

# Determining the emission rates of volatile organic compounds and modeling their dispersion from the petroleum and chemical storage tanks of the largest oil terminal in the southwest of Iran

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## ABSTRACT

This study aimed to investigate the air pollution caused by volatile organic compounds (VOCs) with an emphasis on benzene, toluene, ethylbenzene, and xylene (BTEX). Due to surface evaporation from the storage tanks of the largest petroleum and chemical product terminal in the export port of the southwestern Iran, the field measurements of the emission sources were performed using the TANKS 4.0.9d software, and VOC emission modeling was performed using the PHAST software. Among 36 point sources (32 external floating roof tanks and four internal floating roof tanks), the emission rates of the VOCs of the storage tanks were determined using the TANKS 4.0.9d software in the area of 3.8 km<sup>2</sup> during 12 months (March 2017-January 2018). The highest rate of VOC emissions from the tanks was observed in July, with the highest temperature and wind speed in the region. According to the results, the total emission rate of the VOCs from the storage tanks was 881.74 ton/year, and the highest emission rate was observed in the external floating roof tanks (865.7 ton/year; 98.18%). The contribution of the internal floating roof tanks was 16.04 ton/year (1.81%), and the highest and lowest VOC emission rates in the export port were observed in the light naphtha tank No. 67 and jet naphtha storage tank (56.73 and 4.18 ton/year), respectively. In addition, the highest and lowest BTEX emission rates from the storage tanks were observed in the gasoline tank No. 62 and jet naphtha tanks No. 93 and 94 (0.37 and 0.05 ton/year), respectively.

**Keywords:** Petroleum products, Storage tanks, Volatile organic compounds, TANKS model, PHAST software, Oil terminal

## Introduction

Volatile organic compounds (VOCs) are common air pollutants, which could be harmful to the human health and environment. Some VOCs are classified as potential carcinogens for humans. VOCs have received great attention due to their key role in the atmospheric photochemistry, as well as their

potential side-effects on general health, the largest source of which is oil storage.

Saikomol *et al.*<sup>1</sup> investigated the possible effects of the release of the VOCs emitted from the oil refinery tank area on human health and respiratory issues. The estimations were performed using the United State Environment Protection Agency (U.S.EPA) TANKS 4 emission model for the direct measurement of the gas phase of each liquid stored in the storage tanks. In another study, Ramavandi *et al.*<sup>2</sup> assessed the amount and percentage of the monthly emissions of VOCs in 22 storage tanks in an oil depot in Iran during 12 months in 2014 using the TANKS 4.0.9d software.

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Howari<sup>3</sup> studied the evaporation losses of the VOCs of organic liquids in storage tanks using a Gaussian dispersion model. In the mentioned study, the AERMOD and ALOHA software were also used to simulate the dispersion of VOCs in normal and random scenarios in Sharjah (UAE). Furthermore, Cunningham<sup>4</sup> examined the current methods and software used for calculating the emission rate of VOCs in various industrial fields, concluding that the results of the TANKS software designed for storage tanks were more accurate and could be used without requiring any measurement or monitoring.

Ashrafi *et al.*<sup>5</sup> calculated the vapor losses from the liquids stored in the oil tanks in Assalouyeh region of Iran using TANKS 4.0.9d, and their findings were similar to the AERMOD dispersion model in predicting the distribution of VOCs from liquid storage tanks. On the other hand, Jackson<sup>6</sup> estimated the release of nine VOCs from eight organic fluid tanks in a manufacturing company in Dar Es Salaam (Tanzania) using TANKS 4.9d. In the mentioned study, the total VOC emissions were 853.20 metric tons per year. TANKS 4.9d has been designated for estimating the emissions of organic liquids from storage tanks into the atmosphere.<sup>7</sup> Wei *et al.*<sup>8</sup> aimed to estimate the emission of VOCs in an industrial area, which was an oil refinery in northern China. According to the findings, the monthly production of VOCs in the refinery was 183.5±89.0 tons in March and 538.3±281 tons in June.

Ding *et al.*<sup>9</sup> measured the mixing ratios of 57 VOCs using gas chromatography-mass spectrometry (GC-MS), while Dumanoglu *et al.*<sup>10</sup> collected 160 ambient air samples from 40 sites in Aliaga (Turkey) to determine the climatic, seasonal, and potential sources of VOCs using passive sampling in four seasons in 2009 and 2010. On the other hand, Pandya *et al.*<sup>11</sup> evaluated the VOC concentrations at an oil refinery, and the VOCs were sampled using an activated carbon adsorbent tube, disposed of, and extracted by thermal desorption. Following that, the samples were analyzed by GC-MS. In another research, Masih *et al.*<sup>12</sup>

performed the sampling of benzene, toluene, ethylbenzene, and xylene (BTEX) in India using a low-volume sampling pump (Company SKC U.K. [SKC]; model 220), equipped with coconut-activated charcoal tubes at the flow rate of 250 milliliters per minute for 20-24 hours. The analysis was performed in accordance with the NIOSH 1501 method.

In another research, Pirbadali and Peyghambarzadeh<sup>13</sup> studied the emission of some hazardous pollutants (CO, C<sub>x</sub>H<sub>y</sub>, H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>x</sub>, and CO<sub>2</sub>) from six petrochemical incinerators in two different seasons. In the mentioned study, an air pollutant dispersion model was implemented to predict the dispersion of each pollutant near the industrial area, and the obtained results showed that almost all the pollutants (especially C<sub>x</sub>H<sub>y</sub>) were detected at high concentrations in the residential area near the industrial area.

Aklilu *et al.*<sup>14</sup> investigated the sources of VOCs during the periods of increased hydrocarbon concentrations in the vicinity of a cold heavy oil extraction area in Alberta (Canada). Moreover, Allen<sup>15</sup> stated that the emissions of VOCs and nitrous oxide (NO<sub>x</sub>) from the United States oil and gas supply chain have increased significantly over the past decade. Hoyt and Raun<sup>16</sup> also measured the release of benzene and VOCs from a chemical refinery in the United States, concluding that the estimation of the greenhouse gas emissions from oil refineries and chemical plants is the basis of multiple environmental assessments and policymaking.

According to Hadidi *et al.*,<sup>17</sup> a large proportion of the pollutants in a refinery in Saudi Arabia were obtained from the refining of crude oil in the form of NO<sub>x</sub>, SO<sub>x</sub>, and VOCs. On the same note, Zhang *et al.*<sup>18</sup> measured the volatile organic pollutants at Jinshan second industrial zone in Shanghai (China), while Jiang *et al.*<sup>19</sup> stated that VOCs are the most complex range of the pollutants that are harmful to the human health and environment. To develop the industrial standards of VOC emissions, the most efficient control methods and indicators should be selected depending on the features of the

production process, VOC emission method, and the possible control measures.

Marzocca *et al.*<sup>20</sup> conducted an indoor air quality study at an elementary school in Taranto (southern Italy), and the results of the analysis indicated that BTEX had similar concentrations in the indoor and outdoor air. In addition, Ting *et al.*<sup>21</sup> measured the concentrations of VOCs in Beijing air in the fall of 2005, and the findings were analyzed based on the vertical distribution of the VOCs under the influence of meteorological parameters and transport properties.

Xiong *et al.*<sup>22</sup> examined the levels of environmental VOCs, their potential resources, and the associated health risks in two coastal cities on the Vancouver Metro during 2012-2016. In addition, Cheng *et al.*<sup>23</sup> reviewed a bibliographical analysis of the research focused on the health effects of VOCs in the past 16 years. Soni *et al.*<sup>24</sup> also stated that VOCs are carcinogenic elements that give rise to chemical reactions. Therapeutic processes such as photocatalytic oxidation, plasma degradation, chemical adsorption, and catalytic oxidation were described in the mentioned study, through which the degradation of these contaminants could be achieved. In another study, Hajizadeh *et al.*<sup>25</sup> measured the concentration of four VOCs (benzene, styrene, ethylbenzene, and phenol) in the ambient air of a petrochemical complex in Iran, detecting high levels of ambient VOCs in the recovery and olefin units, while ethylbenzene and phenol levels were lower than the recommended values of the NIOSH and ACGIH.

Wu *et al.*<sup>26</sup> performed a study to address the inequality in the health risks associated with air pollution, and the concentration of VOCs was measured in two communities suspected of air pollution. On the other hand, Zhang *et al.*<sup>27</sup> measured the atmospheric concentrations of carbonyls and BTEX at a sampling site in Beijing (China) during September 2008-August 2010, while Miri *et al.*<sup>28</sup> also measured the concentration of BTEX in the ambient air of Tehran, the capital of Iran. In the mentioned study, the spatial distribution

of BTEX pollution showed the highest concentration on the main roads due to heavy traffic. Similarly, Kanjanasiranint *et al.*<sup>29</sup> investigated the ambient and personal air concentrations of BTEX and carbonyl compounds in Pathumwan, Bangkok (Thailand), which is a dense area with a large surface area. Breton *et al.*<sup>30</sup> assessed the concentrations of BTEX in the urban air of two sites in Merida and Yucatan (Mexico) during 2016-2017.

The present study aimed to determine the emission rate of VOCs using the TANKS 4.09d software and model their dispersion from the petroleum and chemical storage tanks of the largest oil terminal in the southwest of Iran in the PHAST software.

## Materials and Methods

### Study area

The studied oil terminal was located at the northern end of the Persian Gulf in the natural Mahshahr and Khormousa water canal at 30°29' N and 49°5' E (Google Earth aerial map). Fig. 1 shows the geographical location of the study area.

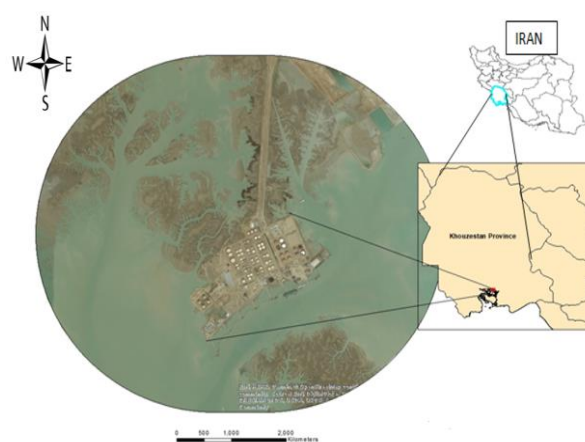


Fig. 1. Location of Mahshahr export port in Khormousa, Khuzestan province, south of Iran

### Meteorological data of the region

The meteorological data of Bandar-e Mahshahr in a five-year period (2012-2017) were analyzed by the software. The highest mean temperature in the region (Mahshahr synoptic station) was 47 °C (observed in July and August), and the lowest mean temperature

was 20 °C (observed in January and December). The highest mean solar radiation coefficient in the region (Mahshahr synoptic station) was 930 (observed in June), and the lowest mean solar radiation coefficient was 520 (observed in December). The highest mean wind speed in the region (Mahshahr synoptic station) was 13 mpy in July, and the lowest mean wind speed was 8 mpy in October. In addition, the highest mean humidity of the region (Mahshahr synoptic station) was 44% in August, and the lowest mean humidity was 17% in January.

### Studied parameters

The studied parameters for the field measurements and software implementation included the data on tanks (product stored in the tank, color, diameter, height, and type of deck support design), and the meteorological data of the area (mean wind speed, mean humidity, mean temperature, and solar radiation coefficient over the five-year period). These data were collected and used in the software. Table 1 shows some of the collected data on the tanks.

Table 1. Specifications of tanks and their contents (external floating roof with height of 10 m)

#	No. of tanks	Content	Tank diameter (m)
1	88-87-77-67	Light naphtha	44
2	106-105-98-97	Light naphtha	35.4
3	53-63-62-61-74-73-72-71	Gasoline	44
4	96-95-86-85	Heavy naphtha	35.4
5	94-93	Jet naphtha	35.4
6	83-76-75	Jet naphtha	44
7	84	Jet naphtha	31
8	1107-1106-1105	Condensate	61
9	TK49	Condensate	44
10	TK69 - TK57	Euro-4 gasoline	44
11	101-92-82	MTBE	35.4
12	91	MTBE	27.8

### Sampling frequency and times

The field measurements were performed on the external floating roof tanks in two stages, including the beginning of the study to

verify the obtained data using the TANKS 4.09d software and at the end of the project for the verification of the polluted areas, the location of which was specified by the PHAST software in the facility area of the port. In addition, the dispersion of the VOCs was modeled over a period of 12 months (March 2017-January 2018) in two hot and cold seasons.

### Field sampling and laboratory analysis method

Activated carbon adsorbent, SKC sampling pump, and NIOSH1501 method were used to absorb the pollutants from the port air. Sampling was performed from 10 sample tanks at the flow rate of 1 L/min and the sampling air volume of approximately 60 L. The adsorbed pollutants were separated from the solid adsorbent using the solvent extraction method (2 mL of carbon disulfide [CS<sub>2</sub>]). The analysis of the adsorbed material in the adsorbent tube was also performed by gas chromatography-mass spectrometry (GC-MS). Afterwards, the emission rates of the pollutants were recorded and compared with the rates obtained from the TANKS 4.09d software.

### Application of TANKS 4.09d software

TANKS 4.09d software program has been developed by the US Environmental Protection Agency (EPA) and the American Petroleum Institute (API) to calculate the emissions from surface evaporations in organic fluid storage tanks (EPA, 1999). In this program, five types of tanks are introduced, and due to the amount of the emitted vapor from the products stored in the export port tanks and field studies, only two types of external floating roof tanks and internal floating roof tanks could be employed (Fig. 2) (Tanks, 2006).

In the present study, the HYSYS software was also used to determine the thermodynamic data of the organic liquids in the tanks. Furthermore, the meteorological data of the region were collected and added to the TANKS 4.09d database, including the mean daily temperature, mean atmospheric pressure,



mean daily maximum ambient temperature, mean daily minimum ambient temperature, mean solar radiation coefficient, and mean wind speed. Fluid specifications such as vapor

pressure and fluid density were also analyzed by the TANKS 4.09d software, and the emission rate from the tanks was calculated.

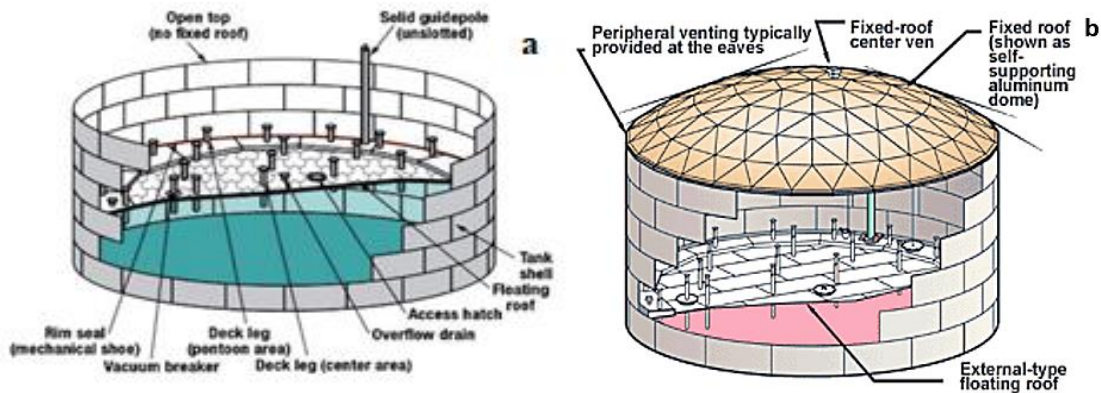


Fig. 2. a) External floating roof tanks (EFRTs), b) Internal floating roof tanks (IFRTs)

**Input data of external and internal floating roof tanks for recording in TANKS 4.09d software**

The input data of the external and internal floating roof tanks included the tank diameter (feet), tank volume (gallons), number of the times the tank is filled and emptied per year, number of the tank columns, effective diameter of the tank columns, inner shell conditions, roof color, roof conditions, primary/secondary seals, deck type, deck fitting type, tank/fluid contents, and tank structure.

**Steps to calculate the solar radiation coefficient**

The solar altitude at the time of day when the sun was visible was obtained at one-hour intervals, and the cloudy fraction of these hours was also estimated during the five-year statistical period. In addition, Eq. 1 was used to calculate the mean value of the solar altitude of each hour and its previous hour, and the solar angle of the hour was also determined.

$$\phi = \left[ \frac{\varphi(tp) + \varphi(t)}{2} \right] \tag{1}$$

In the equation above,  $\varphi$  is the solar altitude, and  $\phi$  shows the solar angle.

In the current research, the clear-sky solar radiation was determined using Eq. 2, as follows:

$$R_0 = 990(\sin \phi) - 30 \tag{2}$$

where  $R_0$  represents the clear-sky solar radiation.

By using the components of the clear-sky solar radiation and cloudy fraction in Eq. 3, the hourly solar radiation was determined, and the monthly mean radiation was also calculated for the statistical five-year period.

$$R = R_0(1 - 0.75n^{3.4}) \tag{3}$$

In the equation above,  $R$  shows the solar radiation, and  $n$  is the cloudy fraction.

**Results and Discussion**

**Output results of TANKS 4.09d software and field measurement for the verification of the software results**

Table 2. Aggregate emission rate of internal floating roof tanks (ton/year) with height of 10 m

#	No. of tanks	Content	Tank diameter (m)	VOCs emission rate
1	82	MTBE	35.4	4.03
2	91	MTBE	35.4	3.99
3	101	MTBE	35.4	4.03
4	92	MTBE	35.4	3.99
Total				16.04

As is shown in Table 2, the aggregate emission rate of the internal floating roof tanks (ton/year) was obtained using the TANKS 4.09d software. Since the floating roof tanks were built and operated at the same time to

maintain the methyl tertiary butyl ether (MTBE) product, they were in the same operational, mechanical, and capacity conditions and had almost the same VOC emission rates (total: 16.04 ton/year).

The emission rates from the rim seal of the floating roof and deck fittings of the tanks were calculated using the TANKS 4.09d software, followed by the field measurements of 10 sample tanks containing six types of petroleum and chemical products. In addition, the field data were compared with the software calculations. The results of the TANKS software, which is designed to calculate the emission rate of VOCs from storage tanks, were observed to be accurate and reliable, and no further measurement and monitoring were

required.

The results of the TANKS software were experimentally examined in the present study. Moreover, the field measurements were performed for the rim seal and deck fitting of 10 tanks with various contents (~30% of tanks; three samples each season). Since no significant differences were observed with the reported software values, the software values were confirmed. On the other hand, the two factors of temperature and wind speed were observed to influence the evaporation and emission of VOCs, and the field measurements were performed at the times of the day with the highest temperature and lowest wind effect for convenience (12-3 PM), with the tank roof was located at the middle height of the body.

Table 3. Emission rates of external floating roof tanks (ton/year)

#	Content	Emission rate					
		VOCs	Benzene	Toluene	Ethylbenzene	Xylenes	BTEX
67	Light Naphtha	56.73	0.08	0.11	0.02	0.04	0.25
77	Light Naphtha	56.71	0.08	0.11	0.11	0.04	0.34
87	Light Naphtha	56.63	0.07	0.11	0.02	0.03	0.23
88	Light Naphtha	56.68	0.08	0.11	0.02	0.04	0.25
97	Light Naphtha	56.71	0.00	0.11	0.02	0.04	0.17
98	Light Naphtha	53.56	0.07	0.11	0.02	0.04	0.24
105	Light Naphtha	53.53	0.07	0.07	0.02	0.07	0.23
106	Light Naphtha	53.53	0.07	0.10	0.02	0.03	0.22
71	Gasoline	25.08	0.04	0.14	0.01	0.05	0.24
72	Gasoline	25.03	0.05	0.14	0.01	0.05	0.25
73	Gasoline	33.90	0.07	0.19	0.02	0.06	0.34
74	Gasoline	33.93	0.07	0.19	0.02	0.06	0.34
61	Gasoline	34.09	0.07	0.20	0.02	0.07	0.36
62	Gasoline	34.16	0.07	0.20	0.02	0.08	0.37
63	Gasoline	33.51	0.06	0.18	0.02	0.07	0.33
53	Gasoline	33.84	0.06	0.18	0.02	0.06	0.32
85	Heavy Naphtha	9.57	0.05	0.09	0.01	0.04	0.19
86	Heavy Naphtha	9.57	0.05	0.08	0.01	0.03	0.17
95	Heavy Naphtha	9.58	0.05	0.08	0.01	0.03	0.17
96	Heavy Naphtha	4.65	0.01	0.02	0.00	0.03	0.06
93	Jet Naphtha	4.65	0.01	0.02	0.00	0.02	0.05
94	Jet Naphtha	4.18	0.01	0.02	0.00	0.02	0.05
75	Jet Naphtha	6.67	0.02	0.02	0.01	0.03	0.08
76	Jet Naphtha	6.67	0.02	0.03	0.01	0.03	0.09
83	Jet Naphtha	4.93	0.02	0.02	0.00	0.02	0.06
84	Jet Naphtha	4.93	0.02	0.02	0.00	0.02	0.06
1105	Condensate	13.48	0.02	0.01	0.01	0.02	0.06
1106	Condensate	13.48	0.02	0.01	0.01	0.02	0.06
1107	Condensate	13.48	0.02	0.01	0.01	0.02	0.06
TK69	Gasoline Uro4	20.74	0.05	0.18	0.02	0.06	0.31
TK57	Gasoline Uro4	20.74	0.05	0.18	0.02	0.06	0.31
TK49	Condensate	20.74	0.02	0.05	0.00	0.01	0.08
Total		865.70	1.45	3.05	0.50	1.28	6.28

According to the information in Table 3, the highest rate of emitted benzene from the external floating roof tanks was observed in the light naphtha tanks No. 67, 77, and 88. In addition, the highest rate of the toluene emitted from the external floating roof tanks was observed in the conventional gasoline tanks No. 61 and 62. The highest rates of ethylbenzene and xylene emitted from the external floating roof tanks were observed in the light naphtha tank No. 77 and conventional gasoline tank No. 62, respectively.

As is shown in the last row of Table 3, the contribution of BTEX was relatively small compared to the total VOCs and estimated at less than 1%. For the total VOCs emitted from the external floating roof tanks, the value was calculated to be 865.7. In addition, the total BTEX emitted from the tanks was  $1.45+3.05+0.5+1.28=6.28$ , which resulted in  $(6.28/865.7)*100=0.72\%$ , indicating that the BTEX emitted from the external floating roof tanks was less than 1% of the VOC emissions from the tanks.

### **Output results of PHAST software**

At this stage and after the required data were entered, the output of the PHAST software was obtained in the form of the side-view diagrams and zoning maps of the pollutants deposited on the ground in the urban areas in two hot and cold seasons. After plotting the side-view diagrams, the cloud footprint diagram and zoning diagram of the pollutant emissions were drawn in the case of the deposition of the intended pollutants on the ground. Furthermore, the pollutant dispersion map and the most polluted area of the export port were examined.

Fig. 3 shows the aggregate VOC emissions from the storage tanks in the hot season. As can be seen in the software output regarding the hot season, the pollutant emissions were in the prevailing wind direction in the hot season (i.e., from northwest to southeast). Fig. 4 depicts the aggregate pollutant emissions from the storage tanks in the cold season. As can be seen in the software output in the cold season, the pollutant

emissions were in the prevailing wind direction in the cold season (i.e., from northeast to southwest). Points 1-6 were selected for the field measurements to verify the emissions obtained by the software.



Fig. 3. VOC emissions from storage tanks in hot season and selected points for field measurements



Fig. 4. VOC emissions from storage tanks in cold season and selected points for field measurements

### **Field measurement results and comparison with the environmental and health standards of the Occupational Exposure Limit-Time Weighted Average (OEL-TWA)**

Table 4 shows the results of the field measurements in the hot and cold seasons and their comparison with the environmental and health standards of OEL-TWA.

The present study aimed to determine the emission rates of VOCs and model their dispersion from the petroleum and chemical storage tanks of the largest oil terminal in the southwest of Iran using the TANKS 4.09d and PHAST software programs. In addition, field

measurements were performed to verify the TANKS 4.09d software and determine the pollutant concentrations in the terminal area of the export port at Abadan Oil Refining Company.

According to the findings, the highest emission rates from the roof were primarily related to the deck fittings (vents, deck supports, vacuum breakers), followed by the rim and seal of the roof and body of the tanks. On the other hand, the highest rate of the emissions from the external floating roof tanks during one year was observed in July due to the higher wind speed, while the lowest emission rate was observed in October. The highest and

lowest emission rates from the internal floating roof tanks during one year occurred in August and January, respectively. In addition, the highest rate of the emitted benzene from the external floating roof tanks was related to the light naphtha tanks No. 67, 77, and 88. The highest rate of the emitted toluene from the external floating roof tanks was related to the conventional gasoline tanks No. 61 and 62, while the highest rates of the emitted ethylbenzene and xylene from the external floating roof tanks were related to the light naphtha tank No. 77 and conventional gasoline tank No. 62, respectively.

Table 4. Field measurement results in cold and hot seasons

Point	Pollutant	Amount on 10-6-2017 ( $\mu\text{g}/\text{m}^3$ )	Amount on 5-5-2018 ( $\mu\text{g}/\text{m}^3$ )	Environment standard ( $\mu\text{g}/\text{m}^3$ )	Allowed/unallowed	Amount on 10-6-2017 (ppm)	Amount on 5-2-2018 (ppm)	TWA (ppm)	Allowed/unallowed
1	B	98	145	5 (Annually)	Unallowed	0.03	0.045	0.5	Allowed
	T	172	210	--	-	0.04	0.05	20	Allowed
	EB	56	29	--	-	0.01	0	20	Allowed
	X	115	70	--	-	0.02	0.01	100	Allowed
2	B	106	213	5 (Annually)	Unallowed	0.03	0.06	0.5	Allowed
	T	197	145	--	-	0.5	0.03	20	Allowed
	EB	61	55	--	-	0.01	0.01	20	Allowed
	X	123	132	--	-	0.02	0.03	100	Allowed
3	B	128	121	5 (Annually)	Unallowed	0.04	0.03	0.5	Allowed
	T	278	190	--	-	0.07	0.05	20	Allowed
	EB	72	29	--	-	0.01	0	20	Allowed
	X	141	90	--	-	0.03	0.02	100	Allowed
4	B	139	232	5 (Annually)	Unallowed	0.04	0.07	0.5	Allowed
	T	225	320	--	-	0.05	0.08	20	Allowed
	EB	78	47	--	-	0.01	0.01	20	Allowed
	X	149	145	--	-	0.03	0.03	100	Allowed
5	B	181	128	5 (Annually)	Unallowed	0.05	0.04	0.5	Allowed
	T	318	190	--	-	0.08	0.05	20	Allowed
	EB	81	24	--	-	0.01	0	20	Allowed
	X	176	55	--	-	0.04	0.01	100	Allowed
6	B	165	230	5 (Annually)	Unallowed	0.05	0.07	0.5	Allowed
	T	320	210	--	-	0.08	0.05	20	Allowed
	EB	88	39	--	-	0.02	0	20	Allowed
	X	189	125	--	-	0.04	0.02	100	Allowed

As is shown in the last row of Table 3, the contribution of BTEX compared to the total VOCs was less than 1%. According to the information in Table 2, since the internal floating roof tanks were built and operated at the same time to maintain the MTBE product, they were in the same operational, mechanical, and capacity conditions and had almost similar

VOC emission rates. The highest and lowest rates of VOC emissions in the export port were related to the light naphtha tank No. 67 and jet naphtha storage tank, with the values estimated at 56.73 and 4.18 ton/year, respectively. In addition, the highest and lowest rates of the BTEX emissions from the storage tanks were related to the gasoline tank No. 62 and jet



naphtha tanks No. 93 and 94, with the values estimated at 0.37 and 0.05 ton/year, respectively.

In the present study, the results of the PHAST software indicated that the highest rate of pollutant deposition on the ground was due to the emission of the VOC vapors from the tanks in stable/fully stable weather conditions. The points with the highest levels of VOCs (particular emphasis on BTEX) were obtained through modeling their dispersion using the PHAST software, which had the highest degree of consistency with the points with the highest levels of the pollutants obtained by the field measurements in the cold and hot seasons in the tank farm, considering that the software modeled the VOC dispersion from each tank separately. Therefore, the verification of the dispersion of VOC emissions was confirmed by the PHAST software.

Given that Mahshahr export port is located near petrochemical companies, the VOCs emitted from the surrounding chemical industries were observed to be dispersed in the area, which influenced the field measurements of the current research. The most polluted points of the export port were point five (port main road) and point six (operational building of the port) in the hot season, which were in the direction of the prevailing wind from the northwest to the southeast, as well as point four (pump house No. 4) in the cold season, which was in the direction of the prevailing wind from the southwest to the northeast.

According to the findings of the current research, the highest rate of benzene emission in the hot season was  $181 \mu\text{g}/\text{m}^3$  (eight-hour emission) in point five (port main road). In addition, the highest rates of other pollutants in the hot season belonged to toluene ( $320 \mu\text{g}/\text{m}^3$ ; eight-hour emission), ethylbenzene ( $88 \mu\text{g}/\text{m}^3$ ; eight-hour emission), and xylene ( $189 \mu\text{g}/\text{m}^3$ ; eight-hour emission) in point six (operational building of the port). The highest rates of VOCs in the cold season belonged to benzene ( $232 \mu\text{g}/\text{m}^3$ ; eight-hour emission), toluene ( $320 \mu\text{g}/\text{m}^3$ ; eight-hour emission), and xylene ( $145 \mu\text{g}/\text{m}^3$ ; eight-hour emission) in point four (area of pump house No. 4), while the highest

rate of ethylbenzene was  $55 \mu\text{g}/\text{m}^3$  (eight-hour emission) in point two (pump house No. 3).

In a similar study, BTEX concentrations were examined in the indoor air of residential buildings and ambient air in Ardabil (Iran), and the results showed that the concentrations of benzene ( $15.18$  vs.  $8.65 \mu\text{g}/\text{m}^3$ ), toluene ( $69.70$  vs.  $40.56 \mu\text{g}/\text{m}^3$ ), ethylbenzene ( $12.07$  vs.  $4.92 \mu\text{g}/\text{m}^3$ ), and xylene ( $48.08$  vs.  $7.44 \mu\text{g}/\text{m}^3$ ) in the indoor air were significantly higher compared to the ambient air. However, the obtained BTEX values were lower compared to the results of the present study. Another research in this regard investigated the levels, sources, and health risks of carbonyls and BTEX in the ambient air of Beijing (China). In the mentioned study, the mean total concentration of BTEX in four seasons was reported to be  $27.2$ ,  $31.9$ ,  $23.2$ , and  $19.1 \mu\text{g}/\text{m}^3$ , respectively, and minimum daily changes occurred all the time in the early afternoon. However, the obtained BTEX values were lower compared to our findings.

According to the information in Table 4, the benzene levels (environmental standard value:  $5 \mu\text{g}/\text{m}^3$  annually) measured at all the points during one year were higher than the annual standard value, while the levels of the BTEX pollutants with the OEL-TWA health standards were measured in the export port during one year and observed to be below the acceptable standard levels. Therefore, they had no adverse effects on the health of the employees in Mahshahr export port during the eight-hour work shift. Table 5 shows the comparison of the values measured with the values of the industrial sites in other countries. Accordingly, the values measured in the present study were lower compared to the values reported in Thailand, while higher than those reported in Mexico and India.

## Conclusion

According to the results, the highest rate of VOC emissions from the tanks was in July, which had the highest temperature and wind speed in the region. In addition, the total rate of the VOCs emitted from the storage tanks of Mahshahr export port facilities was estimated

at 881.74 ton/year, and the highest emission rates from the external and internal floating roof tanks were 865.7 (98.18%) and 16.04 ton/year (1.81%), respectively. The emission rates of benzene, toluene, ethylbenzene, and xylene from the studied tanks were calculated to be 1.45, 3.05, 0.5, and 1.28 ton/year,

respectively. On the other hand, gasoline tank No. 62 had the highest BTEX emissions in the export port during one year (annual emission rate: 0.37 ton/year), while jet naphtha tanks No. 93 and 94 had the lowest BTEX emissions in the export port during one year (annual emission rate: 0.05 ton/year).

Table 5. Comparison of results with similar foreign studies

Country	Research year	VOC (Ton/year)	Benzene ( $\mu\text{g}/\text{m}^3$ )	Toluene ( $\mu\text{g}/\text{m}^3$ )	Ethyl benzene ( $\mu\text{g}/\text{m}^3$ )	Xylene ( $\mu\text{g}/\text{m}^3$ )	Source
Iran-Mahshahr	2018	865.7	232	320	88	189	This study
Mexico	2017	--	40.91	6.87	6.23	13.87	Berton <i>et al.</i> <sup>30</sup>
Thailand	2016	--	589.91	1694.92	96.74	533.75	Kanjanasiranint <i>et al.</i> <sup>29</sup>
India	2006	--	113.35	72.55	9.8	27.65	Pandya <i>et al.</i> <sup>11</sup>
India	2006	--	23.58	18.73	2.91	5.83	Pandya <i>et al.</i> <sup>11</sup>

According to our findings, the highest rate of pollutant deposition on the ground occurred in stable/fully stable weather conditions. The most polluted points of the export port were point five (port main road) and point six (operational building of the port) in the hot season, as well as point four (pump house No. 4) in the cold season. This could be due to the fact that the prevailing northwest wind in the hot season (315 degrees) and southwest wind in the cold season (210 degrees) strongly affect the region.

The timely repair of tank components such as the seals, pressure control valves, insulation, and surface paint could reduce the VOC emissions from the tanks. In addition, it is possible to prevent VOC emissions to the environment by changing the roof and seal design. The recycling of the exhaust gases from air conditioners, as well as regenerating or removing these gases from the environment by biofilters and treatment technologies, could be highly effective in the reduction of air pollutants. Therefore, it is suggested that since the tanks with the highest rate of pollutant emissions were determined in this study, the necessary control programs be adopted for use during operations and for the repair of these tanks to prevent the higher emission of pollutants into the environment. Moreover, the required information should be provided to the relevant authorities. Considering that the polluted areas were identified, proper

programs could be adjusted to examine the personnel who are exposed to BTEX pollutants in case of increased pollution.

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