



Assessing of some important gas condensate pollution factors along horizontal and vertical soil contamination gradients (Sarkhun's gas refinery, Bandar Abbas)

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ABSTRACT

This study was designed due to the appearance of some oil pollution signs around the Sarkhun gas refinery in the city of Bandar Abbas and provided a comprehensive assessment of the current location of hydrocarbon pollution, evaluating some important pollution factors and predicting pollution distribution in the soil around the refinery. Soil samples were taken from different layers, then TOG (Total Oil and Grease) and TPH (Total Petroleum Hydrocarbon) were measured. Total suspended and soluble solids, the amount of initial oil input, and chemical and biochemical oxygen demand were evaluated. Vertical and horizontal pollutants seepages were prepared by Surfer, ArcGIS, and MATLAB. The novelty of this study was a prediction of the release of condensate gas in a specific area (depth of 24 meters of groundwater and the presence of hard surface layers). The results showed that the pollution mostly occurred in the north side of the refinery and TOG and TPH confines from 3633 and 2612 (burning pits) to 7 and 4 mg/Kg soil (south-west of the refinery) respectively, along the slope of the earth layers with more tendencies to Shour river. Abrupt increasing pollution in the east part of the refinery was attributed to the previous breakage of the sewer pipe. The results showed that the deep infiltration was up to the dimensionless depth of 0.2 and in more depth, reduced noticeably. Furthermore, TOG showed severity spreading against TPH in a similar direction. The simulation results showed that by increasing the entering water debit to burning pits, pollution spreading risk will increase, so preventing the pollution extension must be considered.

Keywords: Vados zone, pollution, hydrocarbon, refinery, vapor condensations.

1. Introduction

Studying the soil pollutants' behavior requires the exact identified dominant processes in the transmission of each particular pollutant due to the complexity of the pollutant-soil reaction.

In the conceptual study of modeling, the transfer processes are studied and evaluated to determine the distribution of pollutants in each porous medium (Ebrahimi et al., 2010b). Physical processes of transfer of water-soluble pollutants include diffusion, mechanical dispersion convection. Chemical and biological processes affecting any potential contaminant flow through the soil, are including adsorption, dissolution/precipitation, oxidation, and biodegradation (Emeritus, 2001).

The basic model for pollutant emissions is the application of mass balance to the hypothetical pollutant element in the target environment so that the amount of mass accumulation is always equal to the difference

between the amount of input and output mass (Amali and Rolston, 1993).

For example, in a one-dimensional advection-dispersion model in an unsteady state and the emission from the source in stepwise developed by Ogata (1970), if the contamination does not react, the porous media is homogenous and isotropic, the condition is an unsteady state, and the contaminant concentration is equal to zero that is far away from the source:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} \quad [1]$$

Where V_x (L/T) represents groundwater velocity, D_L (D²/L) is hydrodynamic dispersion coefficient along the L:(M) direction, c (M/L³) is contaminant concentration, and L stands for direction of contaminant

dispersion along x and t is time (USEPA, 1998). Biological and chemical reactions are not concerned. Many attempts have been made to solve this equation analytically. Finally, the complete solution was introduced by Ogata (1970).

This model is mostly applicable for predicting contamination dispersion in the laboratory and is not suitable for larger scales (Ebrahimi et al., 2010b). However, this model by neglecting some available occurrences, including sorption and biodegradation is a conservative stuffed model (Ebrahimi et al., 2010a).

The two-dimensional transfer including diffusion equation and contaminant transfer with finite difference method (application of longitudinal and transverse hydrodynamic diffusion coefficient) which is based on the x and y axis for flow is shown as follows:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} + \lambda c = D_{xx} \frac{\partial^2 c}{\partial x^2} + D_{yy} \frac{\partial^2 c}{\partial y^2} \quad [2]$$

In the two-dimensional transmission of pollutants, the boundary conditions of steps and impacts are considered. In the boundary conditions of pulse mode, the accidental entry of pollutants into the soil and groundwater environment occurs due to any unforeseen occurrence (Ebrahimi et al., 2010b). In the step boundary conditions, the permanent pollutants occur through entering the soil and groundwater environment (Ebrahimi et al., 2010a). The output of the program is also different in these two modes. In the pulse mode, the peak of the graph moves over time, while in the step boundary conditions, quasi-stable conditions are found over time.

In three-dimensional models for the unsteady-state case in which the emission from the source is a pulsed manner, the Baestsle model was investigated. Baestsel initiated his studies on three-dimensional modeling in 1969. The assumptions that he made were: 1- contaminant does not react and the condition is unsteady state. 2- Contaminant dispersion is done by convective and diffusion and 3- the geology of the area is homogeneous and isotropic.

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} = D_{xx} \frac{\partial^2 c}{\partial x^2} + D_{yy} \frac{\partial^2 c}{\partial y^2} + D_{zz} \frac{\partial^2 c}{\partial z^2} \quad [3]$$

Where D_{xx} , D_{yy} , and D_{zz} are diffusion coefficients along the x , y , and z directions.

This study was designed according to the appearance and occurrence of some signs of deep and surface oil pollution around the Sarkhun gas refinery in Bandar Abbas. The main objectives of this paper as the first attempt in the region were to investigate the possible establishment of the current hydrocarbon pollution, the characteristics and environmental assessment and measuring some important factors of oil pollution in the soil surrounding the refinery, and to predict the three-dimensional distribution of pollutants by preparing

statistical maps of pollution emissions by the use of Surfer and ArcGIS software and simulation through MATLAB software. The novelty of the applied method in this study was the prediction of the release of hydrocarbon pollutants in a specific area with a depth of 24 meters of groundwater and the presence of hard surface layers and especially, the release of gas condensate.

2. Materials and Methods

2.1. Study area

The hydrology balance-sheet of Sarkhun watershed plain locates at $27^\circ 21'$ to $27^\circ 21' N$ and $56^\circ 10'$ to $56^\circ 28' E$; and consists of two sub-watersheds including north- and south-Sarkhun that both have the direction and slope towards east-west. The area of Sarkhun's refinery is placed at the 50-kilometers northeast of Bandarabbas, and it mostly has Marne and sandstone structure which often does not have any groundwater source. Furthermore, the investigation of pollution sources shows that the refinery is fed by 13 wells under the control of South Zagros Company with a capacity of 500 million m^3/day (Ebrahimi et al., 2010b).

The accumulated wastewater includes the exterior wastewater, the wastewater made by washing units, the wastewater that is produced at the time of repairing, the displacing caused by the reversed osmosis, and the rainfall of the remediate and un-remediation sites. All of the wastewaters are led towards two basins including wet and dry swage reservoir basins and then by the use of pump and tube lines are led to a burning pit discontinuously. The rainwater of the remediate sites, the wastewater which is made by washing units, and the wastewater that is produced at the repairing time through a closed channel which is placed around the site, are led to the burning pit directly, and the rainwater of un-remediate sites through another channel, which is open and is placed in the refinery, is led towards a river. Also, the hygienic wastewaters are led to the package system of hygienic wastewater refining (Ebrahimi et al., 2010a).

Noting the continuous aridity for more than 11 years in the Sarkhun region and its effect on groundwater as well as the distribution of rainfall over the decade, groundwater balance has declined 6 meters over 13 years. Also, the number of wells has decreased from 430 to 311 (Bazrafshan et al., 2016). Afterward, according to the Sarkhun plain location and the investigation of the pollution probable sources, practical procedures were begun.

2.2. Sampling methods

The selection of 22 borehole locations in this research was done by examining possible sources of pollution leakage, records of the existence of pollution sources, studying geological, geographical, and hydrological maps, and the existence of standards and basic statistical



Figure 1. The appearance of some drilled boreholes for sampling in order to create a general view of the area

information. These wells (Figure 1) were manually drilled until reaching the existing impervious shells, and after checking the existing layers, samples were taken from different layers (Ebrahimi et al., 2010b). In the digging process, especially at the east part of the refinery, some wells reached the water, which shows the existence of hardpan and other impenetrable substrates and also rainwater gathering over this layer.

The presence of fluvial layers in some of the northern wells has been observed at a depth of one meter and in the eastern wells in the surface layers. Sampling from the soil, at a special depth and after digging wells, was done by the use of a sampler tube, which is made of PVC and has 15 cm and 20cm diameter and height, respectively. To preserve the soil variable properties; Before analysis, soil samples were stored at -4°C (Domenico and Franklin, 1990).

Then TSS (Total Suspended Solid), TDS (Total Dissolved Solid), BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), pH, T (Temperature), and Oil tests (USEPA, 2003) were performed to determine the quality of the effluent, considering the main possible source of feeding the burning holes (the main possible source of contamination).

2.3. Hydrocarbon pollutants analysis

After investigating the soil's physical and chemical properties, pollution was determined by the use of TOG/TPH (InfraCal by Wilks Enterprise INC, USA) on the basis of standard method and extracting with solvent, being absorbed by IR at the 2940 cm^{-1} frequency, which is one of these standard methods of EPA413.2 and ASTM D3921 (USEPA, 2003; ASTM, 1999).

Soil samples were analyzed by USEPA 413.2 analysis method for all petroleum hydrocarbons using InfraCal TOG / TPH analyzer, Model CVH. Tetrachloroethylene (TCE) was the used extraction solvent. After passing the necessary time transferring the contaminant from the soil environment to the solvent medium, a clear yellow or white liquid was collected and transferred to the transfer chamber, and it was read. Purification was performed by a silica sulfate gel column to distinguish the polar and non-polar contaminants. In this case, the data shown and read before silica gel is TOG, and the data that is shown and read after silica gel is TPH. Since this method is more suitable for screening purposes, samples extracts with higher contamination levels were examined by GC-MS. GC-MS analysis was performed using an Agilent Technologies 6890N-GC combined with an Agilent-Mass selective detector 5973N mass spectrometer with HP-5ms, 30m, I.D = 0.25 mm, 0.25 column film. The oven temperature program was 40 to 300°C at $10^{\circ}\text{C}/\text{min}$, followed by an isothermal step at 300°C for 10 minutes. The helium carrier gas had a flow rate of 1 ml per minute. MS was performed on selected ion monitoring.

2.4. Geo-statistical analysis

After sampling and their analysis, the pollution mapping of the site was done by the use of geo-statistic techniques (Chilès, 1999; Bivand et al., 2008b). In classical statistics, the data of a society are independent of each other, but sometimes the data are dependent on each other due to their location (Ebrahimi et al., 2010a,b). With this aim, the samples were analyzed by the use of Surfer and ArcGIS software, and then the suitable

models with the least error were chosen. Simultaneously with geo-statistical studies and using the best pollution emission estimates, hydrocarbon pollution emission simulations were performed with MATLAB software.

In studying the existing pollution spreading, on contrary to classical statistics principles, the observations are dependent (Baehr and Hult, 1991). But it is disregarding leads to losing beneficial information. Furthermore, the unknown data can be predicted based on known data in that area and mean square error by the use of geo-statistic techniques (White and Oostrom, 1996).

The Variogram Functions are the base of Geo-Statistical studies and they are defined as below:

$$\gamma(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [z(x+h) - z(x)]^2 \quad [4]$$

Where $N(h)$ represents the number of sampling pairs for each distance h , $z(x)$ is the observed variable, and $z(x+h)$ is the observed variable for distance h from $z(x)$ which is determined by VARIOWIN software. For drawing a variogram as a means of determining space (multidimensional) structure, first γ was measured for different h values, and then the obtained results were plotted for different h values. After normalizing the data which is gained through the experiment, by the use of Arc GIS software, the suitable variogram conceptual model was determined for the results of TPH and TOG experiments (Webster and Oliver, 2007).

The parametric investigation of fit empirical variogram models, the Gaussian model showed the best model for both pollution types TOG and TPH. The following equation shows the Gaussian model and its parameters

$$\gamma(h) = c_0 + c(1 - \exp\left(-\frac{h^2}{a^2}\right)) \quad [5]$$

Where α represents amplitude, c stands for threshold value, c_0 stands for nugget effect, $\gamma(h)$ is variogram and h is the distance (Bivand et al., 2008a). Then the best interpolation with the Mean Biases Error (MBE) was determined by the use of the software. The best model was the Kriging method for TOG's data and Kriging and Spline with Tension method for TPH's data. Then, the map of level lines for TOG and TPH pollutions with the determination of sampling places was made (Diggle and Ribeiro Jr, 2007).

3. Results and Discussion

3.1. Soil properties of the area around the Sarkhun refinery

In the study of some physicochemical properties of soil in the Sarkhun region, based on the determined percentage of sand, silt, and clay, the grain size characteristics of the region were shown to be silty fine grainy sand that varies between 90-60% sand, and it has

a small proportion of fine-grain sand and silt. The type of soil to the depth of hard surface, except in areas located in the margins of floodplains or almost rocky areas, is more than the type of fine-grained sand, with medium to high capability (Table 1).

Experiments on soil moisture and compaction properties showed that most soils are dense to semi-dense with a dry density of 1.94 to 2.06 g/cm³. The relative humidity in dry seasons varies in amount from 1.8 to 2.4 percent and in rainy seasons the moisture content is higher.

In the results obtained from Table 1, quantitative and qualitative observations of soil texture, porosity, and high specific gravity in the soils of the region, the presence of arid and semi-arid climate and low moisture content on the other hand, in addition to the relatively high depth of infiltration impenetrable (between 80 to 200 cm) in most of the studied routes showed that transferring and releasing the diffuse gas condensate is done in the unsaturated area of the upper part of the hard floor, which needs further investigation on how to release besides finding out the affecting mechanisms.

3.2. Hydrocarbon pollution emission sources, type of pollutants, and wastewater characteristics

The results obtained from the analysis of contaminated soil or water make it possible to estimate the potential for contamination. One of the most common quantitative methods is the use of gas chromatography/mass spectrometry.

The results by Gas Chromatography-Mass Spectrometer (GCMS) showed probable released pollutants entering burning pits which include: Nitrogen, Methane, Ethane, Propane, i-Butane, n-Butane, i-Pentane, n-Pentane, 2, 2-Dimethyle Butane, 2- Methyl Pentane, 3- Methyl Pentane, n-Hexane, 2,3 Dimethyle Pentane, 2,2,4- Trimethyle pentane, n-Heptane, Methyl Cyclohexane, 2,5- Dimethyle Hexane, Toluene, 2,3,4- Tromethye pentane, 3- Methye Heptane, n-Octane, 1-Trance- 2-Dimethyle Cyclo Hexane, 2,2- dimethyl-3 Ethyle Pentane, Ethyle Cyclo Hexane, Ethyle Benzene, n- Nonane, N- Propyle Benzene, 1,2,4-Trimethyl Benzene, UnDecane, DoDecane, TriDecane, TetraDecane, Penta Decane, and Heavier, Di Ethanol Amin (DEA), Di Etalol Glycol (DEG).

In the investigation of the source of contamination, possible gradual leakage and accumulation in the soil around the refinery from two sewage storage tanks entering the burning pits, the results of TSS, TDS, BOD, COD, pH, T-tests were obtained as shown in Figure 2 and 3. An important criterion in measuring the severity of wastewater and effluent pollution is the chemical and biochemical oxygen requirements, which the results are shown in Figure 2. Thus, the severity of the contamination is attributed to the amount of organic or inorganic contamination that is capable of oxidation, and the total amount of oxygen used to oxidize the contaminant is determined.

Table 1. The results of some mechanical, physicochemical, and soil studies of boreholes in the area around the Sarkhun refinery

Issue	X	Y	Soil Texture	Moisture (%)	Dry Bulk Density (g/cm ³)	Wet Bulk Density (g/cm ³)	Saturation rate (%)	D ₆₀	Porosity	BedRock Situation (cm)	pH
TP1	439820	3023260	<i>Well-graded Gravel with Sand</i>	7.1	2.05	2.20	57.18	8.5	0.25	75	9.01
TP2	440150	3022400	<i>Poorly graded Sand with Gravel</i>	8.95	1.95	2.12	64.36	8.6	0.26	90	9.23
TP3	440800	3021110	<i>Poorly graded Gravel with Sand</i>	9	2.03	2.23	67.55	16.0	0.26	80	9.01
TP4	441550	3021160	<i>Well-graded Gravel with Sand</i>	9.8	2.03	2.25	75.32	12.7	-	130	8.97
TP5	442550	3021850	<i>Well-graded Gravel with Sand</i>	9.7	2.02	2.23	74.33	13.1	0.26	160	9.41
TP6	443450	3022630	<i>Poorly graded Gravel with Sand</i>	7.9	2.01	2.17	58.74	12.7	0.26	160	9.35
TP7	443550	3023510	<i>Poorly graded Sand with Gravel</i>	8.0	1.98	2.14	60.12	-	0.25	160	9.39
TP8	442530	3024700	<i>Poorly graded Gravel with Sand</i>	7.32	2.04	2.19	56.51	45.8	0.27	120	9.35
TP9	443150	3024450	<i>Sandy Silt</i>	13.7	1.94	2.10	72.41	-	-	50	8.44
TP10	442310	3023850	<i>Poorly graded Gravel with Sand</i>	12.3	1.96	2.13	62.87	16.3	0.28	under 200	8.9
TP11	443110	3024270	<i>Poorly graded Gravel with Sand</i>	8.6	2.02	2.21	71.52	12.7	0.26	200	8.73
TP12	443600	3024500	<i>Well-graded Gravel with Sand</i>	9.4	2.02	2.21	71.52	11.2	0.26	180	9.12
TP13	443900	3024510	<i>Poorly graded Gravel with Silt and Sand</i>	7.3	2.04	2.19	64.68	19.7	0.23	170	9.25
TP14	444650	3025565	<i>Well graded Gravel with Silt and Sand</i>	7	2.06	2.20	77.48	21.7	0.25	80	8.9
TP15	443750	3025000	<i>Poorly graded Gravel with Silt and Sand</i>	8.5	2.03	2.20	65.89	11.2	0.26	50	8.3

High values of COD with an average of 1267 and 1863 mg/l in dry and wet storage tanks indicate the high oxidation capacity of its constituent compounds, which in case of possible leakage can be removed from the environment by oxidation.

Large amounts of BOD with an average of 1036 and

1421 mg/l in dry and wet storage tanks indicate the high removal capability of hydrocarbon compounds from the system by microorganisms.

Table 2 shows the results of oil quantities, total suspended solids, and solution of dry and wet storage tanks entering the burning pits.

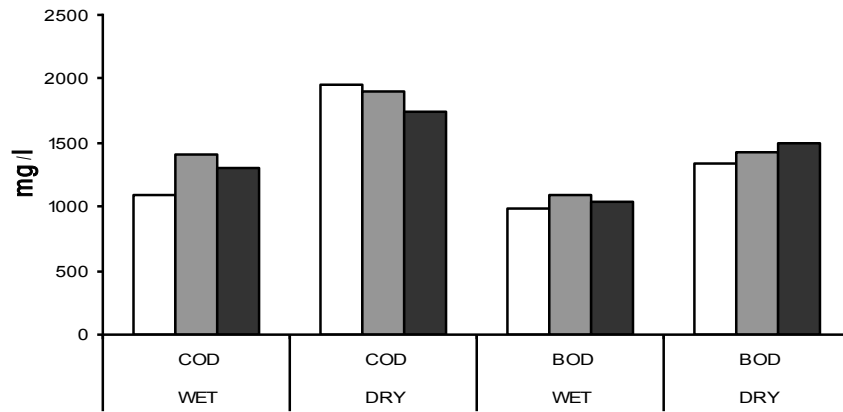


Figure 2. BOD and COD test results of dry and wet sewage storage tanks entering burning pits with three times of iterations

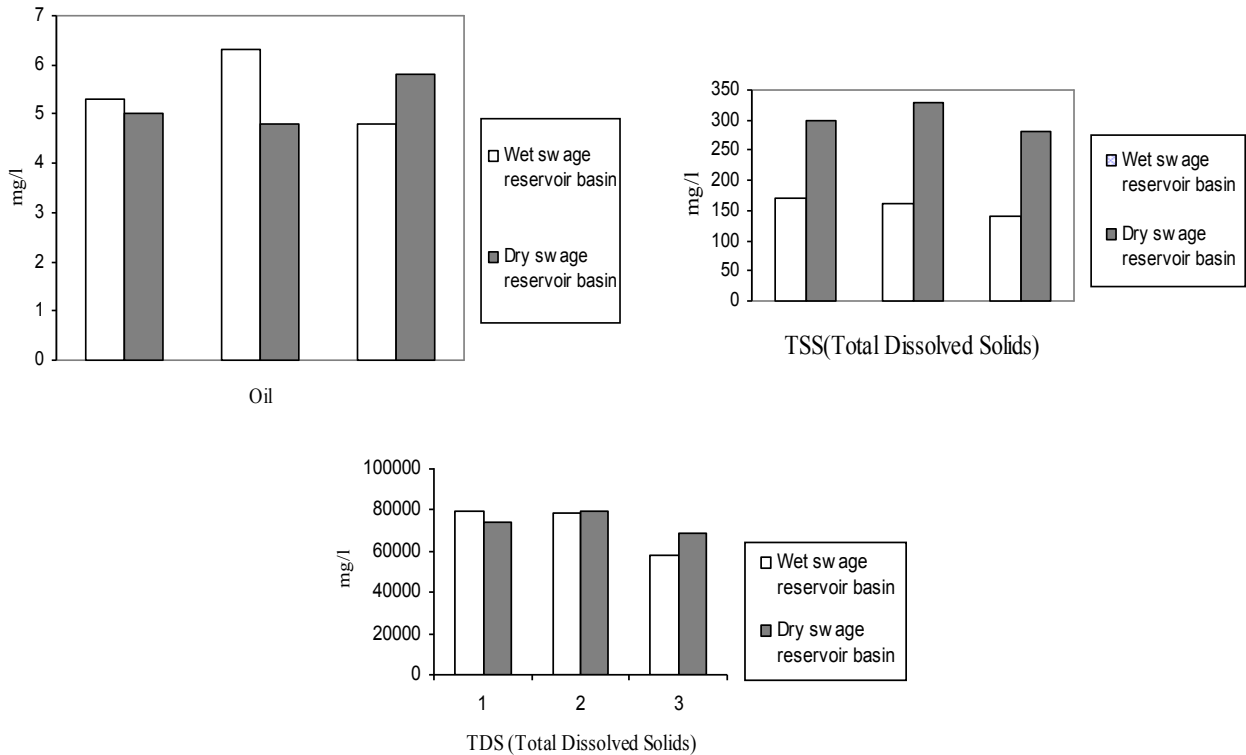


Figure 3. Results of Oil, TDS, and TSS tests of dry and wet sewage storage tanks entering the burning pits with three times repetitions

The amount of oil entering the dry and wet storage tanks with an average of 5.5 and 5.2 mg/l also indicates the initial amount of oil hydrocarbon entering the burning pits, which in case of leakage or infiltration into the environment, is the main cause of hydrocarbon pollution around the refinery.

All suspended and soluble solids, in addition to the

quality of the effluent, anticipate appropriate arrangements for its reuse. The results of TDS tests with an average of 71920 and 74172 mg/l in dry and wet storage tanks indicate a very high amount of soluble solids and the impossibility of reusing it, even if the contaminants are removed.

Table 2. Results of some important effluent parameters in wet and dry sewage basins(S-843, S-844)

	Wet (mg/l)					Dry (mg/l)				
	TDS	TSS	Oil	BOD	COD	TDS	TSS	Oil	BOD	COD
Sampling step 1	79322	170	5.3	980	1100	73770	298	5	1340	1950
Sampling step 2	78596	162	6.3	1095	1400	79606	328.5	4.8	1422	1900
Sampling step 3	57840	142	4.8	1034	1300	69138	282	5.8	1500	1740

3.3. Results of effective factors in determining the conceptual model of pollution emission in the soils around the refinery

The most important emission mechanisms of hydrocarbon and volatile pollutants and VOC compounds widely in the unsaturated soil environment of the refinery area are introduced as follows.

Advection is the mass transport along the main body of flow which is important in the pollution flow's speed. Spreading by advection can be defined by:

$$V_x = \frac{K}{n_e} \cdot \frac{dh}{dl} \quad [6]$$

Where K represents the intrinsic permeability coefficient in porous media, n_e is the dimensionless porosity, dh/dl stands for hydraulic gradient, and V_x is flow mean velocity.

Examination of the conditions prevailing in the underground environment of the soils around the Sarkhun refinery confirmed that in unsaturated soils, especially with low humidity in the area around the refinery, it is reasonable to assume that advection caused by the movement of phases is negligible compared to gaseous diffusion.

Vapor phase diffusion is the mass transport resulting from the concentration gradient of organic chemicals in the gas phase. Gaseous diffusion can be affected by many factors including soil temperature, water content, porosity, contaminant characteristics, and soil properties. It rapidly gets decreased with increasing water content and decreasing porosity.

A lot of research has been done on this subject, and empirical or semi-empirical diffusivity models have been developed to predict the diffusion coefficient in unsaturated soil. Based on the Millington and Quirk diffusivity model, which is considered to give the best predictions of vapor diffusivity (Bruce, 1993; McLachlan et al., 2002):

$$D_g / D_o = \varepsilon^{(10/3)} / \varphi^2 = (\varphi - \theta)^{(10/3)} / \varphi^2 \quad [7]$$

D_g is the vapor phase diffusion coefficient in porous media, D_o stands for the diffusion coefficient in pure air φ stands for the total volumetric porosity, θ represents the volumetric water content, and ε is the volumetric gas-

filled porosity. This model has been widely used in modeling and simulation (Fallah et al., 2013).

Furthermore, the liquid phase diffusion is several orders of magnitude less than the vapor phase diffusion. Therefore, diffusion in the liquid phase is negligible compared to vapor phase diffusion (Diggle and Ribeiro Jr, 2007).

Mechanical dispersion is the movement of some water molecules at a higher or lower speed than the average linear velocity of the contaminant, which causes the soluble contaminants to disperse in different directions. The mechanical diffusion coefficient is the product of the average linear velocity (real) and the dynamic dispersion.

$$D_m = V_x \cdot \alpha \quad [8]$$

In other words, the emission is a function of the flow velocity of the liquid and gas phases. In the study area, due to the prevailing conditions, the dispersion is significant in the gas phase due to the vapor pressure.

Adsorption is the surface interaction of a porous medium that causes the retention or stabilization of contaminant particles and ultimately delays and slows the release of contaminants relative to conditions without adsorption. A constant liquid/solid partition coefficient K_d is widely used in the modeling of organic vapor transport in unsaturated soil. K_d is defined to describe the distribution of volatile organic compounds between liquid and solid phases after equilibrium (Fazlali et al., 2015). The amount of distribution coefficient is highly dependent on soil moisture and in soils of arid areas such as soils around the Sarkhun refinery, it is several times larger than saturated areas (Ebrahimi et al., 2011).

Evaporation is sublimation and evaporation of gas condensate, and oil pollutants are one of the most important ways to leave the soil. The researchers found that the sublimation intensity of volatile organic compounds and condensate from the surface of sandy soil was much faster than that of clay (Tazangi et al., 2020; Karimpoor et al., 2022). Of course, sublimation of volatile organic compounds and condensate from deeper or even groundwater levels can occur; provided that the topsoil does not act as a barrier to gas migration and sublimation (Fingas, 2004). In this study, according to

Table 3. Characteristics and the amount of hydrocarbon pollution at the sampling places

Issue	X (Longitude)	Y (latitude)	TOG	TPH	Issue	X (Longitude)	Y (latitude)	TOG	TPH
			(mg/kg soil)					(mg/kg soil)	
C11	443126	3024767	425	363	N5	443858	3024926	2228	1488
C12	443405	3024721	750	638	N6	444125	3024825	990	650
C13	443409	3024700	700	590	E1	443905	3024735	513	488
C14	443714	3024697	614	501	E2	443878	3024444	325	300
C21	443186	3024508	338	263	E3	443890	3024316	288	263
C22	443408	3024507	320	311	S3	443732	3024005	163	150
C24	443700	3024520	263	253	S2	443428	3023987	188	163
C34	443711	3024300	214	205	W1	442828	3024725	322	299
N1	442889	3024897	1427	1028	W3	443095	3024258	238	221
N2	443124	3024872	2325	1788	G1	443335	3024318	17	-
N3	443507	3024896	3991	3100	G2	443492	3024458	14	5
N4	443690	3024870	3633	2612	G3	443415	3024230	7	4

the prevailing climate and soil studies, evaporation is an important and effective factor in the concentration of pollution.

There are many important factors involved in the leakage of hydrocarbon pollutants in a concept model. The next step is modeling with Millington and Quirk models to predict unknown parameters (Christakos, 1992).

3.4. Results of the investigation on pollution vertical and horizontal spreading according to the sampling places by Geo-Statistic studies

According to the site condition, wells were dug manually up to the hardpans and after investigating the existing stratifications, samples were taken from different layers. Results of TOG/TPH experiments around Sarkhun refinery at the sampling places are shown in Table 3.

Then, after gathering quantitative results of TOG/TPH experiments around the Sarkhun refinery at the sampling places, Geo-Statistic studies were done

In the next step of the Geo-statistics studies, the level-lines mapping was done by the use of Surfer software, as it is presented below, and then, sampling places, as well as sources of pollution, were both determined.

Investigation of the level-lines maps showed that the lines are mostly compacted, and high amounts of pollution have been taken in the soil in the north area around the refinery. Whereas in the west and central points of the studied site, the long distance of the level lines shows less pollution amount. Therefore, each

horizontal line represents an equal amount of emitted pollution (in terms of mg of pollutant/kg of soil). In addition, the points drawn around it are the places of burning pits, which are likely to be the source of pollution according to the shape. Furthermore, these maps showed that pollution spreading toward the east of the refinery was more than the western part.

The three-dimension map of TOG and TPH pollution concentration, which exists in the studied site, is shown below in Figures 4 and 5, on the longitude and latitude basis with the pollution level-lines and by consideration of the level line maps and situation of sampling places.

The investigation of TOG and TPH's three-dimensional quantitative map of pollution spreading showed the direction and path of spreading pollution. Furthermore, the quantity domain of hydrocarbon transport was from 3633 to 7 mgr pollution/kg Soil for TOG and 2612 to 4 mgr pollution/kg Soil for TPH. High quantities were obtained from burning pits, and the least amounts were in the east and west of refiner soils. TOG hydrocarbon pollution spreading was more intensive than TPH (Figure 5).

The three-dimension maps of TOG and TPH pollution concentration have been shown in Figure 5 on the longitude and latitude basis with the pollution level lines by considering the level line maps and the situation of sampling places. In both pollution spreading maps, in the eastern parts of soils around the refinery, hydrocarbon pollution amount increased abruptly. Studies showed that this cause is related to brooked pipe number 8, which occurred a few years ago. For more

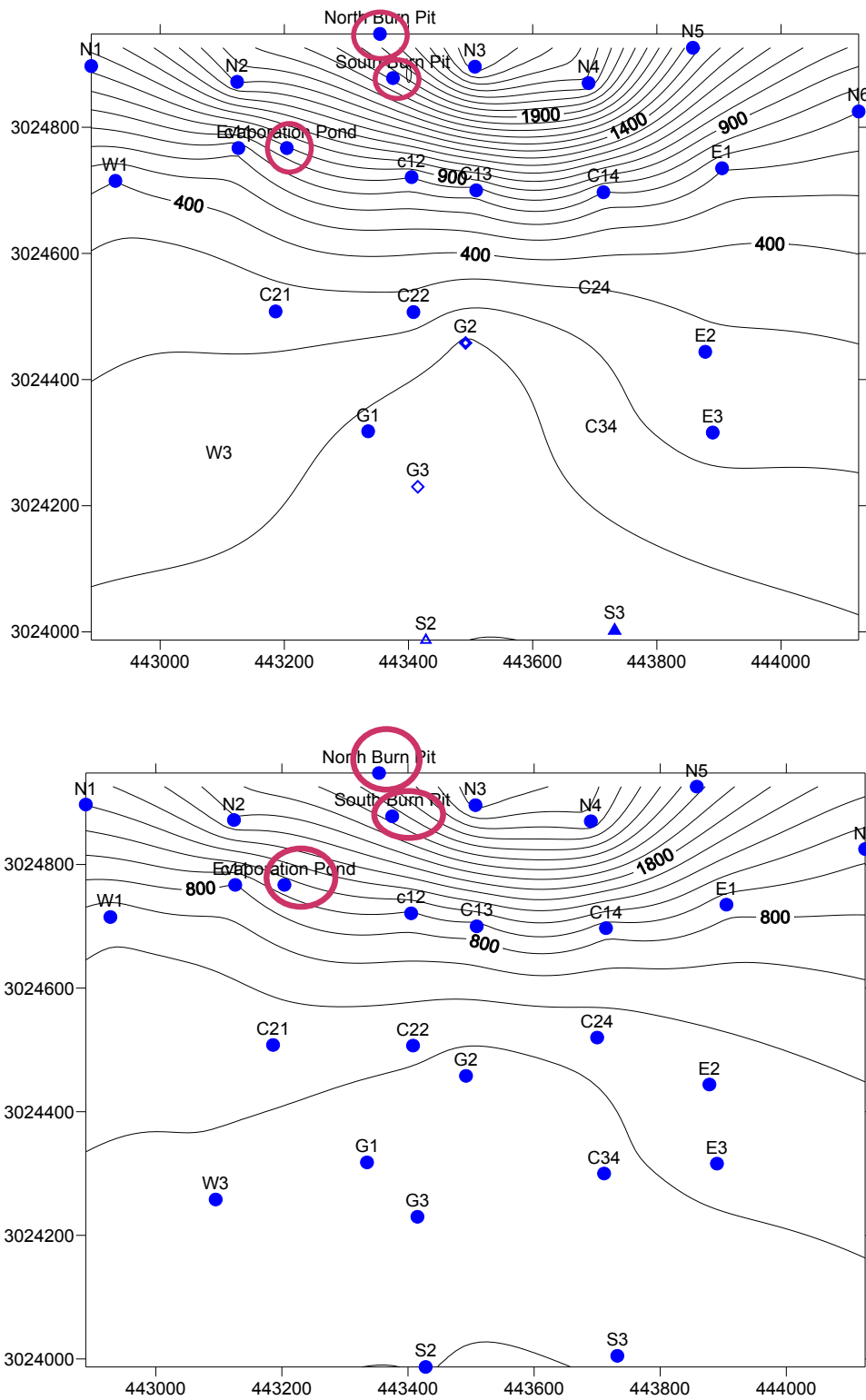


Figure 4. Location of drilled boreholes and sources of pollution based on hydrocarbon pollution and determination of pollution level lines for TOG (left) and TPH (right)

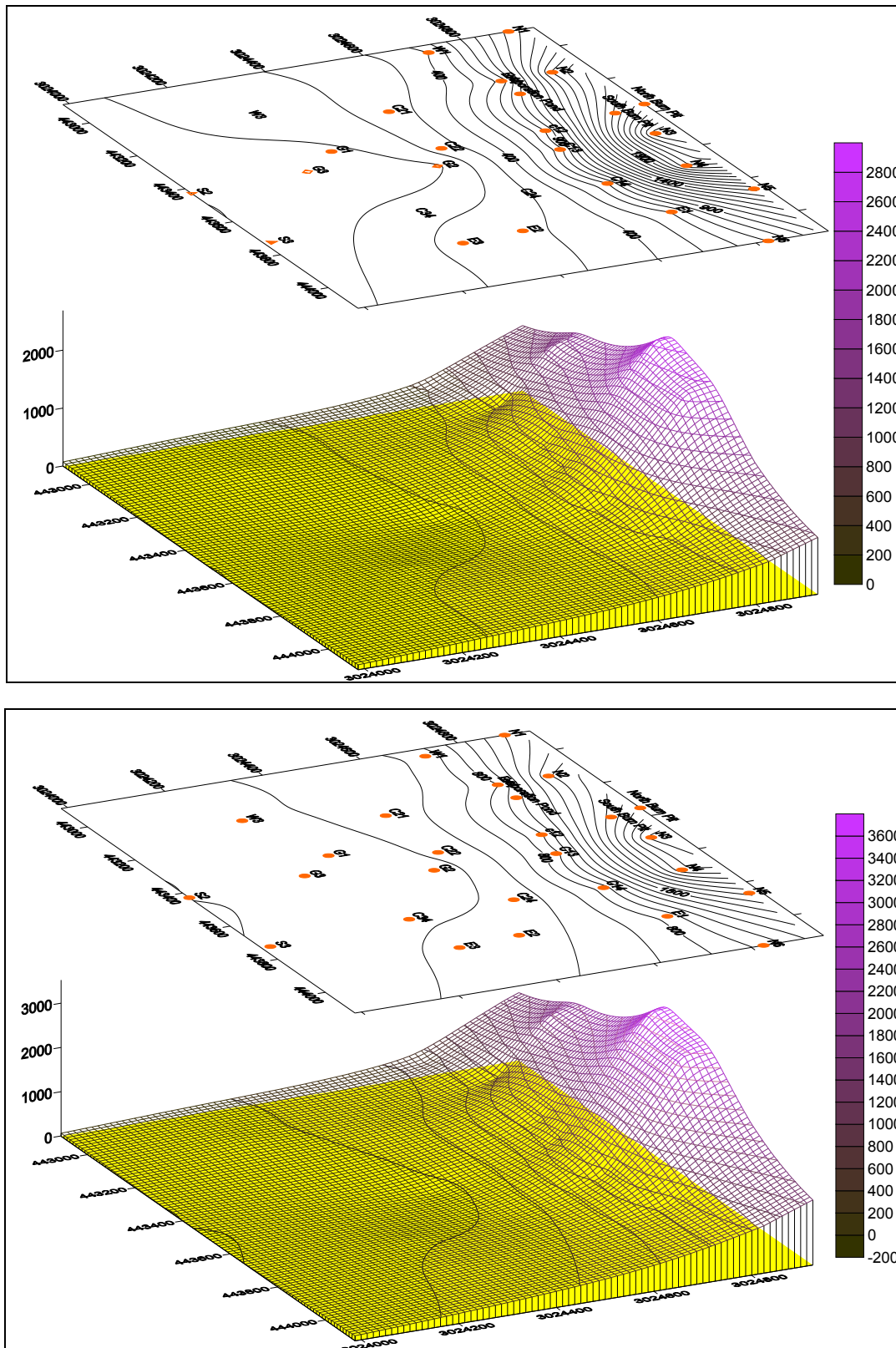


Figure 5. Three-dimensional image of the superimposition of the mining site map and the sources of pollution based on the extracted values obtained and estimated at the site, TOG (left) and TPH (right) (ppm)

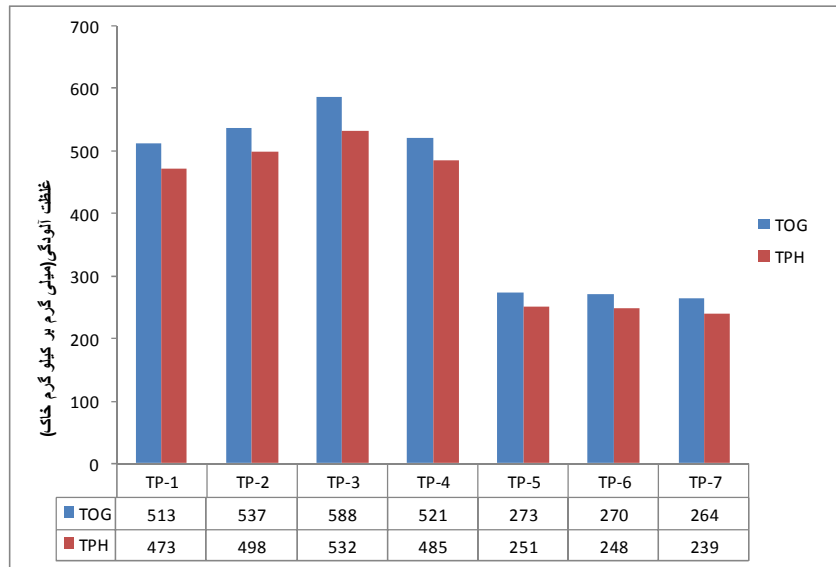


Figure 6. TOG and TPH in the location of sampling places around the broken part of pipe no. 8.

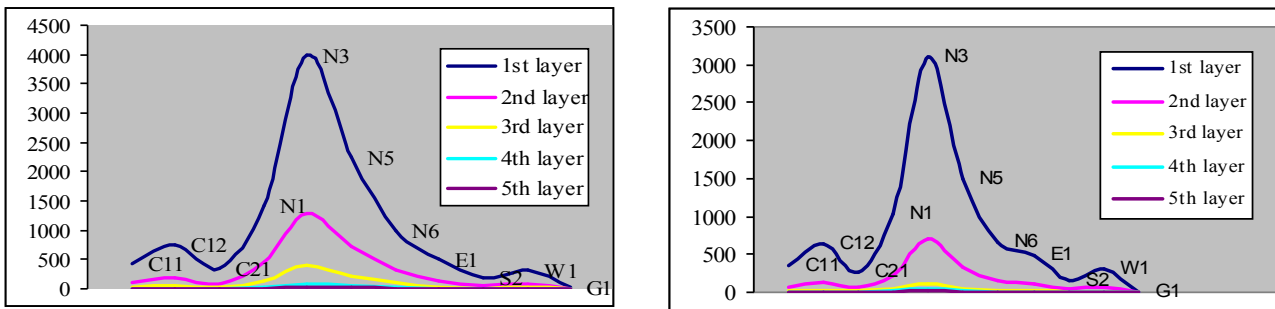


Figure 7. In-situ vertical contamination profile from boreholes at dimensionless depth for TOG (Left) and TPH (Right) contamination.

investigation on how pollution spreads and its quantity deals, sampling places TP-1 to TP-7 appliances around the broken pipe and measuring the amount of TPH and TOG changes based on mg/kg soil were performed.

As it is observed in Figure 6, the results showed that most of the hydrocarbon pollutants were obtained from sample TP-3 that occurred near the broken pipe. In TP-1, TP-2, and TP-4 sites, amounts of pollutants were similar and comparable but in TP-5, TP-6, and TP-7 sites, in path supreme Shour River, the amount of TPH and TOG pollution decreased. For many reasons such as smaller amount of pollutants which were gained from the east of the refinery against the north of the refinery (around burning pits), emission of this pollution source, passing a long time after breakage event rather, in the investigation of pollution spreading quantity and its modeling, this source was eliminated and burning pits and evaporation pond were used as the main sources.

The next step was providing a deep-seated profile of TOG and TPH pollutions, by gathering the data from

various layers and Geo-Statistical maps of whole soils around the refinery. The following figure shows the total pollution concentration in different dimensionless depths of soil. Choosing the dimensionless depths was because of the varied diameter of soil layers in different sites and the unsteadiness in the depth of bedrock. In fact, choosing dimensionless depths of the soil gives a good vision of the depths in which the polluted soil samples were collected.

At each point of the refinery, dimensionless depth is defined as follows (Ebrahimi et al., 2011):

$$z = \frac{h_i}{h_{max}} \quad [9]$$

Where Z stands for dimensionless depths, h_i is the depth of layer from which samples were collected, and h_{max} stands for depth from the soil surface to bedrock. In Figure 5, dimensionless depths 0.2, 0.4, 0.6, 0.8, and 1 represent layers 1 to 5 (from soil surface to bedrock),

actuality. It shows that TOG and TPH pollution deep-seated seepage profile curves in some sampling places. As it is shown in the curves, the most pollution seepage was in dimensionless depth equal to 0.2, and by increasing depth from the soil surface, the amount of the obtained pollution decreased noticeably. On the other hand, the most existing concentration of hydrocarbon pollutant was in the surface layer of soils around the Sarkhun refinery. This diagram is a good guide for managing pollution emissions and determining the best treatment method.

3.5. Modeling results with the software MATLAB

In simulating the emission of gas condensate in the soils around the Sarkhun refinery, after examining and determining the conceptual model of pollution emission and the factors involved, based on the prevailing conditions in the region, the basic principles were considered in the model, and the genetics algorithm was considered for unknown parameters. The general equation of governing mass transfer is as follows (Ebrahimi et al., 2011):

$$\rho DC_g / Dt = -\rho D_g \nabla^2 C_g + r_A \tag{10}$$

Where D_g is the diffusion coefficient of the pollutant in the porous media ρ represents soil density, C_g stands for pollutant concentration, and r_A is the biodegradation rate.

However, the existing conditions showed that since there is no flow in the form of displacement in the soil, the semester related to displacement in the above equation ought to be omitted, and the equation will be simplified as follows:

$$\rho \partial C_g / \partial t = -\rho D_g \nabla^2 C_g + r_A \tag{11}$$

In the above equation, r_A represents the biodegradation reaction, which in this region is due to the presence of different types of chemical contaminants in the soil that inhibit each other in biodegradation, and on the other hand, very high concentrations of these pollutants that cause disruption. Therefore, by the elimination of r_A :

$$\rho \partial C_g / \partial t = -\rho D_g \nabla^2 C_g \tag{12}$$

By consideration of thermodynamic relationships:

$$\begin{cases} C_S = K_d C_L \\ C_L = \frac{C_G}{\gamma H_C} \end{cases} \Rightarrow C_G = \frac{\gamma H_C}{K_d} C_S$$

$$\frac{\gamma H_C}{K_d} = \alpha$$

$$\Rightarrow C_G = \alpha C_S \tag{13}$$

Where C_s is pollutant concentration in soil, C_l is soil concentration in underground moisture, K_d is the distribution coefficient between soil and water, H_c is the Henry coefficient for pollutants, and γ is the thermodynamic correction coefficient.

$$\rho \partial(\alpha C_S) / \partial t = -\rho D_g \nabla^2(\alpha C_S) \tag{14}$$

According to the fact that coefficient α is dependent on soil and pollutant properties, and considering that in the study area (based on the experiments) soil properties do not change much and the type of pollutant does not change, α can be considered fixed, and it is eliminated from both sides of the equation:

$$\rho \partial C_S / \partial t = -\rho D_g \nabla^2 C_S \tag{15}$$

Finally, by considering the entrance duration of pollutants in soil, it is reasonable to assume that this process is in steady state conditions. So by the elimination of the left side of the equation:

$$\rho D_g \nabla^2 C_S = 0 \tag{16}$$

This is the final equation, by many compressions, that must be solved by initial and boundary conditions:

$$\text{At } z=0, x < x_{\text{source}}, y < y_{\text{source}},$$

$$0 < x < x_{\text{max}}, 0 < y < y_{\text{max}}: C=0 \tag{17}$$

$$\text{At } z=0, x=x_{\text{source}}, y=y_{\text{source}}=0: C=C_{\text{source}}$$

$$\text{At } z=z_{\text{max}}: \partial C / \partial z=0$$

$$\text{At } x=0: C=0$$

$$\text{At } x=x_{\text{max}}: C=0$$

$$\text{At } y=0: C=0$$

$$\text{At } y=y_{\text{max}}: C=0$$

Then, the extension of the equation by the Finite Volume method was performed, because the Finite Element method was unpractical. The mainsprings of this failure were an excellent solution domain and a lack of suitable hardware.

Hence, the surface integral of available derivation in elements was done, and the problem was solved by the Finite Volume method. The comparative error in simulation in comparison with getting results of experiments was only a maximum of 12%. Finally, the results of the investigation on pollutions vertical and horizontal spreading were done (Figure 7).

In Figures 8 and 9, the x-axis represents the east-west direction, the y-axis represents the north-south direction, and the z-axis represents the average concentration of pollutants in the region in milligrams per kilogram of soil. The dot (0,0) in this figure indicates the lower-left corner of the refinery (southwest). As can be seen,

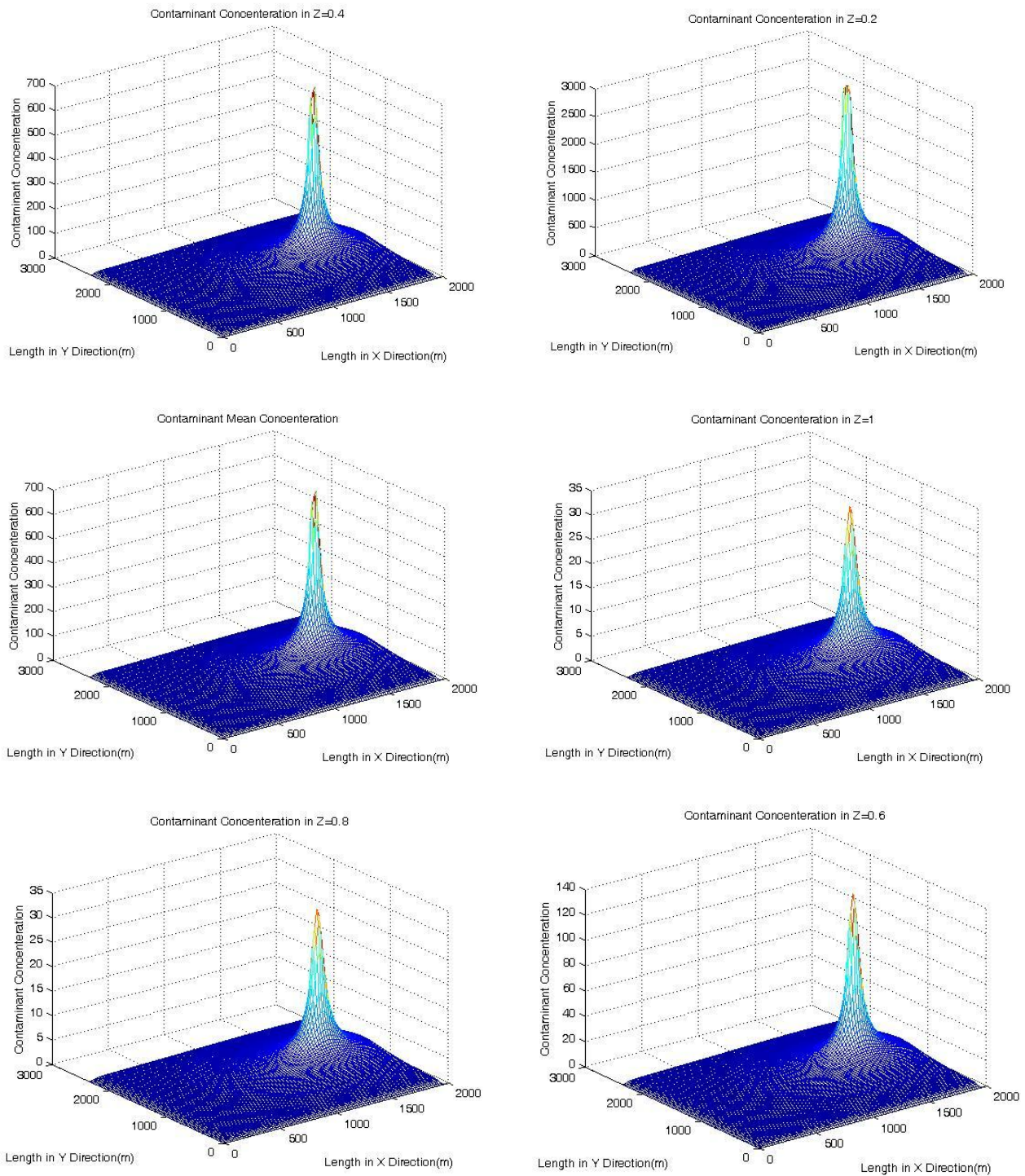


Figure 8. Mean TOG concentration and concentration at dimensionless depths 0.2, 0.4, 0.6, 0.8 in soil around Sarkhun refinery

simulations by MATLAB software show that the concentration of contaminants in the area around the burning pits has its maximum value; and on the other hand, with increasing dimensionless depth, the amount of

TOG and TPH contamination has decreased sharply.

Based on the modeling results, and paying attention to the mechanism of transmission of pollutants in the region, if the inflow of water entering the burning pit

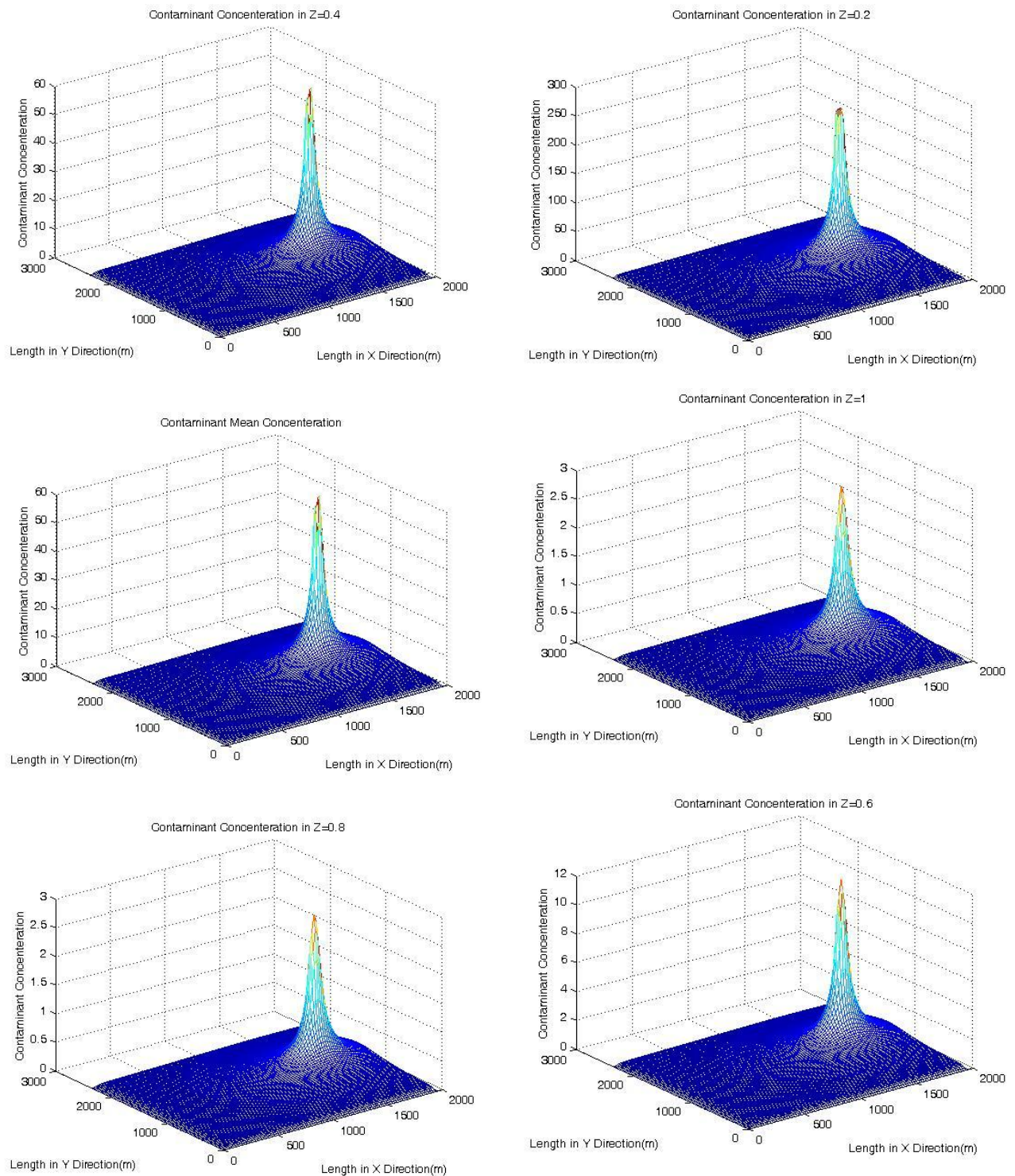


Figure 9. Mean TPH concentration and concentration at dimensionless depths 0.2, 0.4, 0.6, 0.8 in the soil around Sarkhun refinery

increases, there would be a high risk of increasing the scale of pollution, because of that, appropriate measures should be considered to prevent the spread of pollution. The results of this study can be used for estimating the

spread of pollution in any part of the study area at any time, monitoring user planning, and selecting the most appropriate method.

4. Conclusion

Examination of the existence and release of hydrocarbon pollution in the area around the Sarkhun refinery showed that this area has unique conditions, and in practice, many of the laws governing the release and transfer of hydrocarbons in this area need to be revised and amended. The results showed that in practice, due to the presence of groundwater aquifer at a depth of 24 meters in the area on the one hand, and the high hard impermeable buckets, on the other hand, the transfer and diffusion of soil in the enclosed area above the hardpan is mainly done by releasing the gas condensate. Large values of COD and BOD parameters in both dry and wet storage tanks of wastewater entering the burning pits indicated the high ability of oxidizing and removing hydrocarbon compounds from the system by microorganisms; in case of possible leakage. The large amounts of oil entering the reservoirs also indicated the initial amount of oil hydrocarbons entering the burning pits, which in the event of a leak or infiltration into the environment formed the main source of hydrocarbon pollution of the soil around the refinery. The results of tests of all suspended and soluble solids in dry and wet storage tanks indicate a very high amount of suspended and soluble solids and the impossibility of reusing them, even if their contaminants are removed. This, in addition to the quality of the effluent, requires efforts on providing appropriate arrangements for its reuse. Examining existing pollutants and determining their type and amount can be a good guide for not only making decisions about refinery wastewater management besides treatment plans but also for determining the best treatment system. The main parts of hydrocarbon pollution are the north and center part of the area around the refinery, especially around the burning pits (the pollution-causing sources). Furthermore, the results revealed that from the pollution spread point due to pipe breakage, TOG, and TPH pollutants have been moving towards Shour River in a consonant way and along the slope with a greater inclination to the east and the river. According to this matter, the pollution existence and its spread in the northern and western parts of the pipe breakage location were much less, and the main spread and extension were towards Shour River. Due to the elimination and stopping of this pollution caused after pipe breakage happening, the amount of sampling pollution in the place of sampling was much less than the pollution amounts in the northern parts of the refinery (around the burning pits). So, the main sources of pollution were burning pits and evaporation basins. Their way and their transportation level were gained from the place of burning pits towards the whole area and with more tendencies to the eastern side and Shour River and along the slope of the earth layers. The prepared maps of infiltration of TPH and TOG have shown that the deep infiltration was up to the depth of 0.2, and in more depth,

the pollution spread reduced noticeably.

The most important processes affecting the transport of volatile pollutants and gaseous condensates in the soils around the Sarkhun refinery were based on surface adsorption, diffusion, and gravity to reach the hardpan followed by the horizontal transfer of gaseous condensate. This release is influenced by chemical and biological processes that affect the contaminant flow in the soil, including climate-induced evaporation, oxidation, and biodegradation by local microorganisms. Although in this study the most important center of contamination was identified to be the burning pits, the spread of contamination from complete non-observance of safety and prevention during operation, possible leakage from storage tanks, leakage from runoff collection channels, especially during refinery operations for inspection were also some other important factors of contamination which were observed and maintained. The quantitative investigation of pollution spread maps and investigation of spread mechanisms revealed a high risk of increasing the pollution in the case of the increasing flow of entered water to burning pits. Therefore, the required preparation to prevent the pollution extension must be considered. On the other hand, since the lack of information resources consistent with climate conditions in Iran has always been a problem in studies, this research is considered appropriate to provide a valuable tool for future similar research guidelines. The results of this study will also form the basis for future similar studies in the world.

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