



ORIGINAL ARTICLE

Sources and Seasonal Variance of Ambient Volatile Organic Compounds in the Oil-Based Chemical Industry from 2020 to 2021: A Case Study of Iraq

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ABSTRACT: The measurement and analysis of pollutants is undoubtedly the first step in controlling them because, without complete knowledge of the quality and quantity of pollutants, it will not be possible to compare them with the permitted limits and ultimately control them. This descriptive-analytical study focused on the oil refineries and chemical industries. Approximately 279 air samples from 18 complexes in an industrial area were collected for this study in the winter of 2020 and 334 samples in the summer of 2021. In this study, 14 volatile organic compounds (VOCs) were examined, measured, and sampled using procedures recommended by the National Institute for Occupational Safety & Health (NIOSH). Finally, GC/FID and GC/MS devices were used to analyze the samples. SPSS version 22.0 was used to analyze the results. In this study, it was determined that the mean of the majority of the compounds in all of the complexes was higher in the summer than in the winter ($p < 0.05$). Additionally, according to the findings, in both the winter and summer seasons, the average ratio of benzene to BTX, BTEX, and all VOCs showed the highest percentage (67.2%) and the average ratio of xylene concentration to these three variables showed the lowest percentage (3.15-7.35%). The findings of this study indicate that the multiplicity of pollution sources and the accumulation of numerous complexes in this area have increased the amount of pollution spread throughout the region's air. As a result, it is advised to use engineering solutions to reduce the amount of pollution.

INTRODUCTION

Oil and natural gas are crucial for the global supply of energy. There can be a significant amount of volatile organic compounds (VOCs) released during the exploration, drilling, transportation, and processing in oil and gas regions. Tens of thousands of chemical

compounds with different physical, chemical, and physiological properties have been discovered and used as raw materials, intermediate materials, and final products, which is the leading cause of air pollution in cities and workplaces [1–3]. Both urban residents and

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industrial workers have experienced health issues due to these substances [4,5]. Due to their detrimental effects on health, occupational exposure to VOCs is one of the concerns in modern societies. Without a doubt, monitoring and evaluating the contaminants is the first step in pollution regulation [6]. Variable sources produce and emit VOCs, which have the potential to be hazardous to human health. When VOCs are exposed to sunlight,

photochemical reactions take place in the atmosphere. These reactions can destabilize ecosystems and have devastating effects on both people and the environment, depending on the quantity and type of VOCs released [7–9]. The majority of the planet's total VOC emissions are caused by industrial activity and other human-made processes (Figure 1) [10,11].

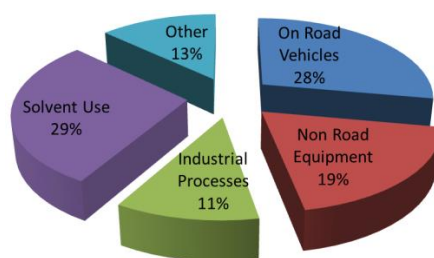


Figure 1. Sources of volatile organic compounds (VOCs).

Vegetation is also an important source for releasing reactive hydrocarbons. Several plant species emit significant amounts of VOCs into the atmosphere. Monoterpenes (C_{10}) like α -pinene, β -pinene, and limonene as well as the hemiterpene (C_5) isoprene make up the majority of the compounds released [12,13]. VOCs are known to have harmful and cancer-causing effects on people and boost the global greenhouse effect [14–16]. They are also known to contribute to the thinning of the stratospheric ozone layer and the production of tropospheric photochemical ozone [8]. During oil refining process, several chemicals are released into the atmosphere including sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbon monoxide (CO), nitrogen oxides (NO_x), and particulate matter (PM) [17,18]. These compounds are emitted primarily through manufacturing operations, storage facilities, pipelines, and crude oil transportation [19]. VOCs pose a serious threat to human health and the environment since they are produced in enormous numbers in oil and other petroleum products, which are used as a source of energy and in the manufacture of other organic chemicals [20–22]. The petrochemical industry uses oil and a select group of basic hydrocarbons (methane, ethane, propane, benzene, toluene, and xylene) to create a range of organic chemicals [23]. Some of these compounds not only have unpleasant smells but also have detrimental effects on health [24]. Exposure to VOCs can cause acute and chronic effects such as respiratory diseases and as a

result increase the risk of some diseases such as asthma [25,26]. They can also affect the nervous system, the immune system and the reproductive system, which include the classic nervous symptoms of fugitive emissions such as feeling tired, headache, dizziness, nausea, lethargy and depression [27,28]. According to the type of composition and concentration, these compounds create various effects on health and hygiene, which include smell disturbance, reduction of lung capacity, and even cancer [29,30]. A high concentration of VOCs has been linked to cancer (e.g., formaldehyde and benzene), birth defects, and other severe diseases in some regions of the United States of America [31–33]. The concentration of VOCs in China is expected to increase by 67% between 2017 and 2026 [34]. We therefore decided to conduct this research to measure and evaluate VOCs and to determine the ratio of pollutants in summer and winter seasons in oil-dependent chemical industries. This decision was made in light of the variety of VOCs and their effects, as well as the importance of people's health and well-being, especially manpower, when exposed to these compounds.

MATERIAL AND METHODS

This research was conducted in complexes in an oil-dependent industrial region using a descriptive-analytical method. For this investigation, approximately 279 samples were collected from 18 complexes in the winter of 2020, and 334 samples were collected in the summer

of 2021. The number of samples was calculated according to the standard deviation and the maximum allowable error from the past studies and considering a 5% chance of a type I error, using the following formula [35]:

$$n = \frac{(Z_{1-\alpha/2})^2 \delta^2}{d^2} \quad (1)$$

Where α is the selected level of significance, $Z_{1-\alpha/2}$ is the value from the standard normal distribution, δ is the standard deviation and d is the tolerated margin of error. The number of necessary samples in each complex have been divided in this study according to the area, labor aspect, and total number of jobs in each complex. In this way, more samples were gathered from complexes with larger areas and greater employee counts; the complex with the most samples were number 3, with 79; the complex with the fewest samples was number 14, with only 6. The samples were collected using a low-flow rate sampling pump and an active charcoal absorber tube made from 100.50 mg coconut shell (Supelco Inc., Bellefonte, PA). In this study, 14 VOCs including benzene, toluene, xylene, styrene, ethylbenzene (EB), chlorobenzene (CIBZ), epichlorohydrin (ECH), tetrahydrofuran (THF), tetrachlorethylene (PCE), methyl ethyl ketone (MEK), n-Hexane, 2-Butanol, acetone, and 1,4-diethylbenzene were examined and analyzed. Sampling of the studied compounds was done in accordance with the methods of 1003, 1010, 1300, 1401, 1500, 1501, 1609, and 2500 of the National Institute for Occupational Safety & Health (NIOSH) [36]. In this study, the qualitative analysis of the compounds in question was done by the GC/MS (gas chromatography-mass spectrometry) device, model CP-3380 and CP-3800 made by Varian Inc., USA, and the quantitative analysis of the compounds was done by the GC/FID (gas chromatographic method with flame ionization detection) (Shimadzu, Japan). To ensure that all desired compounds are identified by the GC and GC/MS devices, as well as to determine the retention time of the compounds, standards of all compounds measured in amounts of 1000, 500, 250, 100, 50, 25, 5 $\mu\text{g ml}^{-1}$ [36] are prepared in the laboratory and injected into GC/FID and GC/MS devices. Both devices utilized an SGE column that had a 25-meter length, an inner diameter of 0.22 mm, and an inner coating diameter of 0.25 μm . In

accordance with the NIOSH-proposed method, carbon disulfide solvent was used throughout the preparation process of the samples. The vials containing the sample were placed in the ultrasonic for 30 minutes so that the pollutant is completely dissolved in the solvent, and then the liquid part above the settled activated charcoal was used. The sample was injected into the GC device using a 10 μl Hamilton syringe and the GC/MS device with a 1 μl Hamilton syringe. Both devices had the same temperature program set which was set for approximately 35 minutes. Also, the injection site temperature was 170°C, the initial column temperature was 40°C, and the maximum temperature was 250°C. The samples were prepared and injected into the device according to the sampling time of the petrochemical complexes. After the end of the analysis time, the amount of chromatographic sub-peak of each injection and its spectrogram were stored inside the device for qualitative diagnosis. Due to the non-normality of the obtained data, the Mann-Whitney non-parametric test was used to compare the measured quantities in comparable groups. All comparisons were performed using SPSS version 22.0 and at a significance level of less than 0.05.

RESULTS

Tables 1 and 2 show the average concentration of 14 pollutants in summer and winter seasons, respectively. It is evident that the average concentration of all substances—aside from MEK and ECH—was higher in the summer than in the winter. In addition, since some compounds including acetone, THF, and PCE have only been identified and quantified during the summer, the average concentration of these compounds during the winter was considered as zero. The tables also include a list of the permitted limits of exposure to pollutants. In the next step, the average ratio of benzene, toluene, and xylene to BTEX (benzene, toluene, ethylbenzene, and xylene), BTX (benzene, toluene, and xylene) and all VOCs under investigation is estimated and the results are shown in Table 3. The table shows that the average ratio of benzene to BTEX, BTX, and all VOCs has the highest percentage in both winter and summer, while the average ratio of xylene concentration to these three variables has the lowest percentage.

Table 1. The results of the average concentration of compounds of pollutants released in the air of 18 investigated complexes in the summer season in terms of ppm by GC and GC/MS.

	Benzene	Toluene	Styrene	Xylene	Acetone	n-Hexane	THF*	ECH*	2-Butanol	PCE*	CIBZ*	EB	MEK	1,4-Diethylbenzene
Exposure limit	0.5	20	20	100	500	50	50	0.5	100	25	10	20	200	Not defined
C1	1.09	1.38	1.75	3.98	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.12	0.00	0.00
C2	0.65	0.04	0.08	0.04	4.08	20.39	15.89	0.05	0.11	0.03	0.04	0.01	0.04	0.02
C3	0.78	0.78	1.91	0.25	6.49	0.71	6.78	0.08	0.85	4.89	0.05	0.03	0.00	0.01
C4	0.21	9.65	0.87	9.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	12.14	0.00	0.00
C5	0.69	0.08	0.37	0.09	0.54	0.14	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00
C6	0.15	0.21	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C7	0.04	0.00	0.01	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00
C8	0.27	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C9	1.13	0.65	0.16	0.00	4.01	0.00	0.00	0.00	10.06	0.00	0.00	0.00	0.00	0.16
C10	0.03	0.24	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00
C11	3.06	28.16	0.60	0.00	1.24	0.39	0.35	0.00	0.84	0.00	0.00	0.00	0.00	0.18
C12	0.68	0.00	0.15	0.00	0.46	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13	0.24	10.19	1.67	0.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.70	0.00	0.00
C14	0.41	0.00	1.33	0.14	0.38	0.18	0.00	0.00	0.21	0.09	0.00	0.00	0.00	0.00
C15	0.56	0.00	0.08	0.00	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C16	0.00	0.37	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00
C17	0.35	0.07	0.00	0.05	0.60	0.09	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C18	0.51	0.20	0.50	0.00	1.18	0.00	0.66	0.00	0.30	0.00	0.00	0.00	0.00	0.00
Total	0.61	2.30	0.96	1.18	2.04	1.54	2.67	0.02	0.62	1.14	0.04	1.68	3.15	0.01

*Ethylbenzene: EB; Chlorobenzene: CIBZ; Tetrachlorethylene: PCE; Tetrahydrofuran: THF; Methyl Ethyl Ketone: MEK; Epichlorohydrin: ECH.

Table 2. The results of the average concentration of compounds of pollutants released in the air of 18 investigated complexes in the winter season in terms of ppm by GC and GC/MS.

	Benzene	Toluene	Styrene	Xylene	Acetone	n-Hexane	THF*	ECH*	2-Butanol	PCE*	CIBZ*	EB	MEK	1,4-Diethylbenzene
Exposure limit	0.5	20	20	100	500	50	50	0.5	100	25	10	20	200	Not defined
C1	0.17	0.34	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.03	0.00
C2	0.18	0.06	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0.00	0.00
C3	0.21	0.20	0.00	0.23	0.00	0.06	0.00	0.02	0.05	0.00	0.00	0.02	0.00	0.00
C4	0.79	2.22	0.00	1.87	0.00	0.00	0.00	0.24	0.04	0.00	0.00	0.30	0.00	0.00
C5	0.14	0.15	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.01	0.00	0.01
C6	0.11	0.08	0.00	0.03	0.00	0.00	0.00	0.02	0.18	0.00	0.00	0.00	0.03	0.00
C7	0.18	0.12	0.00	0.06	0.00	0.00	0.00	0.00	0.05	0.00	0.01	0.04	0.00	0.00
C8	0.57	0.11	0.00	0.06	0.00	0.00	0.00	0.09	0.08	0.00	0.02	0.04	5.78	0.03
C9	0.21	0.12	0.00	0.02	0.00	0.03	0.00	0.12	0.02	0.00	0.03	0.01	0.03	0.00
C10	0.24	0.40	0.00	0.04	0.00	0.00	0.00	0.03	0.04	0.00	0.33	0.01	0.01	0.01
C11	0.23	0.13	0.00	0.09	0.00	0.00	0.00	0.13	0.02	0.00	0.00	0.06	0.15	0.00
C12	0.16	0.21	0.00	0.02	0.00	0.00	0.00	0.20	0.04	0.00	0.07	0.07	0.24	0.00
C13	0.28	0.33	0.00	0.25	0.00	0.00	0.00	0.28	0.07	0.00	0.01	0.04	0.07	0.00
C14	0.21	0.01	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C15	0.29	0.05	8.87	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.01	0.00
C16	0.27	2.03	0.00	0.01	0.00	0.00	0.00	0.24	0.01	0.00	0.00	0.00	2.48	0.00
C17	0.18	0.24	0.00	0.16	0.00	0.00	0.00	0.17	0.58	0.00	0.01	0.06	0.22	0.00
C18	0.07	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00
Total	0.24	1.04	0.20	0.21	0.00	0.01	0.00	0.07	0.06	0.00	0.03	0.03	0.29	0.00

*Ethylbenzene: EB; Chlorobenzene: CIBZ; Tetrachlorethylene: PCE; Tetrahydrofuran: THF; Methyl Ethyl Ketone: MEK; Epichlorohydrin: ECH.

Table 3. Average ratio (percentage) of benzene (B), toluene (T) and xylene (X) to BTEX, BTEX and all studied VOCs in the air of 18 studied complexes.

		The total concentration of pollutants (ppm)			Ratios (%)								
		BTX	BTEX	VOCs	B/BTX	B/BTEX	B/VOCs	T/BTX	T/BTEX	T/VOCs	X/BTX	X/BTEX	X/VOCs
Summer	Average	69.51	23.42	83.07	67.20	67.20	33.60	28.35	27.30	15.75	7.35	6.30	3.15
	Standard deviation	10.64	68.44	15.10	36.75	36.75	31.50	32.55	32.55	24.15	19.95	17.85	11.55
Winter	Average	45.26	49.46	0.21	64.05	63.00	48.30	30.45	29.40	22.05	9.45	8.40	6.30
	Standard deviation	40.85	49.25	74.66	25.20	26.25	28.35	23.10	22.05	19.95	14.70	13.65	10.50

The average ratio of benzene concentration to BTEX in various complexes is more clearly displayed in Figure 2.

Complexes 14 and 15 have the highest benzene to BTEX ratios in winter and summer, respectively, while complexes 10 and 17 have the lowest benzene ratios in summer and winter, respectively. Figure 3 shows an

example of a chromatogram related to the GC/MS device.

Figure 4 displays the results of this test along with the mean and standard deviation of VOCs during the summer and winter seasons.

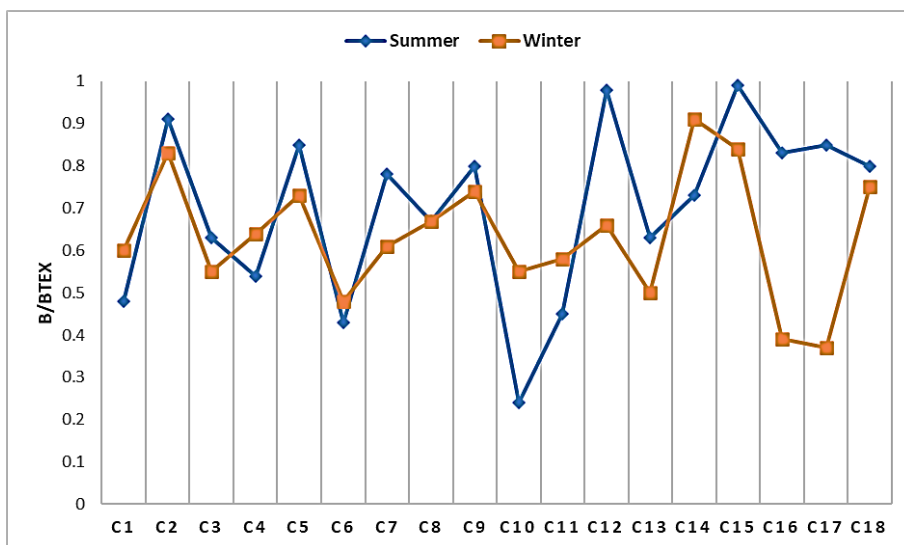


Figure 2. The average ratio of benzene to BTEX in the winter and summer in 18 studied complexes between 2020 and 2021.

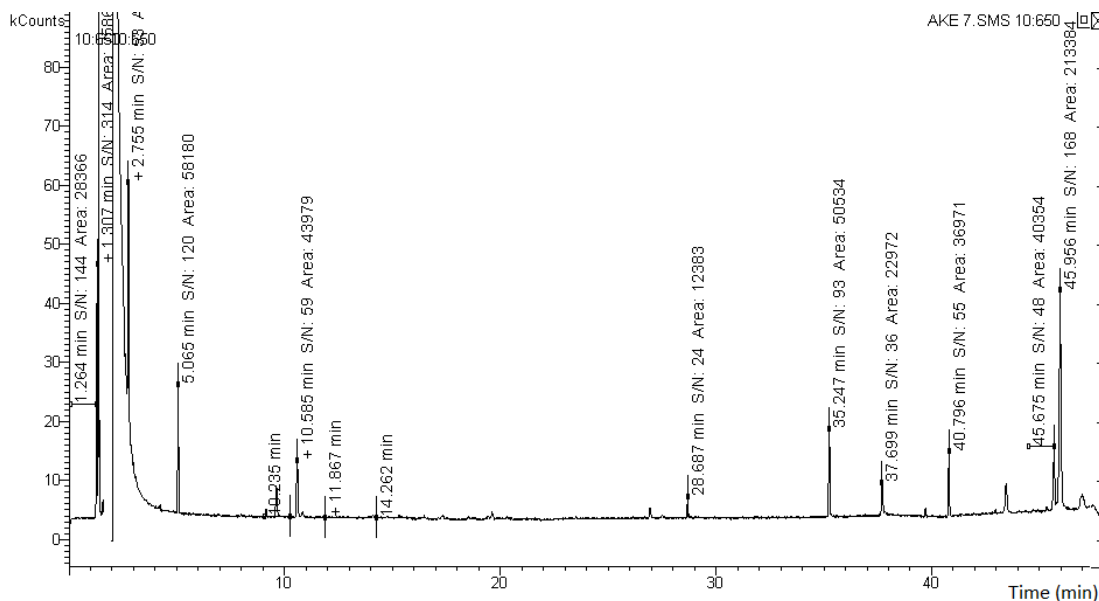


Figure 3. Chromatogram of compounds analysis with GC/MS.

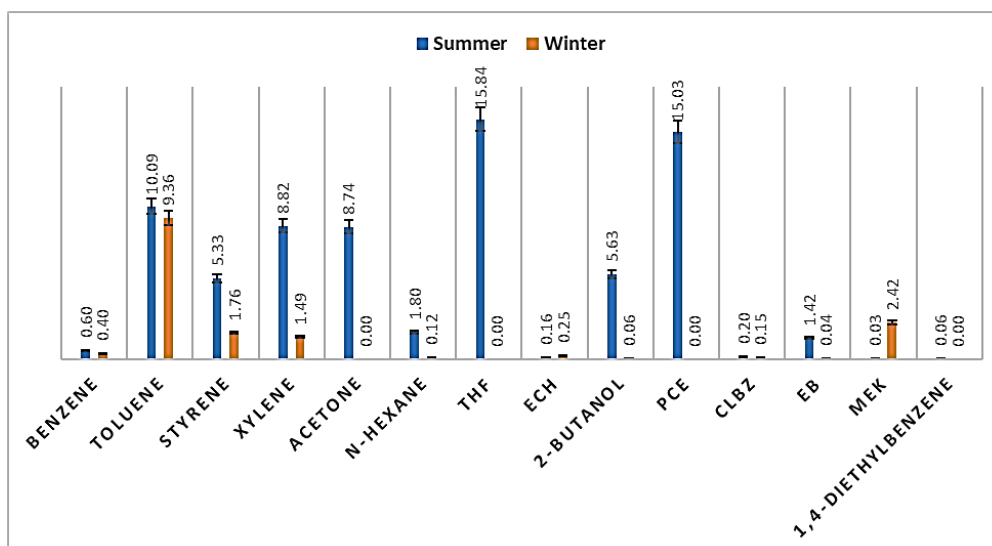


Figure 4. The results of comparing the levels of pollutants in 18 complexes that was under investigation in 2020 and 2021 during the summer and the winter.

According to the Mann-Whitney non-parametric test between results obtained in the summer and winter seasons (Table 4), most of the investigated compounds

had significant differences in the summer and winter seasons.

Table 4. The results of the Mann-Whitney non-parametric test.

Pollutant type	Mann-Whitney test	p-value
Benzene	-3.04	0.031
Toluene	-1.84	0.214
Styrene	-11.70	<0.001
Xylene	-6.20	<0.001
Acetone	-8.22	<0.001
n-Hexane	-2.90	0.008
THF*	-6.00	<0.001
ECH*	-9.08	<0.001
2-Butanol	-4.75	<0.001
PCE*	-2.90	0.008
CIBZ*	-1.55	0.193
EB	-4.27	<0.001
MEK	-5.89	<0.001
1,4-Diethylbenzene	-3.93	<0.001

*Ethylbenzene: EB; Chlorobenzene: CIBZ; Tetrachlorethylene: PCE; Tetrahydrofuran: THF; Methyl Ethyl Ketone: MEK; Epichlorohydrin: ECH.

DISCUSSION

The study was conducted at 18 petrochemical industrial complexes between the winter of 2020 and the summer of 2021. In this study, 14 VOCs that were present in the majority of air samples—more than 40 in total—were looked at and analyzed. The seasons with the highest concentrations of toluene, THF compounds, and toluene were summer and winter, respectively. Toluene had concentrations of 28.16 ppm during the summer and 2.22

ppm during the winter; these values are associated with complexes 11 and 4, respectively. Additionally, complex 3 was found to have the highest concentration of THF, which was measured at 15.89 ppm. The highest concentrations related to benzene are 3.06 ppm in summer and 0.79 ppm in winter, which is significant compared to other compounds. According to the obtained results, it was determined that among all the pollutants,

the average concentration of benzene in the complexes is higher than the occupational exposure limit (OEL). These results are due to the low OEL of benzene which is 0.5 ppm compared to other pollutants. However, due to the low OEL, the concentration of this pollutant is approximately 16 times higher in the summer and more than 9 times higher in the winter, despite the fact that it is less concentrated in both the summer and the winter than other pollutant compounds. Figure 3 provides the average concentration of all compounds in all complexes during the summer and winter seasons. Regardless of ECH and MEK, the average of all pollutants in 18 complexes was found to be higher in the summer than in the winter. These results are consistent with the studies conducted in China [37], as well as the studies conducted in the industrial areas of Turkey [38]. When compared to the winter season, the concentration values in these studies were higher in the summer. The Mann-Whitney non-parametric test was used to conduct statistical tests to compare the average concentrations in the summer and winter seasons since the information related to the concentration of the desired compounds did not follow the normal distribution. According to the results of this test, the average concentration of most of the investigated compounds has a significant difference in summer and winter seasons. In another study, toluene had the highest concentration among other VOCs [39]. These findings are consistent with the results of the current investigation. Also, in a study conducted in the industrial regions of Taiwan, the highest concentrations of VOCs were recorded for toluene [40].

CONCLUSIONS

The seasonal impacts of main emission sources to VOC concentrations were influenced by the variation in ambient temperature and the ensuing shift in emission patterns, according to the analysis of concentration ratios. The results of this study show that the accumulation of a large number of complexes together and the multiplicity of sources of pollution in this region have increased the amount of pollution emitted in the air. Considering the high concentration of benzene compared to other compounds, which are carcinogenic and harmful to humans, it can be said that the implementation of

engineering solutions is a suitable proposal to improve the current situation.

Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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