, and 70 years. Considering the purpose and scope of the present study, health risks were examined only within the power plant. Since there were no settlements surrounding the power plant, the thirty-year course of personnel employment at the power plant was considered as the exposure duration. The IR in exposure assessment depends on the age of individuals and their level of activity at different exposure times.[22] According to the relevant studies, the IR was considered to be 20 m³/d.[9,24]

3) Dose-Response Assessment

Dose-response assessment is the process of determining the relationship between exposure to an agent and the occurrence of an adverse health effect in the exposed

Table 1. Sampling and analysis methods for chemical agents according to the NIOSH guidelines

Pollutant	Method number	Sorbent	Solvent	Flow rate (L/min)	Vol (min-max) (L)	Threshold Limit values	Analysis method	Accuracy	Range studied	Ref
Oil Mist (oil and grease)	5026	Filter MCE, (37 mm)	CCl_4	1-3	20-500	5 mg/m³	Infrared spectrophotometry	±11.8 %	2.5 to 11.7 mg/ m³	18
hydrazine	3503	Bubbler (15 mL 0.1 M HCl)	p-Dimethylaminobenzaldehyde	0.2-1	7-100	0.01 ppm	Spectrophotometry	±17.1%	0.59 to 3.4 mg/m³	19
Sulfuric acid	7908	polytetrafluoroethylene (PTFE), 0.45 µm	Sodium carbonate	1-5	15-2000	0.2 mg/m³	Ion chromatography	-	0.005 - 2.0 mg/sample	20
Sodium hydroxide	7401	Filter PTFE (1 µm)	HCl	1-4	70-1000	2 mg/m³	Acid – base titration	±16.2%	0.76 to 3.9 mg/m³	19
Toluene	1501	Solid sorbent tube	1 mL CS2, stand 30 min with agitation	≤0.20	1-8	20 ppm	Gas chromatography, FID	±10.9%	548 - 2190	21
Hydrogen sulfide	6013	Solid sorbent tube	2 mL 0.2 M NH_4OH + 5 mL 30% H_2O_2	0.2	1.2-40	1 ppm	Ion chromatography	±11.8%	1.4 - 22.0 mg/m³	19
Tetrachloromethane (Carbon tetrachloride)	1003	Solid sorbent tube (coconut shell charcoal, 100 mg/50 mg)	1 mL CS2	0.01 - 0.2	3-150	5 ppm	Gas chromatography	±18.0%	65-299 mg/m³	21
Ammonia	6016	Solid sorbent tube (sulfuric acid treated silica gel)	10 mL deionized water	0.1 - 0.5	0.1-96	25 ppm	Ion chromatography	±14.5%	17 - 68 mg/m³	18

population. In this research, dose-response relationships were assessed for carcinogenic and non-carcinogenic (acute and chronic) risks.

Dose-Response Assessment for Carcinogenic Risks

The toxicity criterion for carcinogenic risks is the cancer slope factor, which, by definition, expresses the upper 95% confidence limit for cancer development. It is assumed that there is a continuous and prolonged exposure to a substance at a specified dose of mg per kg body weight. In health risk assessment, slope factors are considered as inhalation unit risk (IUR). In the health risk assessment of cancer, it is assumed that no threshold levels exist and risks are directly proportional to dose.[15] Dose-response assessment for carcinogenic risks was performed by Eq. 3.[23]

$$CR = ADI \times IUR \quad (3)$$

Where:
CR = Cancer risk (unitless)
ADI = Average daily intake (mg/kg/d)
IUR = Inhalation unit risk $(\mu g/m^3)^{-1}$

For converting IUR $(\mu g/m^3)^{-1}$ to SF (mg/kg/d), Eq. 4 was used to make the CR dimensionless.[25]

$$SF_i = (3.5 \times 10^3) \times IUR \quad (4)$$

Dose-Response Assessment for Non-carcinogenic Risks

Non-cancerous (acute and chronic) risks are calculated by dividing the ADI by a benchmark. Standard values include reference concentration (RFC) and REL.

RFC is continuous inhalation exposure estimate for human populations, which is properly without a significant risk for adverse effects over the lifetime.

REL is concentration or dose levels below which prolonged inhalation exposure is unlikely to lead to adverse health outcomes. The prolonged exposure is an exposure which lasts about 8 years, or 12% of the human lifespan.[15] Dose-response assessment for non-cancer risk is obtained using Eq. 5.[26]

$$HQ = \frac{ADI}{HB} \quad (5)$$

Where HB = Standard Criterion (Benchmark), RFC or REL.

Since the RFC was unavailable for oil mist and sodium hydroxide, the RELs proposed by NIOSH[27] and OEHHA were used for oil mist and sodium hydroxide, respectively. In Eq. 5, for determination of acute non-cancerous risks, instead of the average daily concentration, maximum short-term concentration of a substance $(\mu g/m^3)$ was considered.[15] Table 2 presents the IUR, RFC, and REL values for the emissions under study.

4) Risk Characterization

This was the last stage of exposure assessment. At this stage, for potential non-cancerous effects, if hazard quotient (HQ) ≤ 1, adverse health effects are unlikely; if HQ > 1, there is a potential for non-cancerous effects. To evaluate the total potential non-cancerous effects posed by chemicals (i), the HQ values of all chemicals are aggregated and expressed as hazard index (HI) (Eq. 6).

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

If HI ≤ 1, chronic risks are considered unlikely, while non-cancerous risks are likely to occur if HI > 1. In Table 3, the range of risk has been shown using the HQ and HI indices.

The total cancer risk was also calculated by the total accumulated dose over the exposure period (Eq. 7).[15]

$$CR_T = CR_1 + CR_2 + \ldots \quad (7)$$

CR_T = Cumulative predicted cancer risk for chemicals at a site.

The criteria risk assessment for carcinogenic risks have been presented in Table 4.

Results and Discussion

Demographic Profile of the Workers

All of the workers of the power plant operational units were male whose age ranged between 21 and 50 years old. The nearest residential area, where the workers lived, was located 10 km away from the plant. The values of body weight and inhalation rate were considered as 70 kg (on

Table 2. IUR, RFC, and REL Values of the Measured Gases and Vapors

Pollutant	CAS No	IURi $(Hg/m^3)^{-1}$	RFC, (mg/m^3)	REL chronic (mg/m^3)	REL acute (mg/m^3)	Ref.
Sodium hydroxide	1310-73-2	-	-	-	8.00E+00	15
Sulfuric acid	7664-93-9	-	1.0E-03	-	-	28
Oil Mist	8012-95-1	-	-	5.00E-01	-	27
Hydrazine	302-01-2	4.9 E-03	-	-	-	
Toluene	108-88-3	-	5.0E+00	-	-	
Hydrogen sulfide	7783-06-4	-	2.0E-03	-	-	28
Tetrachloromethane (carbon tetrachloride)	56-23-5	6.0E-06	-	-	-	
Ammonia	7664-41-7	-	5.0E-01	-	-	

Table 3. Range of Hazard Quotient or Hazard Index

Danger Range	Color Code
HQ or HI > 1	Red
HQ or HI ≤ 1	Blue

Table 4. Risk Assessment Criteria for Cancer Risk

Acceptability of Cancer Risk	Estimated Lifetime Individual Excess Cancer Risk
Significant	$>10^{-4}$
Risk should be reduced to "As low as reasonably practicable" (ALARP)	$>10^{-6}$ to 10^{-4}
Insignificant	$\leq 10^{-6}$

Source: Metcalf and Eddy.[29]

average) and 20 m^3/d.[30] In the power plant studied, the work schedule was based on a 12/24 rotating shift pattern. Consequently, exposure frequency was considered to be 208 days per year, and the exposure duration was set at 30 years.

Operational Sites for Gases and Vapors Emissions Using Questionnaire Analysis

Statistical analysis of the questionnaires was performed using ANOVA at the 95% CI by SPSS v20.0 software. The results indicated that four locations, including Industrial Water Treatment Plant, site of Gas Unit, site of Steam Unit, and Repair and Maintenance Unit had the highest amount of gases and vapors emissions. Therefore, sodium hydroxide vapors (in the Unit of Industrial water Treatment Plant) were measured based on short-term emissions. Also, sulfuric acid and ammonia vapors (in the Unit of Industrial water Treatment Plant), oil mist (on the site of Gas Unit), hydrazine vapors (on the site of Steam Unit and at the time of Repair and Maintenance), toluene, hydrogen sulfide, tetrachloromethane (carbon tetrachloride) (in the Repair and Maintenance Unit) were measured based on long-term emissions. Regarding the frequency of the personnel in different units and the analysis of the questionnaires, polluting level of the units in the power plants was determined as shown in Figure 2.

Personnel Exposure Levels With Released Gases And Vapors

During the one-year sampling period, while considering the process of the Industrial Water Treatment Plant unit and system shutdown, it was observed that the highest emission rates of sulfuric acid and sodium hydroxide vapors occurred only during the revival of the de-mineralized water production line. Sampling of these vapors was done only at the time of the line revival in the morning shift and lasted for one working week. This was repeated in four seasons. Other compounds were sampled at three times in the morning, noon, and afternoon, during a working day and the annual average of the measured values was taken into account. Accordingly, the exposure duration was calculated as 2 hours per day for sulfuric acid and sodium hydroxide vapors, and 4 hours per day for other compounds. The sampling was conducted as environmental sampling. Hydrazine injection takes place in a separate industrial shed with a closed system, and operators only enter the shed for inspection at specific times. Additionally, considering the time needed for repair and maintenance, the average duration of exposure to hydrazine vapors was calculated to be 2 hours per day.

Under the mentioned conditions, hydrazine vapor sampling was conducted in the sampling unit (the location of hydrazine storage and its injection into the power plant's steam process) throughout all four seasons as environmental sampling. Additionally, individual sampling took place during the repair and maintenance of the boilers (power plant overhaul) on a typical working day. Following the sampling in units with the highest emission levels, the concentrations of each of the pollutants released in these units were determined. Figures 3 and 4 display the concentrations of the pollutants alongside their ADI.

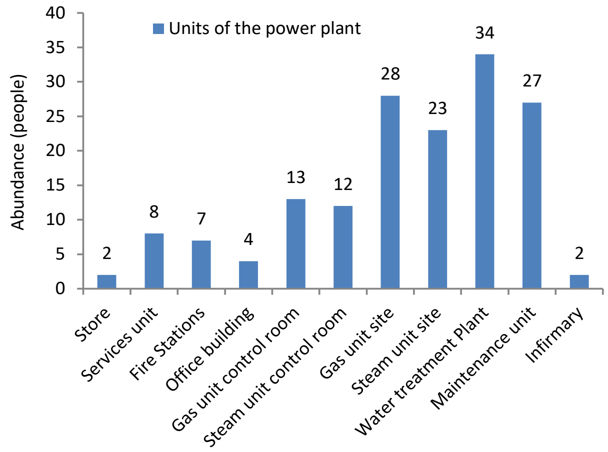

Figure 2. Emission Rate in Different Units in the Power Plant Based on Analyzing the Questionnaires

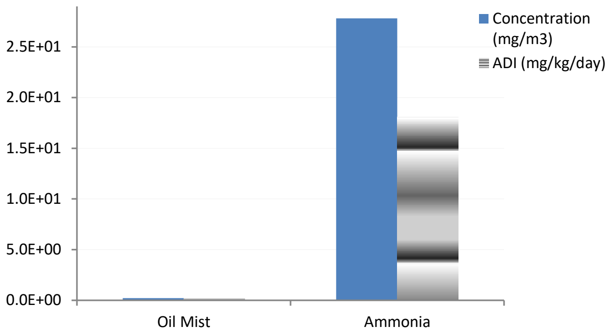

Figure 3. Emissions With the Highest Concentration and ADI

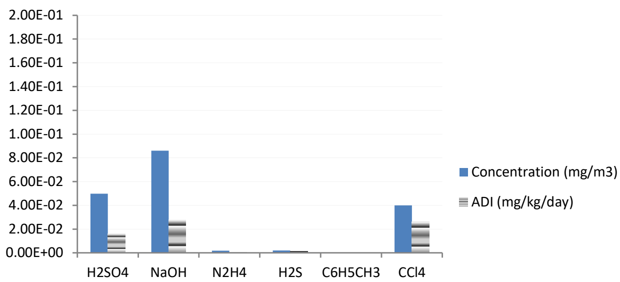

Figure 4. Concentration and ADI of the Pollutants in the Respiratory Air of the Personnel

The results showed that ammonia, with the average annual concentration of 27.8 mg/m^3 in the Industrial Water Treatment Plant Unit, had the highest emission rate and toluene in the Maintenance and Repair Unit, with an average annual concentration of 2.5 E -05 mg/m^3, had the lowest concentration among the pollutants released in the respiratory air of the personnel. Table 5 shows the average concentration of pollutants and their ADI. As seen, the average concentration of the emissions in a descending order was as NH_3 > Oil Mist > NaOH > H_2SO_4 > CCl_4 > H_2S > N_2H_4 > $C_6H_5CH_3$. In addition, the emissions could be sorted based on their ADI values as NH_3 > Oil Mist > NaOH > CCl_4 > H_2SO_4 > H_2S > N_2H_4 > $C_6H_5CH_3$. The results indicated that inhalation of ammonia and its daily absorption through inhalation route had a high risk for the personnel.

Health Risk Assessment Results

The results of health risk assessment have been summarized in Table 6. Among the 8 compounds whose concentration was measured at the combined-cycle power plant following the OEHHA guideline, we assessed the health risks of hydrazine and tetrachloromethane by using the IUR method to characterize the carcinogenic risks.

Non-carcinogenic Risk

According to Eq. 5, non-cancerous risks (HQ) are derived through dividing the ADI value by a reference value.[31] The results of non-cancerous risks for the released emissions showed that sulphuric acid with HQ = 1.6E + 01 and ammonia with HQ = 3.62E + 01, both had HQ > 1 (Table 6). This means that the potential non-cancerous effects were likely to occur. Other compounds, including sodium hydroxide (HQ = 3.50E-03), oil mist (HQ = 2.87E-01), hydrogen sulfide (HQ = 6.61E-01), and toluene (HQ = 3.26E-06) had a HQ < 1. So, it was unlikely that these pollutants had adverse health effects on the personnel.

In order to assess the total potential non-carcinogenic health outcomes caused by the measured vapors, the HQ values of all the chemicals were summed up and expressed as HI. The calculated HI for the mentioned six compounds was equal to 5.34E + 01. Since the HI > 1, there was a possibility for the occurrence of non-carcinogenic risks. There is considerable evidence that chronic (prolonged) irritation and inflammation can lead to cancer.[32,33] In terms of the HQ value, the measured non-carcinogenic emissions were sorted in a descending order as NH_3 > H_2SO_4 > H_2S > Oil Mist > NaOH > $C_6H_5CH_3$.

Carcinogenic Risk

According to the classifications of IARC, carbon tetrachloride and hydrazine are categorized as potential carcinogenic to humans.[34] Moreover, the hydrazine has been introduced as a carcinogenic chemical by DHHS.[35] Accordingly, Eq. 3 was used to measure the individual inhalation exposure to tetrachloromethane and hydrazine as carcinogenic risks. The US EPA estimates the inhalation risk of hydrazine as 4.9E-03 (μg/m^3)$^{-1}$, which was equivalent to 1.72E + 01mgkg^{-1}d^{-1} (Eq.4). The inhalation risk of tetrachloromethane was also 6.0E-06 (μg/m^3)$^{-1}$), which was equivalent to 2.1E-02 mgkg^{-1}d^{-1}.[36] According to Table 6, the carcinogenic risk (CR) was calculated as 9.58E-03 for hydrazine and 5.47E-04 for tetrachloromethane. Therefore, the total carcinogenic risk of the emissions in the power plant was calculated as 1.01E-02. Considering the values of total carcinogenic risk for tetrachloromethane and hydrazine, the total risk of these chemicals falls within the category of significant (i.e. more than 10^{-4}), that belongs to the range of hazardous carcinogenic effects.

To assess potential cancer effects, the likelihood of an individual developing a disease during exposure to chemicals was examined using chemical dose-response data. Generally, the acceptable range for cancer risks proposed by the World Health Organization (WHO) is between 1.0E-04 and 1.0E-06.[37] In the power plant under study, hydrazine is used by both the personnel of the repair and maintenance unit for boiler repair and maintenance, as well as by the personnel of the steam unit to de-oxygenize water in the steam generation process. Consequently, more than 30% of the workers, over their 30-year career period, are directly exposed to this toxic substance. Thus, the risk of exposure to hydrazine is very high for the personnel in these units.

Approximately 25% of the personnel in the plant work in the repair and maintenance unit. These workers, due to the rotation of their workplaces across different units of the plant, have been exposed to all the gases and vapors released in various units during their work activities. Consequently, it was expected that they would have inhaled the vapors of chemicals used in the repair and maintenance unit. In addition, they were exposed to

Table 5. Average Concentration of Pollutants and Their Daily Intake by the Workers

	H_2S0_4	NaOH	Oil Mist	N_2H_4	H_2S	$C_6H_5CH_3$	NH_3	$CC1_4$
Concentration (mg/m^3)	4.97E-02	8.6E-02 (Max)	2.2E-01	1.7E-03	2.0E-03	2.5E-05	2.78E+01	4.0E-02
ADI (mg/kg/d)	1.62E-02	2.80E-02	1.44E-01	5.58E-04	1.32E-03	1.63E-05	1.81E+01	2.61E-02

Table 6. Results of Health Risk Assessment (Carcinogenic and Non-carcinogenic) in the combined-cycle power plant

	H_2SO_4	NaOH	Oil Mist	N_2H_4	H_2S	$C_6H_5CH_3$	NH_3	CCl_4	Total
Cancer risk (CR)				9.58E-03				5.47E-04	1.01E-02
Non-cancer risk (HQ)	1.62E+01	3.50E-03	2.87E-01		6.61E-01	3.26E-06	3.62E+01		5.34E+01

other vapors in different units, particularly sulfuric acid, ammonia, and hydrazine. As a result, the risk of exposure to these personnel was very high.

The personnel of the treatment plant unit (about 7% of the personnel) had a high exposure risk, due to the closed shed and exposure to sulfuric acid, sodium hydroxide and ammonia vapors. They were exposed to inhaling the vapors of these substances at least once during each work shift. Additionally, three operators of the sampling unit, who were also personnel in the treatment plant, were exposed to hydrazine vapors in the closed sampling shed. Consequently, the risk of exposure to these personnel was also high. As previously mentioned, these operators visited the sampling shed at specific times. The personnel at the gas site and the steam site, comprising approximately 10% of the personnel, had a lower exposure risk. This was due to the emissions of oil mist from the chimneys of the gas unit and hydrazine from the blowdown boiler being released into the open air, with minimal connection between their workplaces and the released chemicals. Consequently, the exposure risk for these personnel was very low.

In this study, the average concentration of sulfuric acid in the studied units was 4.97 E-02 mg/m^3. However, the average concentration of sulfuric acid in the study by Lee et al.[7] for a combined cycle power plant in Korea was 4.52E-02 mg/m^3. The mean concentration of sodium hydroxide in the present study was 8.60E-02 mg/m^3, while in the study by Lee et al. it was 1.93 E-01 mg/m^3, which is slightly higher than the measured value in this study. The measured toluene mean concentration in this study was 2.5E-05 mg/m^3. It was 3.70E-01 mg/m^3 in the study by Lee et al.[7] So, the value was higher than the average concentration of toluene in the present study. The levels of hydrazine and ammonia in this study were 1.71E-03 mg/m^3 and 2.78E+01 mg/m^3, respectively, which were reported as Not Detected in the study by Lee et al.[7]

Conclusion

Over the 6-year period of power generation in Iran, based on data reported by the Ministry of Energy between 2010 and 2016, there was an increase in electricity generation from combined-cycle power plants and a decrease in gas and steam power plant production. The acceleration of the construction of combined-cycle gas power plants in Iran can be attributed to the availability of natural gas, the perception of being cleaner compared to other fossil fuels, and, most importantly, the higher efficiency of combined-cycle power plants compared to steam or gas power plants. Consequently, due to the expanding role of combined-cycle power plants in power generation in Iran, this research selected a combined-cycle power plant as its case study.

In this study, measurements of exposure levels and health risk assessment of the workers in different units of a combined-cycle power plant in southwest of Iran were carried out. The aim was to examine the inhalation exposure of the workers who were exposed to the gases and vapors released in their workplace in order to investigate the cancerous and non-cancerous (acute and chronic) risks.

The results indicated that the inhalation of ammonia, followed by sulfuric acid, and their daily absorption through the inhalation route posed a high level of risk, as indicated by HQ values exceeding 1. Additionally, the calculated HI value for non-carcinogenic risks exceeded 1, confirming the likelihood of non-carcinogenic risks occurring. Therefore, due to the ADI of sulfuric acid and ammonia, whose main place of emission is the Industrial Water Treatment Plant Unit, it is necessary to intensify individual care, force the use of personal protective equipment, and reduce working hours in order to decline or eliminate the risk of long-term inhalation. This would be possible through the rules and regulations by the HSE Unit of the power plant. In this regard, it is suggested that the HSE Unit of the power plant perform the inhalation exposure assessment through qualitative model of COSHH (the Control of Substances Hazardous to Health) for initial estimation of emissions and assessment of the workers' inhalation exposure levels. It should be noted that, even for non-cancerous emissions with HQ < 1, it is imperative to implement all safety measures in light of uncertainty.

In the assessment of cancer risk, the risk associated with the vapors of tetrachloromethane and hydrazine exceeded the WHO acceptable limit and fell within the range considered 'significant' (greater than 10^{-4}), indicating hazardous carcinogenic impacts. The carbon tetrachloride and hydrazine are categorized under the Group 2B (as possibly carcinogenic to humans) by IARC.

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Competing Interests

The authors declared no conflict of interest.

Ethical Approval

There were no ethical considerations to be considered in this research.

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