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ORIGINAL ARTICLE

Measurement and Distribution Modeling of volatile Organic compounds (Benzene) in the second oil refineries at Garmsar Industrial Complexes

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ABSTRACT
Hundreds of thousands tons of oil waste or debris from refineries and petrochemical complexes in Iran are refined in the second treatment units and are converted into consumer materials with good quality levels in accordance with cutting-edge standards. These wastes are refined in second treatment units and are converted into consumer materials with good quality levels in accordance with cutting-edge standards. They are then exported around the world and have a good income for the country. The important point in these units is that they do not use customary raw material in other industries in order to contribute to the environmental health. As a result, irreparable environmental damage may occur. This study evaluates environmental pollutions caused by emissions of oil pollution compounds, especially benzene which is known as an indicator of hydrocarbon contamination in the area of second oil treatment unit in the Fajr Industrial Estate of Garmsar. To measure the desired composition, Procedure 1501 of the U.S. National Institute of Occupational Safety and Health (NIOSH) (aromatic hydrocarbons) was used and the results were compared with existing standard values. All measurements were done in the four seasons of spring and summer 2011, and fall and winter 2012. In each measurement, the samples on sorbent tubes containing activated charcoal (coconut shell) were collected and recycled with carbon disulfide. Then using a gas chromatograph with a flame ionization detector, they are analyzed and the value is determined. Along with these samples, wind speed and direction at each station were measured by Testo 350-M/XL. The results showed that released benzene levels are above the standard and accordingly, some suggestions are offered.
Keywords: *Air Pollution, Benzene, Gas chromatography, Volatile Organic Compounds, oil refinery*

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INTRODUCTION

Air pollution is the byproduct of construction in cities and caused by activities such as production, transportation, power generation, recreation, and work. In Iran method of treating with sulfuric acid or acid wash system is being used for re-refining worked oil, stages of the procedure: 1. Solids separation step 2.First distillation section3.acidscatering 4.second distillation stage 5.filter press stage 6.producing all kinds of lubricating The major cause air pollution is incomplete combustion. If complete or theoretical combustion occurs, hydrogen and carbon in the fuel are combined with air and carbon dioxide and water vapor are produced. Impurities in the fuel, poor fuel to air ratio, the formation of byproducts such as carbon monoxide, sulfur oxides, nitrogen oxides, volatile ash, and unburned hydrocarbons which are air pollutants.

Extensive and complex operations in the oil refinery industries release many substances in the environment. Even if the whole process is done well, often some hydrocarbons are entered into the environment. After a period of time, this can cause environmental damage including threats to plant life, animal life and human health.

The concentration of these pollutants in the environment can cause soil and water contamination and toxicity and jeopardizes the health of animals, plants and humans. Volatile organic compounds are fluid or solid that contains organic carbon (carbon bonded to carbon, hydrogen, nitrogen, sulfur) and are being evaporated with remarkable speed, benzene is chemical organic and organic compound.

This study aims to measure volatile organic compounds, especially benzene in the studied area and compare the obtained data with existing standards and finally, to determine the emission level and present strategies for the prevention of air pollution caused by benzene emissions in the studied area.

MATERIALS AND METHODS

Profile of sampling location

The Fajr Industrial Estate of Garmsar, with an area of about 300 acres, is located in the 10th km of Garmsar axis towards Tehran, in the northwest of Garmsar in the latitude and longitude of 35° 14'56"N and 52°14'21". The implementation operations of the estate began in 1992 and it is now an active area which includes steel, chemicals, non-metallic minerals, textile, chemical, food, pharmaceutical, power, and electricity sections. The area of industrial lands is 210 acres in which 293 units are deployed and 60 units are activated.

Air pollution measurement equipment used in this study

Sampling method:

There are several sampling methods such as NIOSH and OSHA for organic vapors based on samples collected using activated charcoal. In order to determine the concentration of benzene and toluene pollutants in this project, the BTEX sampling and compound measurement method in the air according to Procedure 1501 of the U.S. NIOSH (aromatic hydrocarbons) was used [1].

In this method, vapors on sorbent tubes containing activated charcoal (coconut shell) are collected and recycled with carbon disulfide. Then using a gas **chromatography*** with a **flame ionization detector***, they are analyzed and the value is determined [1].

Sampling equipment: The best sampling method of gases and organic vapors is to use sorbents according to NIOSH and OSHA recommendations. The most widely used gas and vapor samplers are sorbent tubes. These tubes have solid sorbents that trap pollutants on their surface. Among sorbets, activated charcoal has the highest application in samplers. About BTEX measurement, activated carbon sorbet (226-01) is presented.

Activated carbon sorbet (code 226-01) has 7 cm in length and 6 mm in diameter. It contains 150 mg of active carbon. Each glass tube containing activated carbon is composed of two separate sections. The front section contains 100 mg and the after section contains 50 mg of active carbon. These two sections are separated by a thin sponge. The biggest problem associated with the collection of chemical compounds in the air by surface sorbent is that the pollutant leaves from the other side of the sorbent. Pollutants leave surface sorbets when the front section of the sorbet is saturated and the pollutant is reentered into the sorbet through the pump sampling suction. For this reason, the U.S. NIHS has recommended sampling with sorbent tubes composed of two sections. When the pollutant value in the after section of the sorbent is more than 0.1 of the **front section***, the pollutant may exit from the other side of the sorbent and therefore, the sample is not acceptable. But if the pollutant in the after section is less than 0.1 of the front section, the pollutant does not leave the sorbent [2].

In this research sampling was done using personal sampling pumps (Model Deluxe) manufactured by SKC England-U.S. with a discharge of 1 L/min and a volume of sampling air of about 60 lit. The sampling location was second oil treatment unit in the Fajr Industrial Estate. For each point, one sample was taken during two seasons.

Moreover, the wind direction and speed at sampling points were measured by Testo 350-M/XL made in Germany. The device has two probed, one for measuring combustion gases and the other for other parameters.

Equipment for laboratory analysis: After sampling, air pollutants were recycled from solid sorbents using the solvent extraction method. Two ml of carbon disulfide was used for recycling. The Gas Chromatography device with detector (FID) was used for the analysis of sorbent tubes. This type of detector is used for the analysis of hydrocarbons.

Profile of the selected stations for measuring air pollutants in the studied area

Selecting sites or measurement stations is an important section of measuring air pollutants. It is discussed in detail separately and here we refer only to the selection process of stations.

First, with initial visits from the industrial estate, 11 second oil treatment units were determined and it was decided to conduct the measurements at these stations during four seasons [3]. According to the conducted surveys, the main areas of benzene production are next to the first distillation and next to the second distillation (exhaust of the distiller gas). Therefore, samples were taken from these sites. In the first distillation section, used oils are heated to a temperature of 300 to 400°C so that molecular bonds between light materials are broken and all solvents exited from oils go to the distiller. In the second distillation section, gas emissions are possible due to the increase in heat.

The average concentration of benzene in the air in rural and urban areas is 1 and 5-20 μg/m^3, respectively [4].

Climate Conclusions of garmsar area in duration(1986-2012)

Average annual minimum temperature	-0.6ºC
Average annual maximum temperature	40.3ºC
The average annual precipitation	124.5 (mm)
wind average speed prevailing wind direction	1.9(m/s) Summer from East to the West Winner from West to the East

Time and duration of measurement:

Field measurements of volatile organic compounds (VOCs) in the Fajr Industrial Estate were done in fall and winter 2011 and spring and summer 2012. In this period, benzene was selected for measurement and it was evaluated. While measuring the pollutant, meteorological parameters such as wind speed and direction were measured. The results are presented in the relevant tables and charts

RESULTS AND DISCUSSION

During four seasons of benzene measurement in the second oil treatment units in the Fajr Industrial Estate, meteorological parameters such as wind velocity, temperature and direction were measured. The results of these measurements for the three main polluting factories are presented in the tables and graphs of this section.

The second treatment company of Aria Takran

The company is located in the northern part of the Fajr industrial estate (Station No. 1). Table (4-1) shows climatic parameters measured in this company in the four seasons.

Benzene

Average benzene concentration in this unit during the sampling period based on Table (4-1) is 20.27 μg/m^3 in fall, 16.49 μg/m^3 in winter, 28.30 in spring and 39.35 μg/m^3 in summer. The following charts show the measured values in this unit.

Table 2: Sampled values of benzene in the second treatment unit of Aria Tkran

Wind Direction	Wind speed (m/s)	Pollutant concentrations (μg/m^3)	Sampling Season	Sampling location
		Benzene		
North to South	4-7	22.32	Fall 2011	Next to the distiller's gas output
North to South	4-7	18.22		Next to the second distillation
West to East	1-3	17.22	Winter 2011	Next to the distiller's gas output
West to East	1-3	15.76		Next to the second distillation
North-west to south-east	4-7	30.11	Spring 21012	Next to the distiller's gas output
North-west to south-east	4-7	26.5		Next to the second distillation
East to West	1-3	40.5	Summer 2012	Next to the distiller's gas output
East to West	1-3	38.21		Next to the second distillation

According to statistical analysis of SPSS, given the season changes, it was found that with increase in the temperature, emission rates and concentrations of VOCs, especially benzene and toluene increase in the factory setting. Thus, the emission rates and concentrations of VOCs have a direct correlation with the increase in seasonal temperature so that summer and winter account for the highest and lowest emissions of VOCs, respectively.

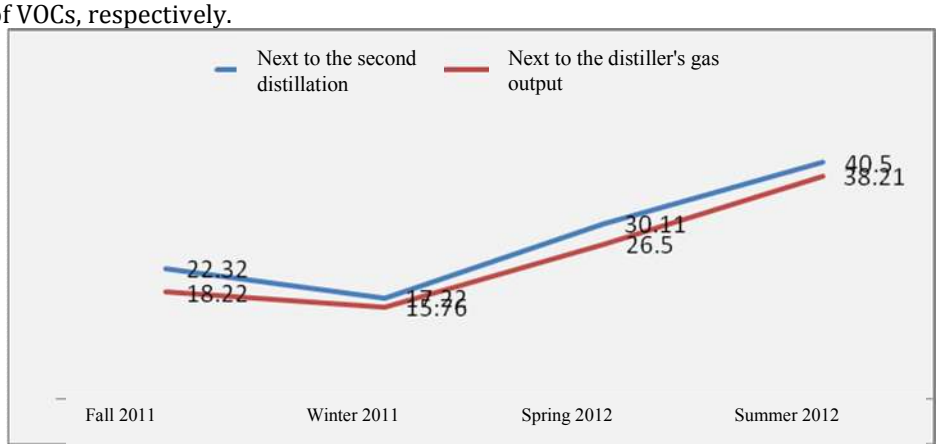


Figure1: Line comparison of benzene concentration values in two points in the second treatment unit of Aria Takran according to season changes

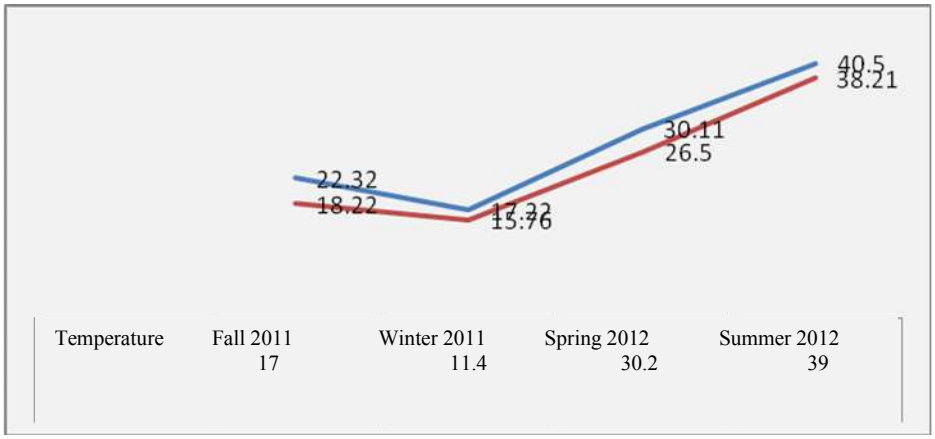


Figure 2: Line comparison of benzene concentration values in two points in the second treatment unit of Aria Takran according to temperature changes

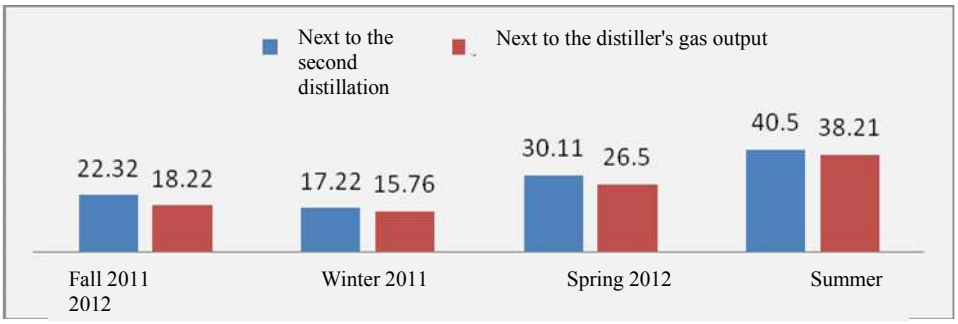


Figure 3: Bar comparison of benzene concentration values in two points in the second treatment unit of Aria Takran according to season changes

The second treatment company of Ojan Grease

This company is located in the northern part of the Fajr industrial estate (Station No. 1). Table (4*3) shows climatic parameters measured in this company in the four seasons.

Benzene

Average benzene concentration in this unit during the sampling period based on Table (4-3) is 39.88 μg/m^3 in fall, 38.93 μg/m^3 in winter, 48.78 in spring and 58.54 μg/m^3 in summer. The following charts show the measured values in this unit.

Table 3: Sampled values of benzene in the second treatment unit of Ojan Grease

Wind Direction	Wind speed (m/s)	Pollutant concentrations (μg/m³)	Sampling Season	Sampling location
		Benzene		
North-west to south-east	1-3	49.32	Fall 2011	Next to the distiller's gas output
North-west to south-east	1-3	30.45		Next to the second distillation
North-west to south-east	1-3	48.52	Winter 2011	Next to the distiller's gas output
North-west to south-east	1-3	29.34		Next to the second distillation
West to East	1-3	55.22	Spring 21012	Next to the distiller's gas output
West to East	1-3	42.35		Next to the second distillation
East to West	1-3	61.66	Summer 2012	Next to the distiller's gas output
East to West	1-3	55.34		Next to the second distillation

According to statistical analysis of SPSS, given the season changes, it was found that with increase in the temperature, emission rates and concentrations of VOCs, especially benzene and toluene increase in the factory setting. Thus, the emission rates and concentrations of VOCs have a direct correlation with the increase in seasonal temperature so that summer and winter account for the highest and lowest emissions of VOCs, respectively.

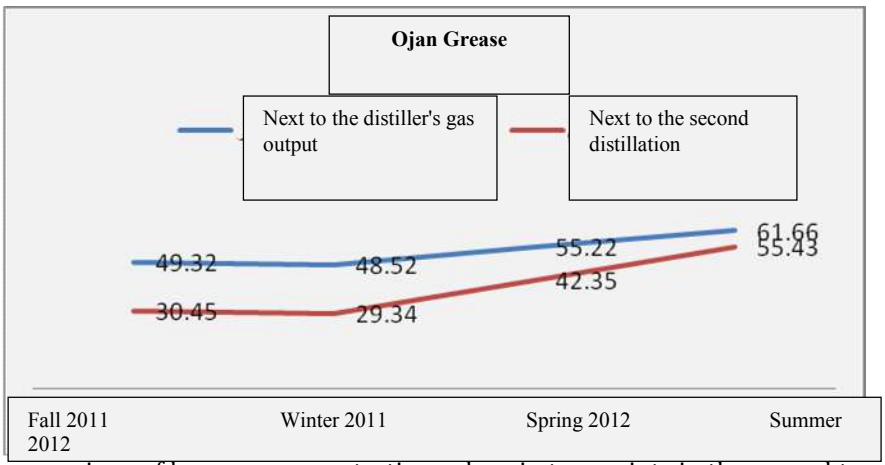


Figure 4: Line comparison of benzene concentration values in two points in the second treatment unit of Ojan Grease according to season changes

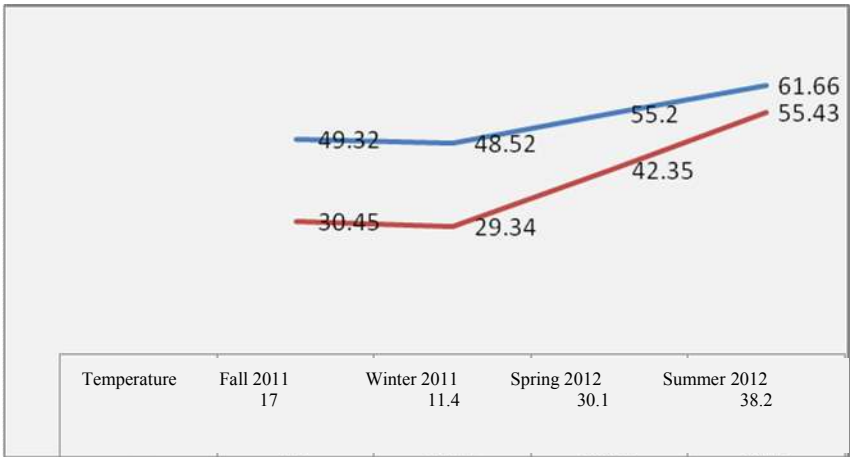


Figure 5: Line comparison of benzene concentration values in two points in the second treatment unit of Ojan Grease according to temperature changes

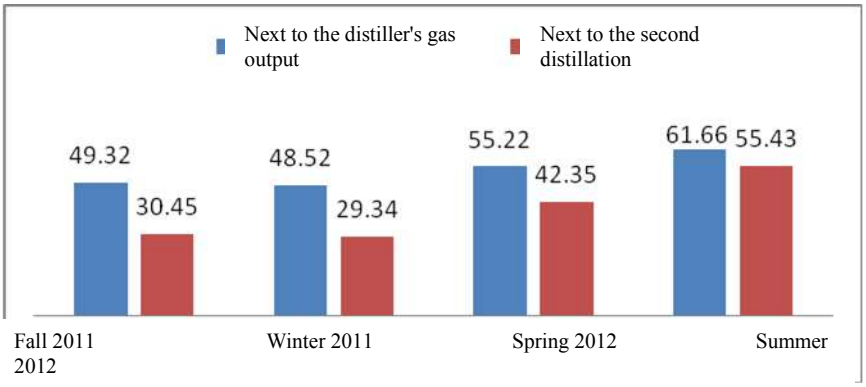


Figure 6: Bar comparison of benzene concentration values in two points in the second treatment unit of Ojan Grease according to season changes

The second treatment company of Tizro Grease

The company is located in the northern part of the Fajr industrial estate (Station No. 1). Table (4-1) shows climatic parameters measured in this company in the four seasons.

Benzene

Average benzene concentration in this unit during the sampling period based on Table (4-7) is 72.36 µg/m³ in fall, 69.70 µg/m³ in winter, 73.66 in spring and 76.55 µg/m³ in summer. The following charts show the measured values in this unit.

Table 4: Sampled values of benzene in the second treatment unit of Tizro Grease

Wind Direction	Wind speed (m/s)	Pollutant concentrations (µg/m³)	Sampling Season	Sampling location
		Benzene		
North-east to south-west	4-7	96.10	Fall 2011	Next to the first distillation
North-east to south-west	4-7	48.63		Next to the first distillation and soil filtering
West to East	1-3	94.11	Winter 2011	Next to the first distillation
West to East	1-3	45.30		Next to the first distillation and soil filtering
North-west to south-east	4-7	98.17	Spring 21012	Next to the first distillation
North-west to south-east	4-7	49.15		Next to the first distillation and soil filtering
East to West	1-3	101.15	Summer 2012	Next to the first distillation
East to West	1-3	52.36		Next to the first distillation and soil filtering

According to statistical analysis of SPSS, given the season changes, it was found that with increase in the temperature, emission rates and concentrations of VOCs, especially benzene and toluene increase in the factory setting. Thus, the emission rates and concentrations of VOCs have a direct correlation with the increase in seasonal temperature so that summer and winter account for the highest and lowest emissions of VOCs, respectively.

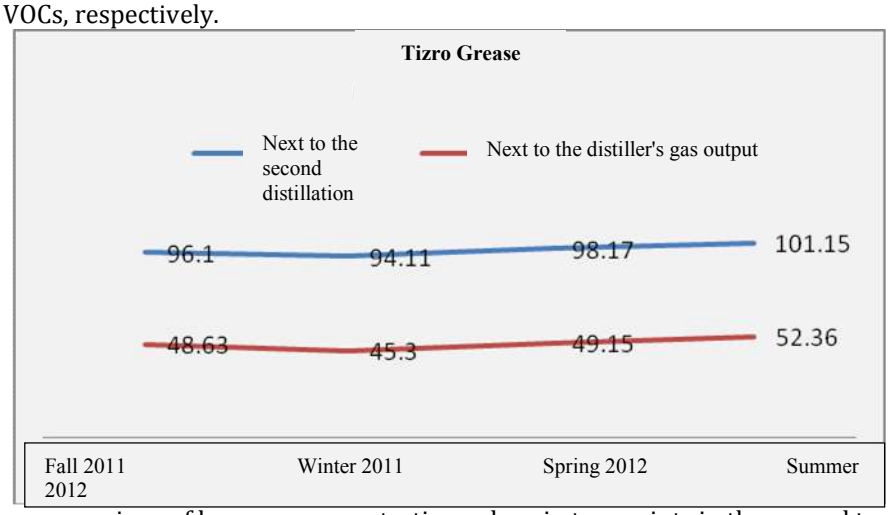


Figure 7: Line comparison of benzene concentration values in two points in the second treatment unit of Tizro Grease according to season changes

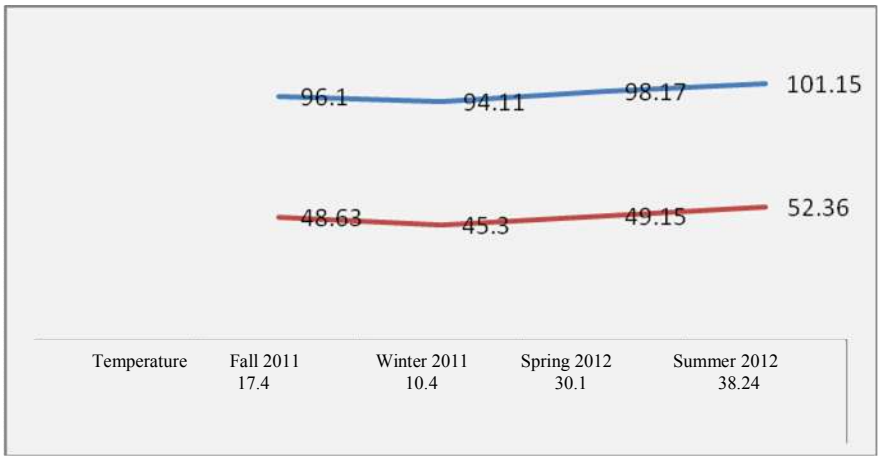


Figure 8: Line comparison of benzene concentration values in two points in the second treatment unit of Tizro Grease according to temperature changes

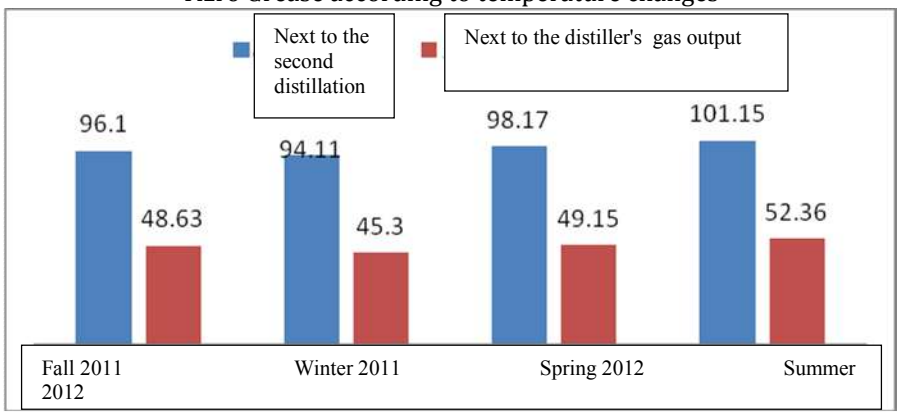


Figure 9: Bar comparison of benzene concentration values in two points in the second treatment unit of Tizro Grease according to season changes

Analysis and interpretation of results

To evaluate and interpret the results, this section compares data from collected samples with existing standards. Finally, given the prevailing wind speed and direction in the area, the amount of benzene emissions and pollution in the estate will be discussed. As previously mentioned, according to the WHO, the annual average benzene concentration in the air of rural and urban areas is 1 and 5-20 μg/m^3, respectively. The annual average concentration of toluene in the air of rural and urban areas is less than 5 μg/m^3 and 5-150 μg/m^3, respectively. Its weekly standard is 69 μg/m^3. As shown in Figures (1-5) and (2-5), emissions of benzene and toluene in the measured stations is more than the standard approved by the WHO.

Figure (5-1) shows seasonal wind roses of Garmsar synoptic station. As can be seen in the figure, the prevailing wind direction in summer is from East to West followed by from North East to South West. In winter, the prevailing wind direction is from West to East followed by from North West to South East, East to West and South West to North East, respectively.

Thus, given the measured values of wind direction and speed at the sampling stations and also the location of Garmsar in the Southeast of Fajr Industrial Estate, it can be concluded that the released benzene and toluene emissions (especially, benzene) may transfer from oil treatment units to Garmsar. Given that emissions are higher than annual standards, environmental and human risks exist for the residents of the region and Garmsar.

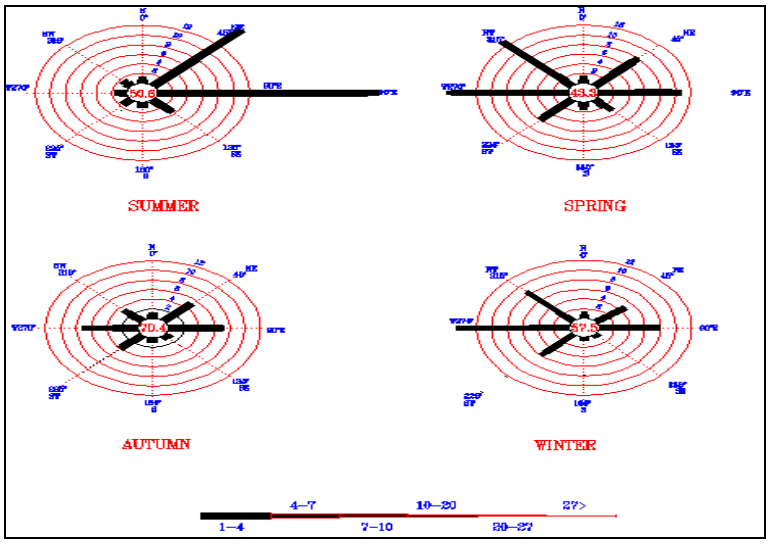
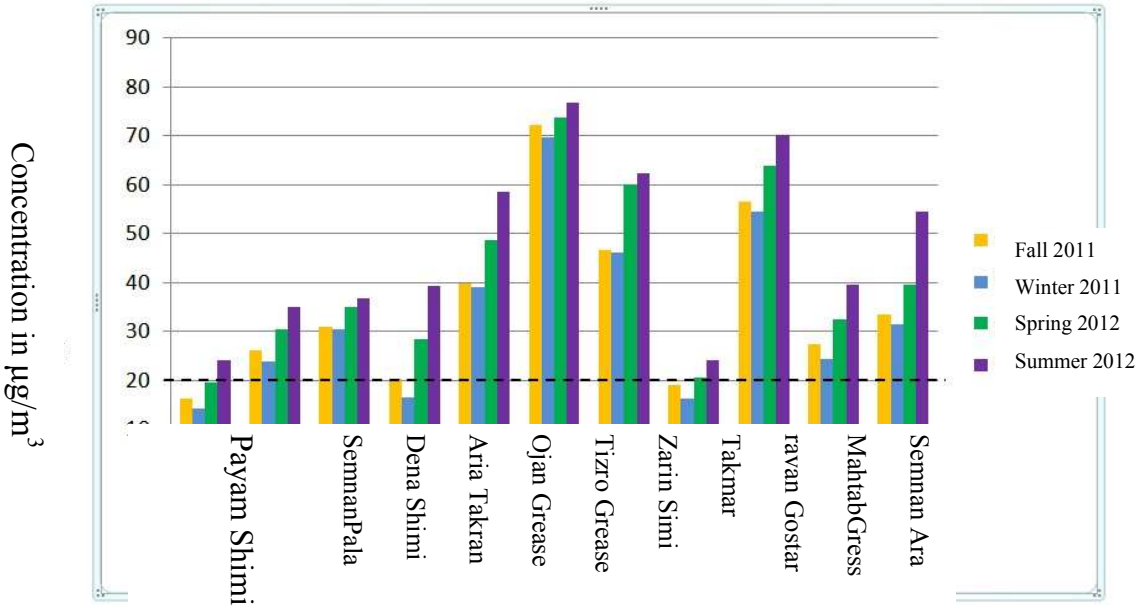


Figure 10: Seasonal windroses of Garmsar synoptic stations



Graph 1: Comparison of the measured benzene values with annual standard of benzene emission in the environment
[Dotted lines are for urban areas and a straight line is for rural areas]

SUGGESTIONS

- If possible, make changes in the process and production stages of units (e.g., mechanizing some processes instead of being manually. It has be done in the bleaching earth injection and slacked lime adding, so the second distillation tank output valve is not opened frequently. Therefore, large amounts of unpleasant odors released in the air are reduced).
- If output emissions are high, it is recommended to use one of the methods provided in the control and treatment methods of BTEX pollutions in the air and the output of systems for absorbing and reducing output emissions
- Specialized inspection of control and treatment systems in order to design and install them in the units

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