

Article

Investigation of the Presence Volatile Organic Compounds (BTEX) in the Ambient Air and Biogases Produced by a Shiraz Landfill in Southern Iran

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Abstract: The generation and emission of volatile organic compounds (VOCs) affects the environment and air quality, playing an important role in global warming, depletion of atmospheric ozone and emission of unpleasant odors, but also directly affect human health. This study investigated the health risks of benzene, toluene, ethylbenzene, xylene (BTEX) compounds and biogas released in and around the municipal landfill. Sampling of the VOCs was carried out by the 1501NIOSH method from 8 points over 5 months. The samples were analyzed for BTEX in the ambient air of the landfill, resulting in 0.03–18.09 ppm concentrations, while for biogases a 0.08–25.2 ppm range was found. Assessment of definite health and potential risks showed that the lifetime cancer risk (LCR) for benzene and hazard quotient (HQ) for the BTEX components in all studied sampling sites are higher than the acceptable standard. The high concentration of benzene measured in ambient air indicated that petroleum compounds containing benzene and its derivatives have the highest value in the category of BTEX compounds among all emissions. Therefore, high concentrations of volatile compounds derived from VOCs, especially benzene, should be reduced at the site with control engineering measures.

Keywords: environmental pollution; volatile organic compounds; BTEX; biogas; health risk assessment; landfill waste

1. Introduction

Economic, demographic and technological advances in modern societies have led to massive municipal solid waste (MSW) production that leads to complications in waste management [1–3]. Landfilling is, if not the most common, one of the most widespread MSW management methods in urban communities worldwide [4]. Due to the prevailing conditions of operation, their emissions pose a serious threat to human health and the environment [5–7]. Landfill gases (LFG) are produced by microbial decomposition of organic matter in anaerobic conditions [8–11] and are generally considered a major source of

atmospheric pollution [12]. LFGs consist of several gases, including CH₄ (55–60% *v/v*), CO₂ (40–45% *v/v*), and more than 200 non-methane volatile organic compounds (NMVOCs), including C₂⁺ alkanes, aromatics and halogenated hydrocarbons. These compounds are classified as volatile organic compounds (VOCs) [13]. On the other hand, if the current trend towards the use of fossil fuels continues, concerns about global consequences such as global warming, rising sea and ocean levels, the extinction of plants and animals, and unprecedented social change, will be inevitable. One way to solve these problems is to use biogas as an alternative to fossil fuels. In fact, biogas reduces carbon dioxide emissions during methane uptake and ensures a cleaner environment, while these are big leaps towards cleaner fuels. Extensive research and many techniques are currently being developed for the quality of methane extracted from biogas [14]. Reduction in emission and biogas upgradation to biomethane became a point of high technical interest since biomethane is intended to be injected into national gas grids or used as a vehicular fuel [15]. Biomethane is a versatile renewable fuel that replaces fossil natural gas and can be used in combined heat and power (CHP) systems, distributed through a small local gas network, dedicated to public transportation, or converted to hydrogen. In addition, vehicle biofuel produced from waste fulfils EU requirements to reduce greenhouse gas emissions by up to 60% compared to current fossil fuels [16].

Volatile organic compounds are a group of human-made or organic compounds that have relatively high vapor pressure at room temperature (25 °C). VOCs are in their gaseous form at vapor pressure over 0.1 mmHg [17]. They pose a significant environmental impact through their role in global warming, depletion of atmospheric ozone, emission of unpleasant waste odors and the influence of photochemical oxidants [18,19]. The most commonly observed VOCs in landfills are benzene, toluene, ethylbenzene, xylenes (BTEX) [20,21]. Such compounds exist in the atmosphere as gas, constituting about 60% of NMVOCs [22], and are regarded as potentially hazardous air pollutants (HAPs) [23].

According to reports by the Toxic and Disease Registration Agency (ATSDR), continued exposure to hazardous compounds, such as VOCs, can have an extremely harmful effect due to the risk of developing various diseases on human health [24,25]. More specifically, the World Health Organization and the International Agency for Research on Cancer (IARC) have identified benzene as a carcinogen in Group A. Investigations show that benzene is a carcinogen causing leukemia by exposure to 3.19 mg/m³ or 1 ppm at NTP (Normal Temperature and Pressure [26,27]). Inhalation of toluene and xylenes causes headache, vertigo and inflammation of the mucous membrane [28]. As a result, the levels of BTEX compounds are used as indices for measuring the harmful effects of human exposure to VOCs [29].

Much research has been conducted worldwide on the levels of BTEX compounds in the air of landfills. Allen and colleagues collected VOCs from seven landfills in the United Kingdom [30] and identified more than 140 VOCs through three adsorbent sampling tubes (Tenax TA, Chromosorb 102, Carbosive SIII), 90 of which were in all 7 landfills observed. In another study, Eklund et al. (1998) reported collection of landfill gases (LFGs) from New York samples using metal canisters in the ambient air, and more than 70 compounds were detected [31]. In twelve sampling points, Zou et al. investigated ambient air in Chinese landfills, collecting gas samples through three adsorbents (Tenax, Carbosive SIII, silica gel). In total, VOCs records were 60 and 38 found in summer and winter, respectively. Schweigkofler and Hardniessner used stainless steel cans to collect gas samples from two landfills in Germany, and experiments detected more than 80 VOCs at these sites [32]. Durmusoglu et al. collected ambient gas samples from landfills through absorbent tubes containing 400 mg Carbograph 1TD. The average benzene, toluene, ethyl benzene and xylene concentrations were measured at 140.3, 771.7, 239.9 and 341.3 micrograms per cubic meter, respectively [33]. While it is clear that the abundance and levels may vary from site to site and the common denominator of VOCs constitutes a point of concern, their generation must be monitored.

In this study, we focus on the landfill in Shiraz, in Southern Iran. It consisted of two sections, old and new sites that received approximately 1070 tons of waste for disposal (including urban, industrial and hospital) per day. In 2013, there was a massive explosion in a landfill that caused the death of seven people. Since then, proper vigilance regarding VOCs as hazardous materials emitted from landfills has increased in order to avoid serious health problems for operators, workers, and nearby residents. Therefore, it is essential to investigate and control emissions of gases produced at landfill sites. Consequently, the present study aimed to identify, determine, and evaluate the health risks of BTEX compounds in the air of landfills, in Shiraz as a case study. In addition, the effect of meteorological variables (wind speed and direction, temperature, pressure and relative humidity) on BTEX emission was investigated.

2. Materials and Methods

2.1. Chemicals and Reagents

All materials used in this work were analytical grade, purchased from Merck Co. (Darmstadt, Germany) and were used as received.

2.2. The Study Area

The Shiraz's landfill is located 18 km southeast of Shiraz on the Shiraz–Sarvestan road in an area called Barmshour with a total area of 5000 hectares (Longitude = 52.69964, Latitude = 29.42650). A view of the location of the study area is shown in Figure 1. Municipal waste was being disposed of in a landfill covering a total area of 2197 hectares. This was the only waste disposal site, so deposits of industrial and hospital waste were also made at the site, as well as deposits of urban solid waste.

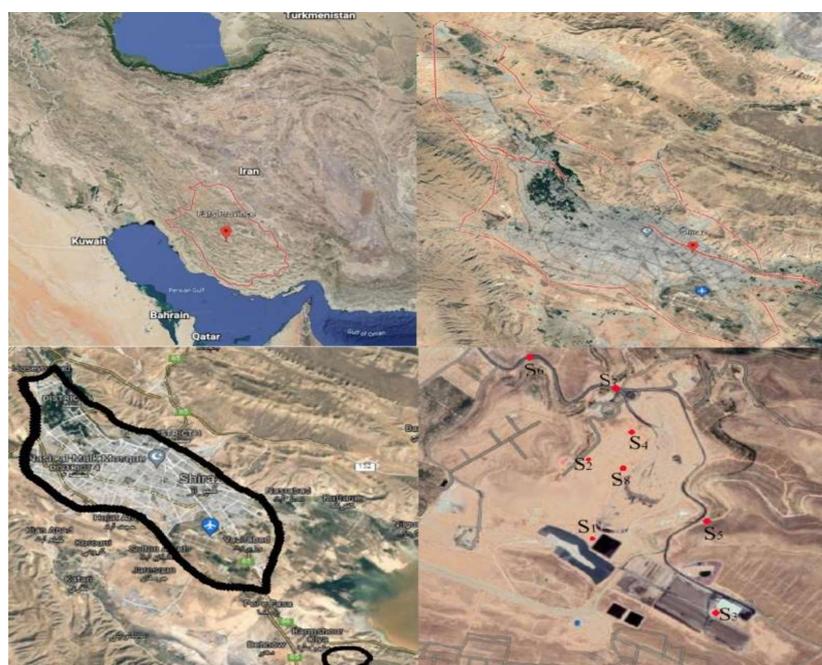


Figure 1. The location of the study area.

Trenches at the landfill were approximately 800 m long and 100 m wide, and 16 m deep. Each landfill layer consisted of 8 m of waste, which was then covered by 1 m of soil. Soil excavated by the trenches was used for the temporary and final covering stages, and new disposal cells in the studied landfill. At the time of research, there was capacity for 2 trenches covering 12 hectares out of the total 40 hectares allocated to waste management in the area. Samples of ambient air from the landfill were investigated for BTEX compounds,

and levels were compared among points at the site. A view of the trenches of the study landfill is shown in Figure 2.



Figure 2. Trenches at the landfill.

The biogas collection pipeline system was also active on site. In this way, they used the active method to collect biogas and then transfer it to the biogas plant to generate electricity. The biogas plant of Shiraz was established in 2007 in an area of 1 acre landfill. This plant with natural consumption gas of 740 m³/h is the largest power plant in the Middle East. The amount of electricity generation in the power plant is 7188 MWh/year. The landfill gas management system is composed of extended sectors of biogas collection, a natural gas transmission network to the consumer, equipment available in the collection area and a gas transmission network, gas preparation system (main and blower condensate trap) and consumer gas system (Feller or power generator) (see Figure 3).



Figure 3. Shiraz biogas power plant with gas collection wells.

2.3. Sampling Points and Collection

A total of 8 sampling points were selected as follows: the leachate basin (point 1), landfill (point 2), composting (point 3), new biogas vent (point 4), a 1-km distance before the landfill (point 5), a 1-km distance after the landfill (point 6), the entrance to the landfill (point 7), and old biogas (point 8). Figure 4 shows the sampling points of the site. Two points 5 and 6 were selected according to prevailing wind direction from southwest to northeast. Six samples were collected from each point and a total of 48 samples were

collected altogether. These samples were collected by 7-cm long adsorbent tubes packed with activated carbon (6 mm OD, and 4-mm, ID, 100/50) and sampling pumps (SKC 224-44MTX), which were situated 1.5–2 m above ground level and calibrated (300 mL min^{-1}), within a period of 2 h. Adsorbent tubes containing two sections of activated carbon with 20–40 mesh separated by a 2 mm layer of polyurethane foam (made by SKC company, Chino Hills, CA, USA) were used. The tube was made of glass. The front section contained 100 mg and the rear section contained 50 mg (50/100) activated carbon.



Figure 4. Sampling points in the site.

Samples were taken during the period from the 3rd of September, 2020, to the 14th of January, 2021, according to the 1501NIOSH standard method. This method recommends taking gases and organic vapor samples using adsorbents such as activated carbon, which have high porosity, large surface area, and thermally stable polymers. Control samples were also taken from each point. Control sampling was performed in the same way as the main sampling features. After control sampling, both sides of the sampling tube were broken and kept in the environment for a moment. Additionally, after putting the lid on it and tagging its identification code, it was transferred to the laboratory along with other samples to be prepared and analyzed in the same way as the main samples. Once each sample had been collected, the ends of the adsorbent tubes were sealed by plastic closing lids. Samples were kept at 4°C pending analysis.

2.4. Extraction of VOCs from the Samples

Extraction of VOC compounds from adsorbents was performed by ultrasound for 15 min with 2 mL of benzene-free carbon disulfide (CS_2) (purity $\geq 99.5\%$ (GC); CAS Number: 75-15-0; Merck Co, Darmstadt, Germany). Additionally, 1-bromododecane (purity $\geq 95.0\%$ (GC); CAS Number: 143-15-7; Merck) was used as an internal standard because it did not interfere with VOCs emitted from municipal landfills [34,35]. Extraction efficiency in the present study for benzene, toluene, ethylbenzene and xylene were 92, 95, 95 and 90%, respectively.

2.5. Analysis of Landfill Gases by Gas Chromatography

The samples were analyzed by gas chromatography (Agilent Technologies 7890A, Santa Clara, CA, USA) equipped with a 7000 triple mass detector and J&W DB-1MS capillary column (Agilent Technologies, Santa Clara, CA, USA) (length 30 m, diameter 0.25 mm and film thickness 0.25 μm). Helium was used as the carrier gas at a flow rate of

1 mL/min. The injection and transfer line temperature were 250 °C [36]. The temperature of the column was first programmed to rise from 45 °C (at which it was kept for 2 min). Then, at a rate of 10 °C/min, it reached a temperature of 240 °C and then was maintained at a stable temperature for 5 min. The quadruple mass spectrometer scanned over the 40–600 amu with an ionizing voltage of 70 eV, using the TIC method. The injection volume was 0.5 µL. BTEX concentrations were determined by the calibration curve, prepared by diluting through CS₂ the standard benzene, toluene, ethylbenzene, and xylenes, and finally 6 calibration points were created (0.5, 1, 10, 50, 100, 150 ppm), which were analyzed along with other samples [37].

2.6. Deterministic and Stochastic Risk Calculation

Determining the extent of the negative effects of petroleum compounds (BTEX) on workers (who are exposed to higher concentrations of these compounds for a longer period) is essential given the adverse health effects of these compounds [38]. Risk assessment associated with chronic exposure to toxic compounds is an accepted method to assess the cancerous effects and non-cancerous risk of hazardous substances [39]. Chronic daily intake (CDI) was measured by inhalation using the following formula (Equation (1)) [40]:

$$CDI = \frac{C \times CF \times IR \times ET \times EF \times ED}{BW \times AT} \quad (1)$$

where C: Composition Concentration (µg/m³), CF: Conversion factor (mg/µg), IR: Inhalation rate (m³/day), ET: Exposure time, EF: Exposure frequency (day/year), ED: Duration of exposure (years), BW: body weight (kg) and AT: average time (days). Equation (2) was used for calculation lifetime cancer risk (LCR) for benzene (Equation (2)):

$$LCR = CDI \times SF \quad (2)$$

where SF: cancer slope factor (mg/kg/day). An LCR greater than 1 × 10⁻⁴ indicates a maximum individual risk for cancer. Normally the LCR should be below 1 × 10⁻⁶ [41]. Non-carcinogenic risk is determined in terms of Hazard quotient (HQ). The HI for BTEX is calculated based on the following equation (Equation (3)):

$$HI = \sum HQ_i = \sum \frac{CDI_i}{RfD_i} \quad (3)$$

where RfD: the reference dose (mg/kg/day). An HI below 1 is considered to be a negligible risk [42].

Health hazard assessment estimates a random distribution to assess the potential for carcinogenic hazards and non-cancerous hazardous compounds. Random calculations consider some variables as random variables, known as the probability distribution [43]. To eliminate the uncertainty factor in the calculations related to health risk estimation, Monte Carlo simulation and sensitivity analysis were performed using Oracle Crystal Ball 11.1.2.3. (Oracle Co., Redwood City, CA, USA) Table 1 shows the parameters selected and used to assess the risk and sensitivity analysis of each variable.

Table 1. Parameters and variables used in the health risk assessment model.

Variable	Unit	Distribution Factor	Values	Ref.
C	$\mu\text{g}\cdot\text{m}^{-3}$	-	-	This study
CF	$\text{mg}\cdot\mu\text{g}^{-1}$	-	10^{-3}	
IR	$\text{m}^3\cdot\text{h}^{-1}$	normal	0.83 ± 0.08	[44]
ET	$\text{h}\cdot\text{day}^{-1}$	fixed	8	
EF	$\text{day}\cdot\text{year}^{-1}$	normal	300 ± 10	
ED	year	fixed	30	
BW	kg	Log-normal	70 ± 13	
AT	year	-	non-carcinogenic = 30 carcinogenic = 70	[45]
SF _{benzene}	mg/kg/day	-	0.029 benzene = 0.00855 toluene = 1.4	
RfD	mg/kg/day	-	ethylbenzene = 0.286 xylene = 0.029	

3. Results and Discussion

3.1. BTEX Concentration

To our knowledge, at the time of writing, no survey had been published to date on concentrations of VOCs (benzene, toluene, ethylbenzene, xylenes) on the landfill site under study. Statistical analysis of the concentration of each BTEX compounds in the air around the landfill and biogas collection valves during the sampling period (3 September 2020–14 January 2021) is shown in Tables 2 and 3. Further results of statistical analysis were shown in Appendix A. The difference observed in the case of maximum and minimum concentrations in the ambient air was due to environmental temperature fluctuations [46,47]. Benzene and vinyl chloride are the most frequently observed VOCs in urban landfills particularly industrial landfills, as they normally receive liquid waste [48,49].

Table 2. Descriptive statistical analysis of BTEX compounds.

Location Compound	In Biogas Collectors				In the Air around the Landfill			
	Max	Min	Mean	Std.	Max	Min	Mean	Std.
Benzene (ppm)	18.09	0.02	3.71	5.06	5.2	0.1	2.34	2.60
Toluene (ppm)	2.02	0.02	0.68	0.68	7.4	0.12	3.43	3.06
Ethylbenzene (ppm)	1.85	0.03	0.61	0.78	25.2	0.24	13.7	10.67
Xylene (ppm)	6.26	0.02	1.3	2.34	5.4	0.08	2	2.9

Table 3. Results of non-cancerous risks of BTEX exposure.

Compound	Max	Min	Mean	Std.
HQ _{Benzene}	2171.27	12.71	674.21	857.28
HQ _{Toluene}	2.95	0.08	1.03	1.00
HQ _{Ethyl benzene}	14.06	0	3.71	5.46
HQ _{Xylene}	464.74	0	91.64	162.50
HI	2172.38	18.05	770.59	817.49
LCR _{Benzene}	0.231	0.001	0.074	0.091

Benzene remains in the atmosphere longer than other BTEX types. Furthermore, benzene concentration rises due to its accumulation. Ethylbenzene and xylenes have higher photoreactivity than benzene and toluene, being reduced during daylight through photochemical reactions. The highest mean VOC concentrations in benzene, followed by xylene, toluene and then ethylbenzene, were measured and recorded as presented in

Table 2. Additionally, a chromatogram of volatile organic compounds at the landfill is shown in Figure 5.

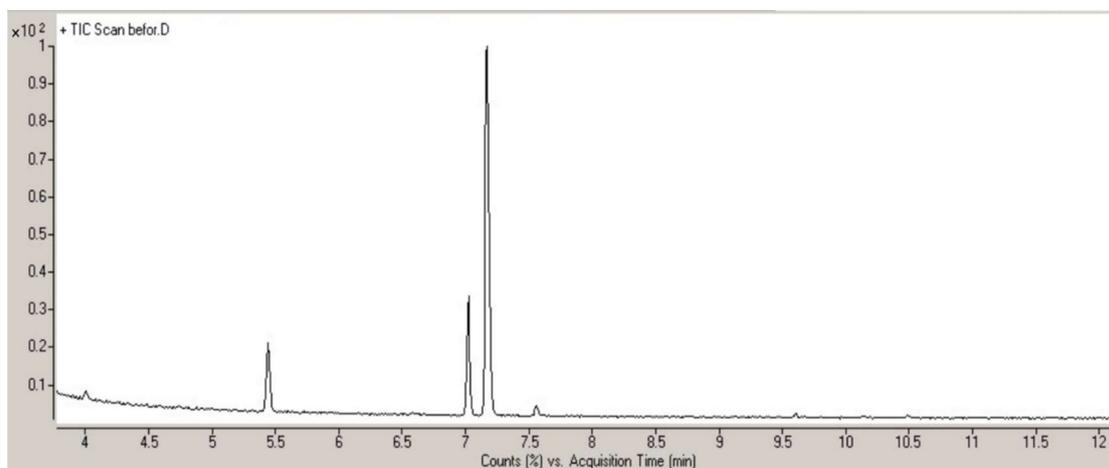


Figure 5. Chromatogram (GC-MS-MS) of volatile organic compounds at a distance of 1 km around the landfill.

3.2. The Effect of Meteorological Parameters on Emissions of VOCs

To investigate the factors affecting emission and concentration of VOCs, the following meteorological parameters, including mean temperature ($16.5\text{ }^{\circ}\text{C}$), atmospheric pressure (899.2 mmHg), relative humidity (30.3%), and wind speed (2.05 ms^{-1}) were measured (Figure 6). Results revealed that atmospheric pressure and wind direction did not significantly affect BTEX emissions. However, the concentrations of compounds showed a notable increase in relation to increased wind speed and decreased temperature. Relative humidity had a direct effect on the emission of VOCs, and high concentrations of VOCs were observed at high humidity.

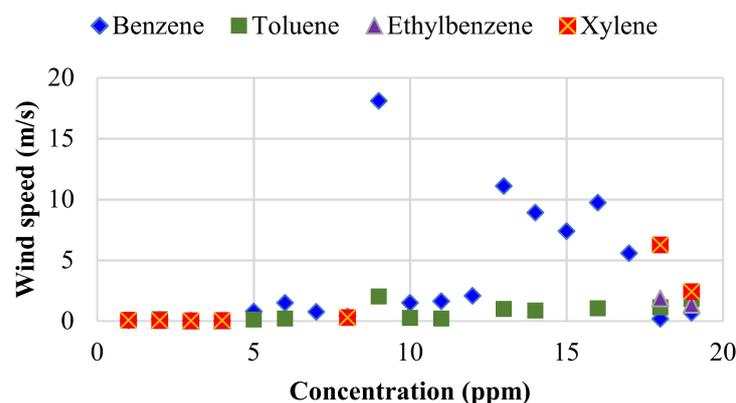


Figure 6. Effect of wind speed (m/s) on emission of VOCs in the ambient air of landfill.

To survey the effect of environmental ventilation on VOCs concentrations, ambient air and landfill gases (LFGs) collection vent system results were compared (Figure 7). Figure 3 shows that, in each of the LFG valves, all BTEX compounds, except benzene, had higher concentrations than the concentrations in the ambient air of the landfill. In LFG valves, the ethyl benzene, toluene, benzene, and xylene concentrations were 64, 16, 11 and 9%, respectively. In terms of the LFG to ambient air concentration ratio (L/A), the estimates for benzene, toluene, ethylbenzene, and xylene were 0.63, 5, 4.22 and 1.5, respectively.

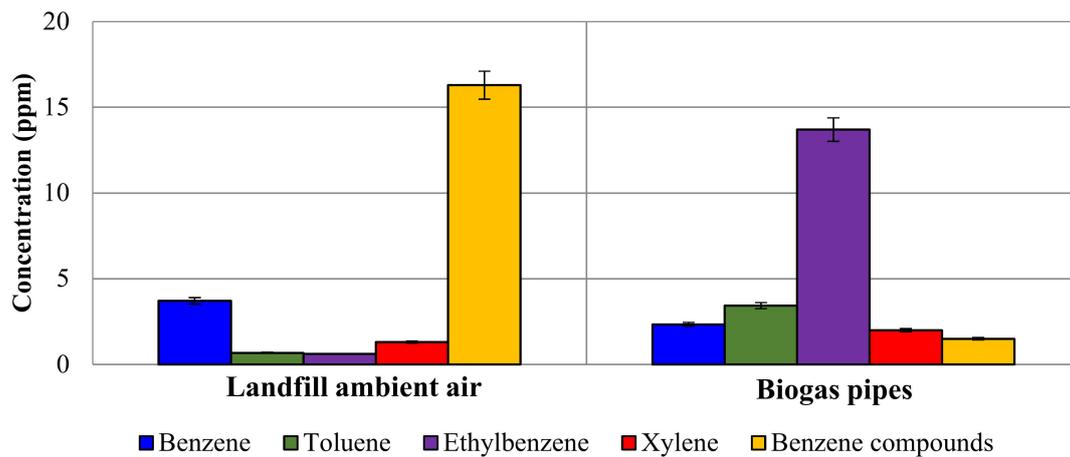


Figure 7. Comparison of VOC concentrations in LFG vents and the ambient air of the landfill.

3.3. Effect of Disposal Time on Concentrations of VOCs

To investigate the time of disposal on concentrations of VOCs emitted, both old and new biogas sites were studied. Our results revealed a significant difference between the two types. Figure 8 shows that all BTEX concentrations were higher in the new biogas collection tubes than in the old biogas vent. This result would have been determined by the volume of gas produced during the time of waste disposal. The ratio of BTEX compounds in the new biogas collection tubes to old biogas was 0.01/1.5. The concentrations of all BTEX compounds in the new biogas vents were determined as several times larger than those in the old ones.

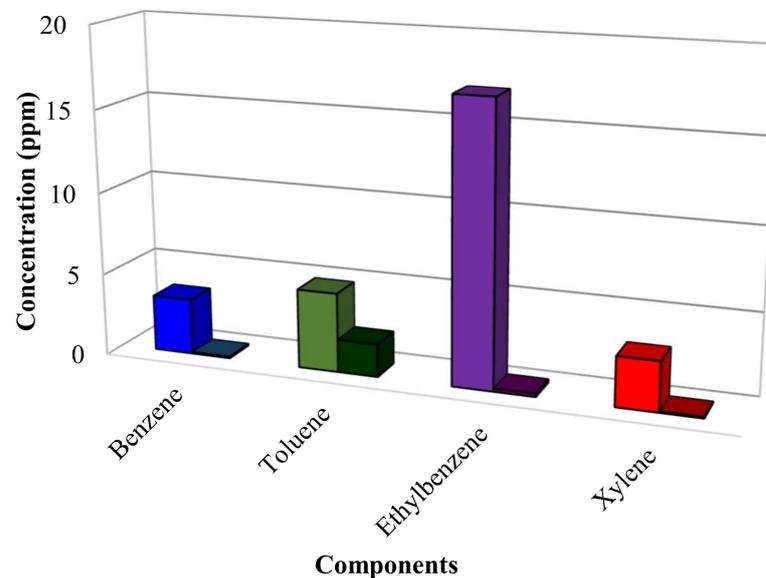


Figure 8. Comparison of VOCs concentrations in old and new biogas collection vents. Left-hand columns: new biogas vent; right-hand columns: old biogas vent.

3.4. Comparison of VOCs Concentrations in Different Countries/Landfill Sites

Comparison of the average concentrations of each BTEX compound in different countries [21,30,50–52] with our study shows that the concentrations of VOCs in our case study site were more intense in ambient air compared to the results of similar surveys. There was a significant difference among concentrations of VOCs in landfills of different countries. The reason for such difference can be attributed to various factors, including compounds (packaged plastics or foam plastics), age and extent of disposed waste, duration of the pre-decomposition stage, meteorological parameters (humidity, temperature, air pressure,

and wind direction), sampling time, typology, and conditions of site operation (landfill coverings or cap). The highest concentrations observed at landfills were related to benzene, while concentrations higher than those measured in this study were reported for other compounds, such as toluene, ethylbenzene and xylene at landfills in Canada.

3.5. Spatial Variation of Concentrations of BTEX at Sampling Points

Figure 6 summarizes the concentrations of BTEX compounds in different sampling points: the leachate basin (point 1), landfill (point 2), composting (point 3), biogas (point 4), a 1-km distance before the disposal site (point 5), a 1-km distance after the disposal site (point 6), the entrance to the disposal site (point 7) and old biogas (point 8). Figure 9 also shows a schematic of the sampling points according to their direction and prevailing wind speed.

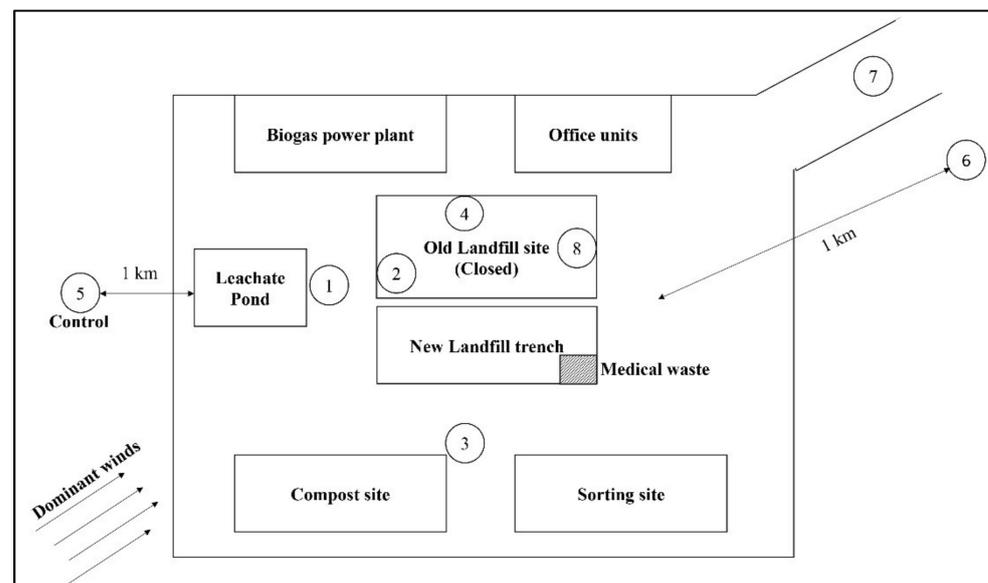


Figure 9. Sampling points according to their direction and prevailing wind speed.

We aim to illustrate the pattern of temporary changes in each of the BTEX compounds in different sampling points in Figure 10. Our investigation showed a remarkable difference in VOC concentrations between the sample points. Sampling points 5 and 6 were within a 1-km distance before and after the disposal site and were located outside the site. Sampling point 7 was in the vicinity of the administrative section and the laborers and employee's recreation area, and the other points were situated within the central part of the landfill.

Higher benzene concentrations were recorded at sampling points 7, 4, 3, 1, 2, 6, 5, and 8, accordingly. A marked increase in benzene concentration at point 7 was attributed to a sudden change in temperature, increased humidity, and decreased wind speed. Point 7 was situated downstream of the prevailing wind and in close proximity to old and new biogases. The reason for benzene concentration at sampling point 8 might have been caused by a change in temperature or a sharp decrease in humidity at the time of sampling.

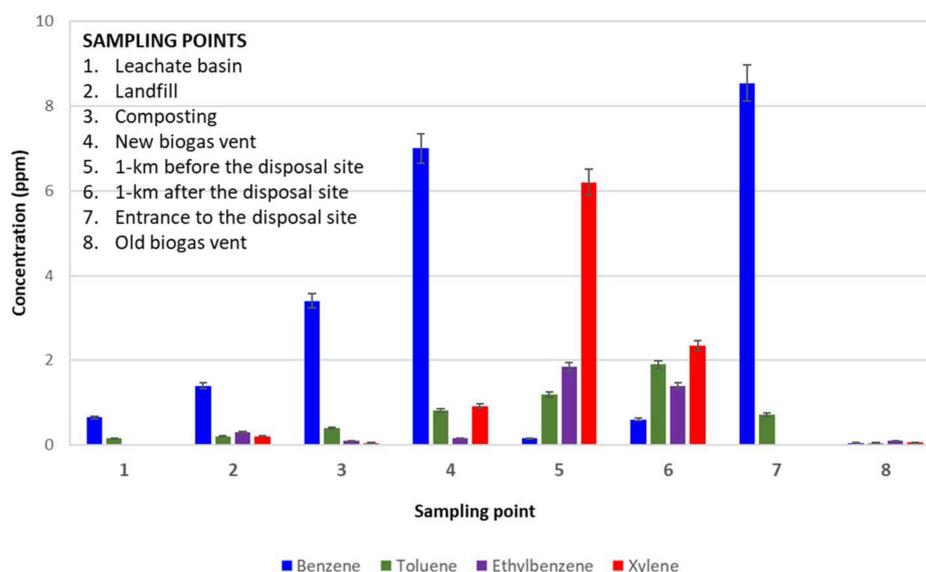


Figure 10. Concentrations of BTEX compounds at different sampling points.

Based on their degree, toluene concentrations were observed at points 6, 5, 4, 7, 3, 2, 1, and 8, respectively. Yet, these degrees exceeded the WHO weekly standards. The European Union has not yet issued standards for toluene concentrations, but the WHO has suggested a weekly concentration of 0.26 ppm in order to protect human health. In the present investigation, the average toluene concentration (0.68 ppm) was higher than the recommended acceptable limit.

Maximum ethylbenzene concentrations were found at sampling points 5, 6, 2, 4, 3, and 8, and at all these points, ethylbenzene concentrations fell within the standard limits. Similarly, higher concentrations of xylenes measured at sampling points were at 5, 6, 2, 4, 3, and 8. At each of these points, concentrations were less than the acceptable standard limit. Photochemical reactions occurring during the summer can reduce concentrations of ethylbenzene and xylenes because these compounds have high photoreactivity and decomposability within a short period. Generally, the type and concentration of VOCs in all sampled points were different, considering the nature of the activity, situation and other factors.

3.6. Deterministic and Stochastic Risk Calculation from BTEX Exposure

The present study evaluated the non-cancerous risk of occupational exposure to BTEX values by inhalation, through the HQ method. In addition, the risk of carcinogenicity due to exposure to benzene was assessed through the risk of lifelong cancer (LCR). Table 3 presents the non-cancerous risks of BTEX exposure. Non-cancer risk assessment showed that the HQ for all studied compounds (benzene, toluene, ethylbenzene and xylene) was too much to inhale and above the acceptable level, indicating a high risk of long-term exposure to these compounds (Table 3). The HQ index goes beyond the standards, meaning that exposure to inhaled chemicals can adversely affect people's health. According to the International Agency for Research on Cancer (IARC), benzene is classified as a carcinogen. The Lifetime Cancer Risk Assessment (LCR) was used to assess the carcinogenic risk of benzene [53]. The mean (standard deviation) LCR estimated for benzene is about 0.001–0.231 (Table 2). According to the value obtained for LCR, the average lifetime carcinogenic risk measured for benzene (0.074) is greater than the maximum acceptable value provided by USEPA (1×10^{-4}), which is a significant risk for cancer workers and people at risk.

To determine the potential health risk and to find the factors affecting the estimated risk, a simulation and Monte Carlo sensitivity analysis was performed using Crystal Ball software. For other uncertainties that may affect the risk assessment results, these values were estimated through sensitivity analysis. The 5th percentile and the 95th percentile of

benzene hazards were 3.26×10^{-3} and 6.92×10^{-2} , respectively (Figure 11). Cancer risk less than or equal to 1 in 1,000,000 ($=1.0 \times 10^{-6}$) is considered insignificant or ineffective. On the other hand, projected risk greater than or equal to 1 in 1000 ($=1.0 \times 10^{-3}$) was defined as a warning for significant risk by the US Supreme Court in 1980. Furthermore, the risk level of 1.0×10^{-4} was recently considered acceptable. Here, benzene's average carcinogenic hazards are more than 1.0×10^{-3} (specifically: 2.31×10^{-2}). Therefore, the risk of benzene carcinogenicity in landfills is highlighted and should not be ignored. Working in this place is potentially dangerous, causing serious health issues.

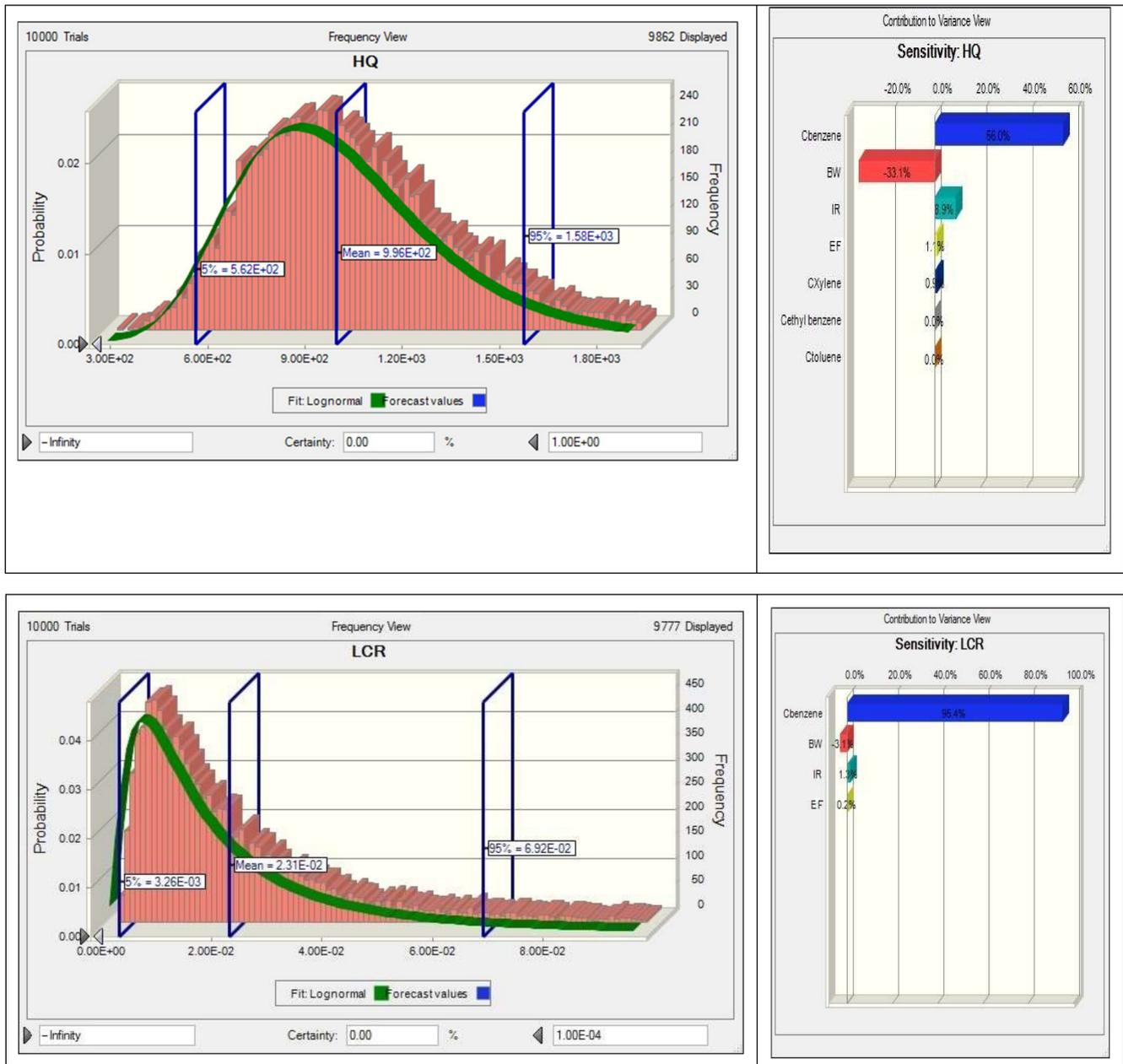


Figure 11. Histogram of HQ and LCR for BTEX components.

The main route of contact with inhaled pollutants is considered. The results of the sensitivity analysis illustrated that benzene concentration (56%) and body weight (−33.1%) had the highest outcome on variables in calculating the non-cancer risk of the BTEX component, while other combined parameters had less effect on the risk of cancer (less than 1). Benzene concentration (95.4%), inhalation rate (1.3%), and exposure frequency (0.2%)

are the most important variables to assess cancer risk. On the other hand, bodyweight (−3.1) has a reverse effect on the risk of cancer. This study shows that the concentration of VOCs, as one of the most important factors affecting health, should be minimized in the workplace. Therefore, using efficient monitoring and protection methods, occupational exposure to VOC should be reduced.

4. Conclusions

This study aimed to investigate the quantity (concentration) and quality (type) of VOCs in landfills in southern Iran. In this evaluation, samples of air around the landfill and biogas collection valves were prepared daily, and then the studied parameters were measured and compared with other studies and standard values. The presence of NMVOCs in the landfill site was an indicator of volatile compounds in disposed waste. Higher concentrations were determined among VOCs in benzene (3.7 ppm), followed by xylenes (1.3 ppm), toluene (0.68 ppm), and ethylbenzene (0.61 ppm). Emissions of benzene appear to be the most critical cause for concern in the studied landfill, due to its carcinogenic character, and its emissions exceeding the acceptable limits.

Considering the hazardous impacts of such compounds, although concentrations were not high compared to other gases in the disposal site (less than 1% of the total volume), the most commonly observed VOCs in ambient air of the site were inherently toxic, and in some cases carcinogenic, and would have a critical effect on the quality of air in the region. This level of exposure would also affect people living in the vicinity (the nearest village was 4 km far from the site).

The non-carcinogenic risk (HQ) from BTEX compounds, via implementation of risk assessment techniques and possible methods for assessing the negative effects of different factors on health, was found to be higher than the permissible levels. In assessing the potential adverse health effects, the carcinogenic risk of benzene was calculated to be higher than the allowable limit (1.0×10^{-4}). The sensitivity analysis showed that the measured concentration of benzene through workers' respiration was considered the most important factor for measuring carcinogenic and non-cancerous risks. Therefore, implementing effective protection measures is an important step to reduce workers' exposure to risk factors. Thus, we suggest that personal protective equipment (PPE) specifically designed for eliminating inhaled VOC and fit tested to each employee have to be implemented. Additionally, we recommended decreasing employees' working time span or occasionally change their workspace from a site to another site sequentially. Finally, biological monitoring of the metabolites of these compounds is also recommended for future studies.

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Appendix A

Tables A1 and A2 provide data related to statistical analysis.

Table A1. Statistical analysis of BTEX compounds in the air around the landfill (ppm).

Compounds	Max.	Min.	Average		Standard Deviation
	Statistical	Statistical	Statistical	Std. Error	
Benzene	18.09	0.02	3.71	1.16	5.06
Toluene	2.02	0.02	0.68	0.18	0.68
Ethylbenzene	1.85	0.03	0.61	0.31	0.78
Xylene	6.26	0.02	1.3	0.88	2.34
Benzene derivatives	43.09	2	16.29	13.40	23.21

Table A2. Statistical analysis of BETX Compounds in biogas pipes (ppm).

Compounds	Max.	Min.	Average	Standard Deviation
Benzene	5.2	0.1	2.34	2.60
Toluene	7.4	0.12	3.43	0.306
Ethylbenzene	25.2	0.024	0.137	0.1067
Xylene	5.4	0.008	2	2.9
Benzene derivatives	2.4	0.7	1.5	0.7

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