

EVALUATION OF OIL AND GREASE CONTAMINATION OF EUPHRATES RIVER IN AL KUFA RIVER STATION DURING 2010-2011

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ABSTRACT

The effects of pollution sources on receiving water quality are diverse and depend on the type and concentration of pollutants. The present study was conducted on Al Kufa river in Al-Kufa city in the aim of studying the contamination levels of oil and grease, with some water quality parameters (NO₃, pH, T.U., Cl,) and selected climatic parameters (precipitated dust particles, temperature, dust storm, and rain) were depended. Samples of raw water were collected and analyzed from Kufa river station during a period of fifteen months, starting from October 2010 to December 2011. The purpose is to assess the level of parameters measured and their effects on the river. Statistical analysis used to describe the relations between oil and grease and the other parameters and a regression analysis was performed by "Data Fit" program version 8.0 Software. This study showed that discharging domestic sewage and industrial waste water from adjacent areas, caused oil and grease contamination of levels more than Iraqi standard limits in 64 times .The highest values of oil and grease recorded in heavy rainy months impacted by runoff from land, the second highest values of oil and grease occurred in high level of weather temperatures. Finally, oil and grease levels, also increased according to precipitated dust particles, and dust storm which will lead to use more amounts of oil and grease due to different activities, followed by discharging of polluted waters to sewers or into river directly.

Keywords: oil and grease, nitrate, hydrogen Ion concentration, turbidity, chloride, precipitated dust particles, regression models.

تقييم التلوث بالزيوت والشحوم في نهر الفرات

في محطة شط الكوفة للفترة (2010-2011)

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الخلاصة

يختلف تأثير مصادر الملوثات على المسطحات المائية حسب نوع وتركيز تلك الملوثات. هذه الدراسة اختصت بدراسة مستويات التلوث بالنفط والزيوت مع بعض مكونات الماء (النترات، أيون الهيدروجين، العكورة، الكلورايد) وبعض خصائص المناخ (الغبار المتساقط، درجة الحرارة، عواصف الغبار، والأمطار) بنهر الكوفة في مدينة الكوفة. تم أخذ عينات ومن ثم تحليلها من مياه النهر من محطة الكوفة وبواقع نموذجين شهرياً من تشرين الأول في العام 2010 وحتى نهاية كانون الأول في العام 2011. الهدف لمعرفة تأثير تلك الملوثات على مياه النهر من خلال التحليل الإحصائي لمعرفة درجة الارتباط فيما بينها وباستخدام برنامج Software "Data Fit" program version 8.0. بينت الدراسة بأن تصريف مياه الصرف الصحي وبعض الأنشطة الصناعية في المناطق المجاورة تسبب زيادة في مستويات التلوث بالنفط والزيوت تصل إلى 64 مرة أعلى من الحدود المسموح بها في المواصفات العراقية. كما وأن أعلى مستويات التلوث بالنفط كانت في أشهر تساقط المطر الذي يتسبب بسحب تلك الملوثات إلى المجاري ومن ثم وصولها إلى النهر، وعند ارتفاع درجات حرارة الجو. وأخيراً فقد بينت الدراسة بأن ارتفاع مستويات التلوث بالنفط والزيوت كان في فترات زيادة تساقط الغبار والعواصف الترابية وما ينتج عنها من نشاطات وأعمال تؤدي إلى زيادة استعمال المشتقات النفطية ومن ثم تصريفها إلى شبكات المجاري أو إلى النهر مباشرة.

كلمات رئيسية: الزيوت والشحوم، النترات، أيون الهيدروجين، العكورة، الكلورايد، الغبار المتساقط، نمذجة الانحدار.

1.INTRODUCTION

Water, is used for many purposes associated with human activity. In its natural state it occurs in and on the ground in subsurface and surface reservoirs. The quality and reliability of a water source will vary considerably, both in time and space. This means that characteristics (chemical, physical, and biological) will differ greatly depending upon the location and type of the source. It also means that a given source may vary over the seasons of the year (Pfafflin and Ziegler, 2006).

Water pollution can be defined as the presence in water of enough harmful or objectionable material to damage the water's quality (Pankratz, 2001). Water pollutants are categorized as *point* source or *nonpoint* source, the former being identified as all *dry* weather pollutants that enter watercourses through pipes or channels. Storm drainage, even though the water may enter watercourses by pipes or channels, it is considered a nonpoint source pollution. Other nonpoint source comes from agricultural runoff, construction sites, and other land disturbances (Weiner and Matthews, 2003).

Traditionally, in United States, water quality standards are classified as the following nine parameters: dissolved oxygen (DO), pH, coliform, temperature, floating solids (oil–grease), settleable solids, turbidity–color, taste–odors, and toxic substances (Corbitt, 2004). Pollution from petroleum compounds (“oil pollution”) first came to public attention with the Torrey Canyon disaster in 1967. The huge tanker loaded with crude oil plowed into a reef in the English Channel. Despite British and French attempts to burn the oil, almost all of it leaked out and fouled French and English beaches. Eventually, straw was used to soak up the oil and detergents were applied to disperse the oil (detergents were later found to be harmful to the coastal ecology) (Weiner and Matthews, 2003).

Abriola and Pinder (1985) formulated a one-dimensional finite difference model which included immiscible organic flow, water flow, and equilibrium inter-phase transfer between the immiscible organic phase, the water phase, and a static gas phase. The results of this simulation were described to demonstrate the numerical algorithms incorporated in the model as cited by (Sleep and Sykes, 1989).

Kaluarachchi and Parker (1989) presented an isothermal two-dimensional finite element model named MOFAT-2D for three phase flow and transport by allowing for interphase mass exchange. This model is based on Galerkin's weighted residual approach and an upstream weighting technique to predict simultaneous flow of water and oil in a three fluid phase system with gas assumed constant at atmospheric pressure.

Euphrates river has a large importance for Iraqi environmental researchers because of the detrimental effect of pollutants resulting from treated and untreated domestic wastewater, treated and untreated industrial wastewater and farming and agricultural pollutants.

Al-Mayahi, 2005 studied the pollution by petroleum in sediments of three stations at shatt Al-Arab River. Samples were collected monthly from October 2003 to September 2004. Spectrofluorometric method was used to determine the total petroleum hydrocarbons and using Basra crude oil as standard. Many ecological parameters also were determined for three selected stations. Values: salinity, pH, dissolved oxygen, BOD₅, total organic carbon (TOC), nitrates and phosphates were investigated, and he showed that the measured values fluctuated according time and space of human activities.

A large number of populations of Iraq reside along the banks of Euphrates and Tigris rivers so that the utility of such water for bathing and recreation purposes cannot be aesthetically good. The polluted water especially by oil and grease are also difficult to be easily treated and it is found that the treatment plants have to be increased in handling such water.

The objective of the study is to evaluate oil and grease contamination of Euphrates river at Al Kufa river station.

2. STUDY AREA

Kufa is a city in Iraq, about 170 kilometers south of Baghdad (capital of Iraq), and 10 kilometers northeast of Najaf. It is located on the banks of the Euphrates river. Euphrates river branches after Al-Kifil town directly about (1Km) to two branches (first one is Shatt Al Kufa and another branch named Al Abbasia river). The main sources of water for this river are rain water, stored water as lake and reservoirs.

Al Kufa station is located on the Euphrates river/Shatt al-Kufa, near the Al Kufa water treatment plant for surface water monitoring, at coordinates (E044.4075, N32.03941) figure (1). The water level at the station is not stable, in the summer decline is attributed to its lowest level so that the bottom of the river can be seen in some areas near the station, and in winter the water levels are not rising as required, and the center of the river is not covered with water even in winter and the rainy season. The nature of the land surrounding the station is agricultural land, with some residential buildings at a distance (100 m to the south) and farming land on the other side.

Al Kufa river passes through many towns and villages thus it represents the main source for different uses such as:

- Irrigation: Irrigation for large agricultural areas locating on both sides of the river.
- Water supply systems: Water supply for many water treatment plants such as Al-Najaf and Al-Kufa water treatment plants.
- Industrial purposes: The main source for all industrial activities in the area.

In addition to these main uses, the river receives many pollutants discharged by different sources, including:

- Careless use of pesticides can contaminate water sources and make the water unsuitable for drinking. Wastes of animals and plants from agricultural areas are discharged to the river on both sides.
- Municipal wastes: Municipal wastes are discharged from Northern drainage of Al Kufa (2 km / north) and raw waste water discharged from Al Jimaah zone at 1 km / north of station.
- Industrial wastes: Many industries discharge wastewater to the river such as soft drink factory and many private industries.

3. MODEL FORMATION

Data of oil and grease concentrations, some water quality parameters, and climatic conditions factors of the Euphrates river (at Kufa river station) are being analyzed monthly, and the pollution levels are being determined.

In present study the statistical models are described the relations between parameters of water quality. The regression analysis was done by using "Data Fit" program version 8.0 software .

Also, two statistical methods were utilized for analyzing data collected from the sampling site: correlation analyses, regression variable (t-ratio and Prob(t)), and Variance analyses (Prob (F)). Correlation analyses were performed on the individual water quality parameters to identify relationships between them. Variance analysis to determine the overall significance of the regression model

Accordingly, multiple non-linear regression models in three forms were used for each design requirements to choose which form gives the best fitting of data. The regression models that were proposed and investigated can be seen in table (1).

4. DATA ANALYSIS

This research covers the study and analysis the pair of monthly water quality parameters of surface water for Euphrates river at Al Kufa river station, and climatic conditions factors involved.

Data for Euphrates river in Al Kufa station were collected, from the period extended from October 2010 to December 2011. These data represent the nitrate (NO_3), hydrogen ion concentration (pH), turbidity unit (T.U.), chloride (Cl), precipitated dust particles (PM, g/m^2), mean max. temperature (T), dust storm (DS), and monthly rain totals (Ra) as independent variables, and oil & grease (O&G) as dependent variable, as shown in table (2).

The samples of water parameters were tested in the laboratory in environment directorate of Al Najaf city. Partition-Gravimetric Method used to quantify oil and grease in samples taken. The Apparatus comprised:

- a. Separatory funnel, 2-L, with TFE* stopcock.
- b. Distilling flask, 125-mL.
- c. Liquid funnel, glass.
- d. Filter paper, 11-cm diam.
- e. Centrifuge, capable of spinning at least four 100-mL glass centrifuge tubes at 2400 rpm.
- f. Centrifuge tubes, 100-mL, glass.
- g. Water bath, capable of maintaining 85°C .
- h. Vacuum pump .
- i. Distilling adapter with drip tip.
- j. Ice bath.
- k. Waste receptacle, for used solvent.
- l. Desiccator.

*Teflon

While the reagents used are included:

- a. Hydrochloric , 1:1: Mix equal volumes of either acid and reagent water.
- b. Sodium sulfate, Na_2SO_4 , anhydrous crystal.
- c. Freon 113 .

Procedure of analysis can be summarized as an oily water sample is extracted by a solvent. After separating the solvent (now containing oil) from the water sample, it is placed into a flask, which has been weighed beforehand. The flask is placed into a temperature controlled water bath, and the solvent is evaporated at a specific temperature, condensed and collected. After the solvent is evaporated, the flask now containing the residual oil, is dried and weighed. Knowing the weight of the empty flask, the amount of residual oil can be calculated, this method is dependent and used in USA EPA. (USEPA, 1998).

Climatic parameters used in present study were measured by the digital climatic station in education faculty for girls in university of kufa.

Figure (2) shows the variations of oil and grease with time compared with some allowable limits according to Iraqi and United States standards in Al-Kufa river station. Monthly variations of NO_3 , pH, T.U., Cl, and PM are shown by Figure. (3) to (7), while temperature, dust storm, and rain variations are represented by figure 8 during the period of study.

Table (3) shows analysis of variance (ANOVA) for the regression model obtained, the Prob (F) = 0.11, which means that there is a 89 % chance that at least one parameter is not equal to zero depending on the hypothesis used, therefore, the best significant relationship between the dependent variable and regression model is confirmed.

Table (4) shows the data statistics of the water quality parameters .The optimum correlation equation was found in the rank A of an exponential form with coefficient of determination R^2 equal to 0.791, was shown in table (5).

The correlation matrix is shown in table (6), and table (7) shows regression variables results and 95% confidence intervals.

Figure (9) shows the plot of the model represents the parameters of Euphrates river at Al Kufa river station during study period.

5. DISCUSSION

The environmental impact of most releases of petroleum wastes would be minimal if the wastes remained at their points of release. Unfortunately, wastes can migrate away from a release point by a number of pathways (Reis, 1996).

From figure (2) oil and grease ranged in Al Kufa river station throughout the study period between 0.3-6.4 mg/l, as Iraqi standard limits 0.1 mg/l, those concentrations range from 3 to 64 times greater than Iraqi standards. The highest value recorded was 6.4 mg/l in February, but the lowest value was 0.3 mg/l in November. The highest values 5.1, 6.4, 5.1 mg/l in January, February, and March, respectively, which recorded in heavy monthly rain fall of 20.7, 15.1, 13.5 mm, respectively. This agreed well with result gained by Hunter et al., 1979 that presented a relationship between runoff and load. Rain precipitation caused oil washing into surface water as runoff from roads and parking lots (Nathanson, 2000). The word "runoff" indicates rainwater or snowmelt carried across land to water. Runoff arises from *non-point sources*, and carries almost anything that water can carry as oil, grease, dirt, trash, animal waste, microorganisms, and chemical pollutants, including metals, pesticides, and fertilizers (Hill, 2004). The variation of temperature, dust storm and rain with time during the period of the study is given in figure (8). Table (6) shows that the temperature has high negative correlation (-0.89) with rain agreed very well Iraqi climatic conditions.

Figures (3 to 7) show monthly variations with Iraqi standard limits of NO_3 , pH, T.U., Cl, and PM during the period of the study. The value of oil & grease 5.1 mg/l in March, increased according to high values of NO_3 , pH, Cl as a result of sewage discharged to Al Kufa river from northern drainage of Al Kufa (2 km/north) and raw waste water discharged from Al Jimaah zone at 1 km / north of the station,

particularly in fertilizing season in neighbor area taking in consideration that agricultural, industrial, and domestic wastewaters discharged to surface waters are a source of chlorides and nitrates (Metcalf & Eddy, 2004). Also, The value of oil & grease (6.3 mg/l) in July, increased according to high values of turbidity as a result of sewage discharged to Al Kufa river, this agreed very well with the result obtained by (Hunter et al., 1979) that showed of runoff increase the fraction of hydrocarbons associated with the particulates increased.

In addition, the oil and grease increased to reach 6.3 mg/l in July according to PM, T and DS values 153.85 , 46.1, 0.5 , respectively. This is a result of washing, polishing and lubricating of different types of vehicles covered by dust through the dusty weather by using oil products in large number of garages, some of them treating wastes in preliminary method and others discharging wastes to sewers affecting oil and grease increasing, especially when sewage is discharged to the river without treatment in wastewater treatment plant or illegal sewer pipe discharges.

Direct releases of oil into river were observed. Second highest oil & grease value recorded in July (6.3) with high level of temperature, its sources were from diesel agriculture motors located on river banks, motor and other recreational boats in summer season release up to 30% of their fuel (Hill, 2004). Oil products were also discharged from different sizes of motors for electricity generation in all Al Najaf and Al Kufa quarters (residential, industrial and commercial zones) during working time especially through cooling processes by water and allow to water-oil mixture entering sewers to reach Al Kufa river.

High oil and grease concentrations in Shatt Al Kufa is also from grease formed in sewage which includes fats, waxes, free fatty acids, calcium, magnesium, soaps, mineral oils and other non-fatty materials (Singh and Singh, 2007). The sewage from kitchens, slaughter houses and restaurants contains grease (Steel and McGhee, 1979; Meenambal et. al., 2005; Singh, 2007), therefore, oil and grease find their way to Shatt Al Kufa from raw waste water discharged directly from Al Jimaah zone at 1 km / north of station.

Other sources of oil and grease in Al Kufa river are spills, oil leaking from vehicles, or released during accidents. In addition, petroleum hydrocarbons from atmospheric sources (e.g., automobile exhaust fumes) are deposited daily on road surfaces. When it rains, these oily deposits wash into nearby streams (Weiner and Matthews, 2003). This principle agreed well with the statistical analysis of the present study concerning the highest value of oil and grease through raining months and dust storm periods, as the particulate emissions are discharged from sources mentioned above, they are more rapidly separated and dispersed by the swiftly moving air, particulate smaller than 1 μm tend to remain suspension in the atmosphere indefinitely, whereas those larger than 1 μm tend to settle out under the force of gravity (Nathanson, 2000). The particulates coated with petroleum hydrocarbons are settled, either precipitate directly on Al kufa river or full deposited on road surfaces and reaches to river with rain.

6. CONCLUSIONS

The following conclusions are drawn on the basis of the results obtained from the present analysis:

1. Oil and grease ranged in Al Kufa river station throughout the study period between 0.3-6.4 mg/l, those concentrations range from 3 to 64 times greater than Iraqi standard limits.
2. The highest values of oil and grease were recorded in heavy rainy months, caused oil washing into surface water in runoff from roads and parks.

3. The value of oil & grease in March, increased according to high values of NO₃, pH, T.U., Cl as a result of sewage discharged to Al Kufa river from northern drainage of Al Kufa and raw waste water discharged from Al Jimaah zone.

4. It was noticed that the oil and grease increased according to PM, T and DS values as result of different activities involves, followed by discharging of polluted waters to sewers or into river directly.

7. RECOMMENDATIONS

-Iraqi legislations should be severely restricting the discharge of oil & grease and other toxic substances by requiring pretreatment of wastewater.

-Conduct more studies on the relationships between different types of pollutants and human and animal health.

-Environmental monitoring programs to control the oil and grease contamination of Al Kufa river, and how they are affected by various environmental factors.

-Further studies on other potential pollutants in Al Kufa river and the hydrocarbon compounds such as pesticides and other residues in the river water and sediment.

-More studies on the relationships between air pollution from industrial and traffic sources within river water and sediment.

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Table (1): The proposed models.

Rank	Equation Description
A	$y = \exp(ax_1 + bx_2 + \dots + j_k x_k + M)$
B	$y = ax_1 + bx_2 + \dots + j_k x_k + M$
C	$y = a x_1 + b x_2 + \dots + j_k x_k$

Where;

y = dependent variable.

x₁, x₂, ..., x_k = the independent variables.

a, b, c, ...j_k = model coefficients, and

M = model constant term.

Table (2): Description of independent and dependent variables in Al Kufa river station.

<i>Type of variables</i>	<i>Variables</i>	<i>Detail</i>
<i>Independent</i>	X ₁	Nitrate (NO ₃ , mg/L)
	X ₂	Hydrogen Ion concentration (pH)
	X ₃	Turbidity unit (T.U., NTU)
	X ₄	Chloride (Cl, mg/L)
	X ₅	Precipitated dust particles (PM, g/m ² /month)
	X ₆	Mean Max. Temperature (T, °C)
	X ₇	Dust Storm (DS, No. of days)
	X ₈	Monthly rain totals, (Ra, mm)
<i>Dependent</i>	Y	Oil & Grease (O&G, mg/L)

Table (3): Variance analysis of variables in Al-Kufa river station

Variance Analysis					
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	8	56.3780773	7.047259662	2.837972003	0.11029
Error	6	14.89921603	2.483202672		
Total	14	71.27729333			

Table (4): Data Statistics of variables in Al Kufa river station

Variable	X1, NO ₃	X2, pH	X3, T.U	X4, Cl	X5, PM	X6, T	X7, DS	X8, Ra	Y, O&G
Number of Points	15	15	15	15	15	15	15	15	15
Missing Points	0	0	0	0	0	0	0	0	0
Maximum Value	8.85	8.65	39.2	234.7	823.74	46.3	3.5	20.7	6.4
Minimum Value	2.6	6.48	2.95	129.7	15.33	18.2	0	0	0.3
Range	6.25	2.17	36.25	105	808.41	28.1	3.5	20.7	6.1
Average	6.96733333	7.81	17.464	179.406666	167.45	30.03333333	0.8	9.10666666	3.05066666
Standard Deviation	1.7601358	0.5732738	10.107770	30.274072	256.29058	10.103405	1.207121	7.5663226	2.2563765

Table (5): Model Selected of variables in Al Kufa river station

Rank	Model	Std Error	Residual Sum	Residual Avg.	RSS	R ²	Ra ²
A	$a^2x_1 + b^2x_2 + c^2x_3 + d^2x_4 + e^2x_5 + f^2x_6 + g^2x_7 + h^2x_8 + i$	1.5758	3.769217531	0.251281169	14.899216	0.79096826	0.512259
B	$a^2x_1 + b^2x_2 + c^2x_3 - d^2x_4 + e^2x_5 + f^2x_6 + g^2x_7 - h^2x_8 + i$	2.2169	2.04281E-14	1.36187E-15	29.4897843	0.58626677	0.03462
C	$a^2x_1 + b^2x_2 + c^2x_3 - d^2x_4 + e^2x_5 + f^2x_6 + g^2x_7 - h^2x_8$	2.0526	-0.006724963	-0.000448331	29.4939637	0.58620814	0.17241

Table (6): Correlation matrix of variables in AlKufa river station

	X1, NO ₃	X2, pH	X3, T.U	X4, Cl	X5, PM	X6, T	X7, DS	X8, Ra	Y, O&G
X1, NO ₃	1								
X2, pH	0.34176056	1							
X3, T.U	0.05337900	0.04214696	1						
X4, Cl	0.0281790	-0.1194745	-0.6983032	1					
X5, PM	0.14446519	-0.1766155	0.06844531	-0.4118016	1				
X6, T	0.25952756	-0.3491751	0.5361165	-0.5457593	0.36549184	1			
X7, DS	0.22967968	0.14502241	-0.1073830	-0.1613297	0.64258691	0.22065123	1		
X8, Ra	-0.0899375	0.2361754	-0.6728314	0.68999777	-0.2759301	-0.8925515	-0.1034655	1	
Y, O&G	0.11470081	0.37559150	-0.1325180	-0.0415189	-0.3263598	-0.009052	0.1204234	0.0899481	1

Table (7): Regression coefficients results and 95% confidence intervals

Regression Variable Results				
Var.	Value	Standard Error	t-ratio	Prob(t)
a	-0.3461478	0.205221244	-1.686705499	0.14263
b	1.023656105	0.631589036	1.620762943	0.1562
c	-0.07315679	0.067695274	-1.080677958	0.32135
d	-0.037297617	0.01922619	-1.939938045	0.10045
e	-0.014236224	0.006336813	-2.246590356	0.06575
f	0.279992317	0.157939786	1.772778881	0.12664
g	0.395297331	0.230554953	1.71454712	0.13725
h	0.258707332	0.149817547	1.726815972	0.13495
i	-6.579121525	6.479378199	-1.015393966	0.3491

95% Confidence Intervals				
Var.	Value	95% (+/-)	Lower Limit	Upper Limit
a	-0.3461478	0.502155861	-0.848303661	0.156008061
b	1.023656105	1.545435212	-0.521779107	2.569091317
c	-0.07315679	0.165643565	-0.238800355	0.092486775
d	-0.037297617	0.047044563	-0.08434218	0.009746947
e	-0.014236224	0.015505548	-0.029741772	0.001269325
f	0.279992317	0.386462862	-0.106470545	0.666455179
g	0.395297331	0.564144915	-0.168847584	0.959442246
h	0.258707332	0.366588555	-0.107881222	0.625295887
i	-6.579121525	15.85439051	-22.43351204	9.275268989



Figure (1): Map of the studying area in the national context.

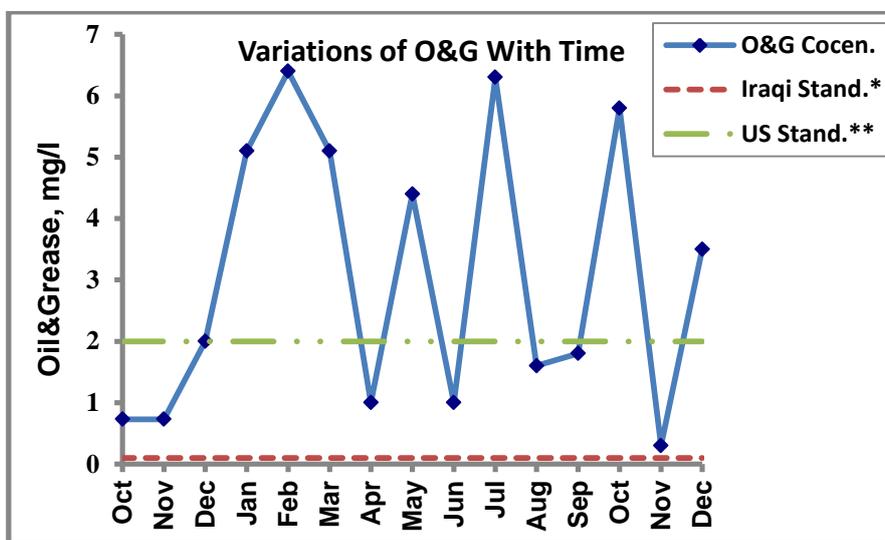


Figure (2): Variations of oil and grease with time compared with some allowable limits according to Iraqi and US Standards in Al-Kufa river station.

* *Source:* Iraqi environmental legislations book

***Source:* Maximum allowable values in United States related to type of use published by California (Liu, 1999).

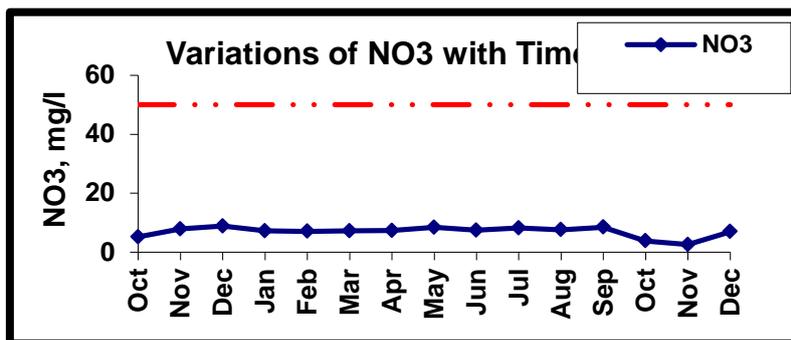


Figure (3): Variations of NO₃ with Time

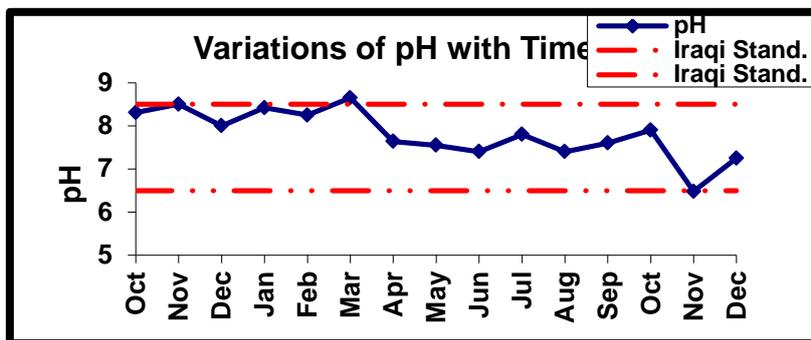


Figure (4): Variations of pH with Time

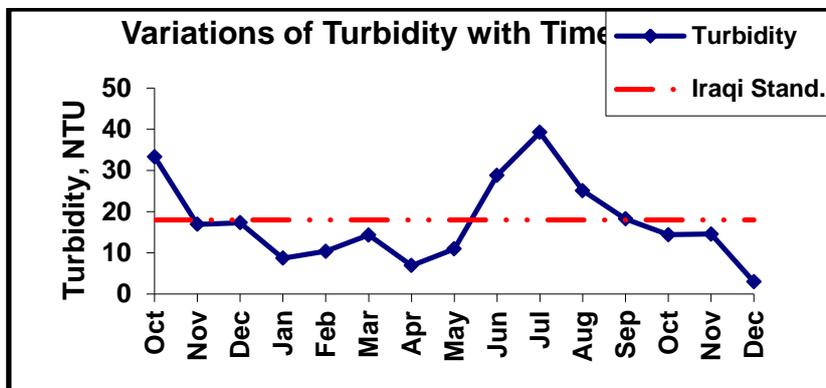


Figure (5): Variations of Turbidity with Time

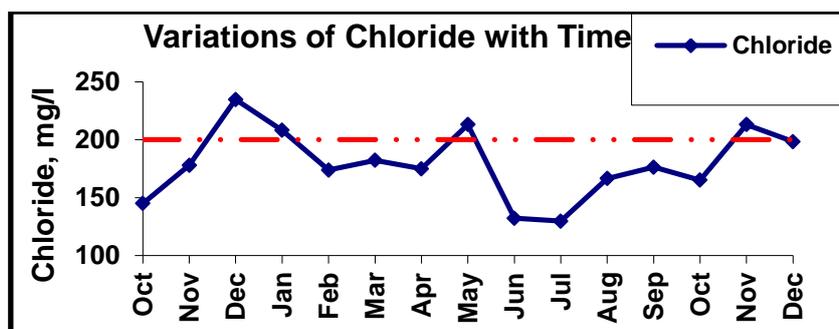


Figure (6): Variations of Chloride with Time

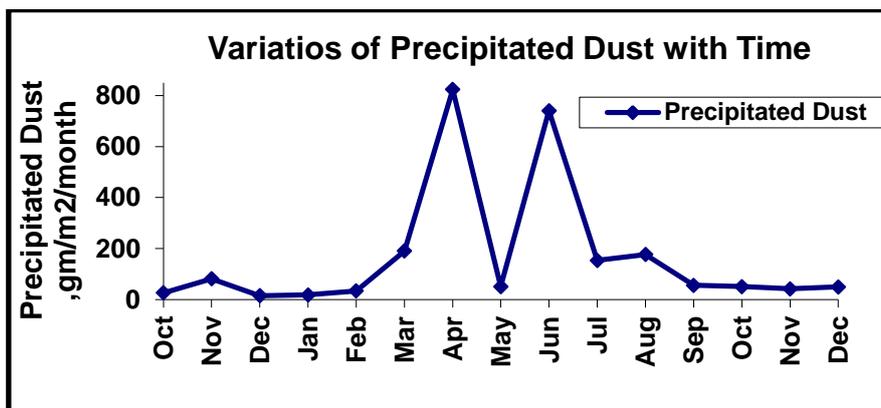


Figure (7): Variations of Precipitated Dust Particles with Time

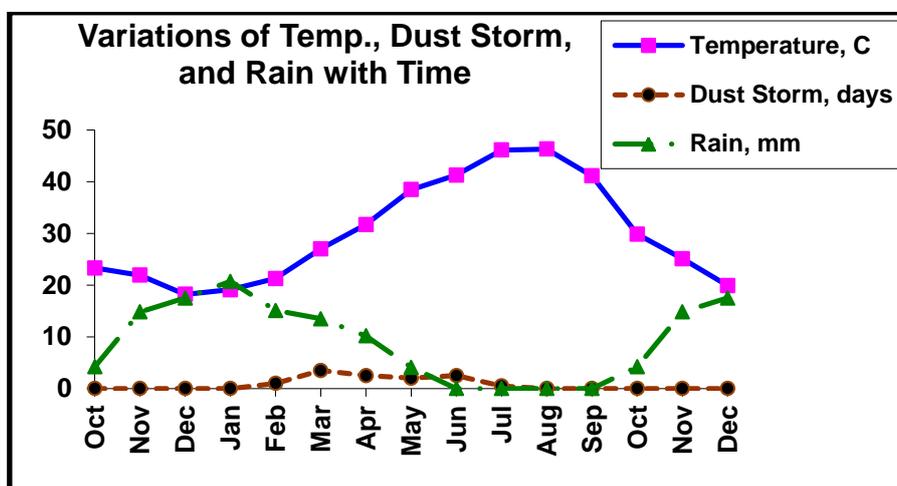


Figure (8): Variations of Temperature, Dust Storm and Rain with Time

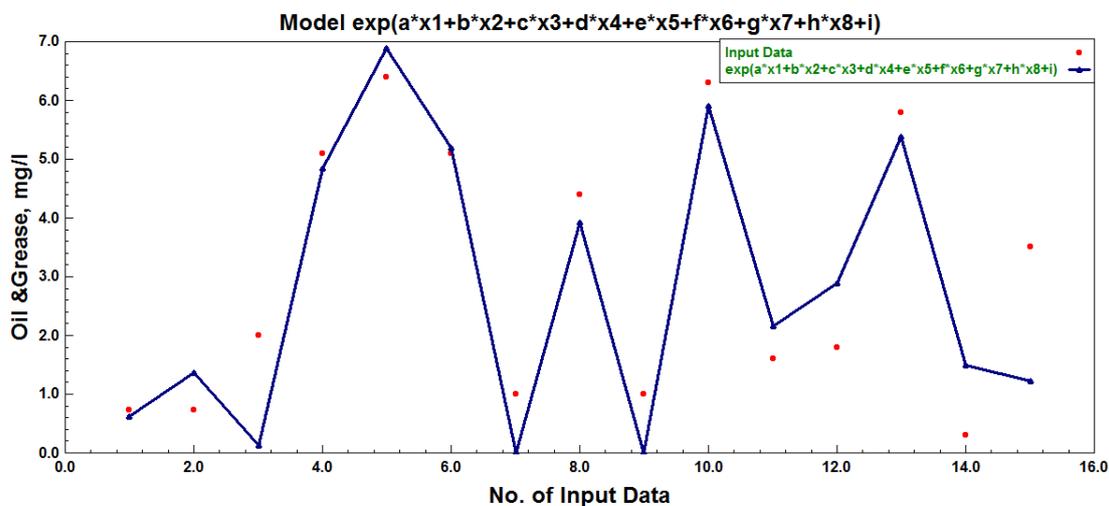


Figure (9): Plot model of parameters used in AL Kufa river station