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OIL AND GREASE CONTAMINATION OF EUPHRATES RIVER

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Abstract

The environmental impact of most releases of petroleum wastes would be minimal if the wastes remained at their points of release. However, wastes can migrate away from a release point by a number of pathways. The present study was conducted on Al Manatherah river in Al Manatherah city in the aim of studying the contamination levels of oil and grease, with some water quality parameters (NO_3, 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 Al Manatherah 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 May. 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, turbidity, chloride, precipitated dust particles, regression models.*

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1. INTRODUCTION

Water that may be considered absolutely pure is not to be found in nature. Even rainwater which is in fact, distilled water, collects impurities such as dust, gases, bacteria etc. during its passage through the atmosphere. The portion of rainwater which flows over the surface and called run-off picks up organic and suspended matter, whereas the portion percolating through the ground has got mineralogical, organic and inorganic matter which it gathers while traversing through the underground strata before reaching the water table (Duggal, 2008).

Oil is a natural product which results from plant remains fossilized over millions of years, under marine conditions. It is not surprising, therefore, that all components of oil are readily biodegradable by bacteria, although different components degrade at different rates, tars being one of the slowest. When oil is spilled on water body, being light, it is spreads over the surface as a slick. The lighter components, which are also often the most toxic, either evaporate or dissolve in the water. Immiscible components become emulsified and dispersed in the water, while heavy residues form tar balls. The immiscible fraction forms a water-in-oil emulsion called" chocolate mousse", which contains about 75 per cent water. This forms sticky brown masses when it comes ashore and causes major problems on tourist beaches and river banks (Kiely, 1997).

Generally, petroleum contains about 85 per cent carbon 12 per cent hydrogen. The remaining 3 per cent is composed of small amounts of oxygen, nitrogen, and sulfur. Some products and by-products of oil refining are gasoline, kerosene, lubricants, gas oil and fuel oil, wax, asphalt, petroleum coke, miscellaneous materials such as petrolatum and insecticides (Nemerow, 1971).

Oil is washed into surface waters in runoff from roads and parking lots, and groundwater can be polluted from leaking underground tanks. Accidental oil spills from large transport tankers at water bodies occasionally occur, causing significant environmental damage. Oil spills at surface water may eventually move toward shore, affecting aquatic life and damaging recreation areas (Nathanson, 2000). The acute effect of oil on birds, fish, and other aquatic organisms is well cataloged; the subtle effects of oil on aquatic life is not so well understood and is potentially more harmful (Weiner and Matthews, 2003).

Prior to 1940, most municipal wastewater was generated from domestic sources. After 1940, as industrial development in the United States grew significantly, increasing amounts of industrial wastewater have been and continue to be discharged to municipal collection systems. The amounts of heavy metals and synthesized organic compounds generated by industrial activities have increased, and some 10,000 new organic compounds are added each year. Many of these compounds are now found in the wastewater from most municipalities and communities (Metcalf & Eddy, 2004).

BOD is reduced and SS are removed by wastewater treatment, but heavy metals, motor oil, refractory organic compounds, radioactive materials, and similar exotic pollutants are not readily handled this way. Communities usually severely restrict the discharge of such substances by requiring pretreatment of wastewater.

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Hunter et al., 1979, showed that the runoff from an urban area was found to contain on the average 3.69 mg/1 total hydrocarbons. Of the total hydrocarbons, 69.6% were aliphatic and 30.4% aromatic. In addition, 86.4% were associated with the particulate materials present and only 13.6% with the soluble constituents. However, as the runoff increased the fraction of hydrocarbons associated with the particulates also increased. No relationship was found between load and the time since prior rainfall, but a relationship was observed between runoff and load. Preliminary analysis indicates that the primary source of these hydrocarbons may be crankcase oil.

From previous studies done by Iraqi researchers, there is no study that deal with measurement and monitoring of oil and grease in water bodies specifically. So, this paper in our companion paper (Alikhan, 2014) will be used to observe oil and grease contamination of Euphrates river at Al Manatherah river station.

2. STUDY AREA

Al Manatherah city is located about 15 km south of Al Najaf city, and the location of Al Manatherah station is on the Euphrates river/ Al Kufa river, near the Al Manatherah water treatment plant for surface water monitoring, at coordinates (E044.49070, N31.90693). The water level at the station is not stable at a certain depth, according to the season of the year, 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 even 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 (figure 1).
The nature of the land surrounding the station is agricultural land, with some residential building.

Euphrates river near Al Manatherah station receives many pollutants discharged by different sources, including:

- ***i.*** Al Barakiah waste water treatment plant at 10 km north.
- ***ii.*** 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.
- ***iii.*** Contaminated water discharged from many drainage channels located at 750 meters north and 1000 m south.

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

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Fig. 1: Map of the studying area in the national context.

3. MODEL FORMATION

Data of oil and grease concentrations, some water quality parameters, and climatic conditions factors of the Euphrates river (at Al Manatherah 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).

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Table (1): The proposed models.

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

Where;

y = dependent variables.

$x_1, x_2, \ldots, x_k$ = the independent variables.

a, b, c, …j_k = are model coefficients,
and M = model constant term.

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 Manatherah river station, and climatic conditions factors involved.

Data for Euphrates river in Al Manatherah 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 used were tested in the laboratory in environment directorate of Al Najaf city.

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

Type of variables	*Variables*	*Detail*
Independent	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, ºC)
	X_7	Dust Storm (DS, No. of days)

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	X_8	Monthly rain totals, (Ra, mm)
Dependent	Y	Oil & Grease (O&G, mg/L)

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

Table (3) shows analysis of variance (ANOVA) for regression model obtained, the Prob (F) = 0.82 . Table (4) shows the data statistics of water quality parameters used in present study, the optimum correlation equation from rank A in an exponential form with coefficient of determination R^2 equal to 0.40, was shown in table (5).
The correlation matrix is shown in table (6), and table (7) shows regression variables results and 95% confidence intervals.

Fig (9) shows the plot model of parameters used of Euphrates river at Al Manatherah river station during study period.

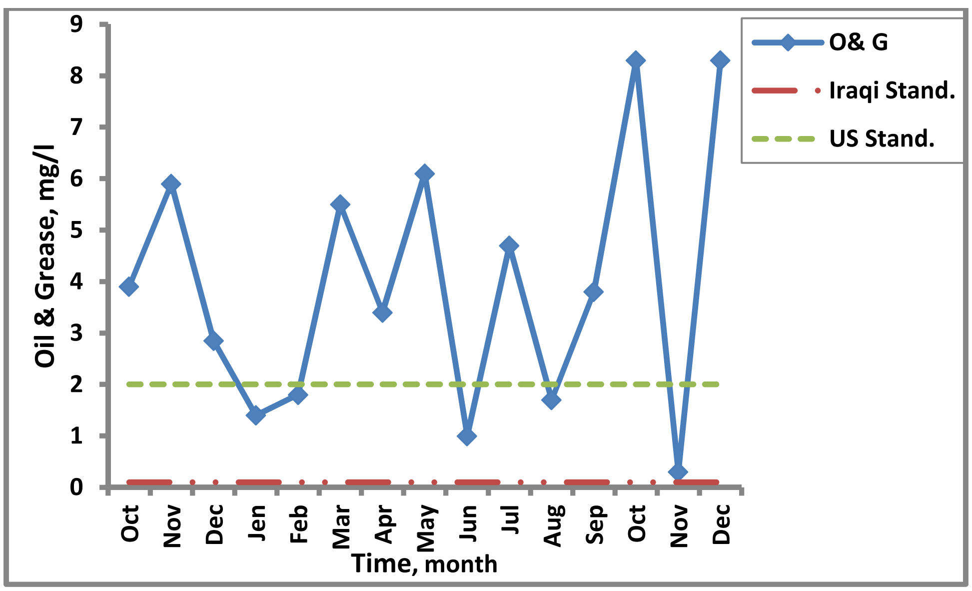

Figure (2): Variations of O&G with time compared with some allowable limits according to Iraqi and US Standards in Al Manatherah river station.

* *Source:* Iraqi environmental legislations book

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

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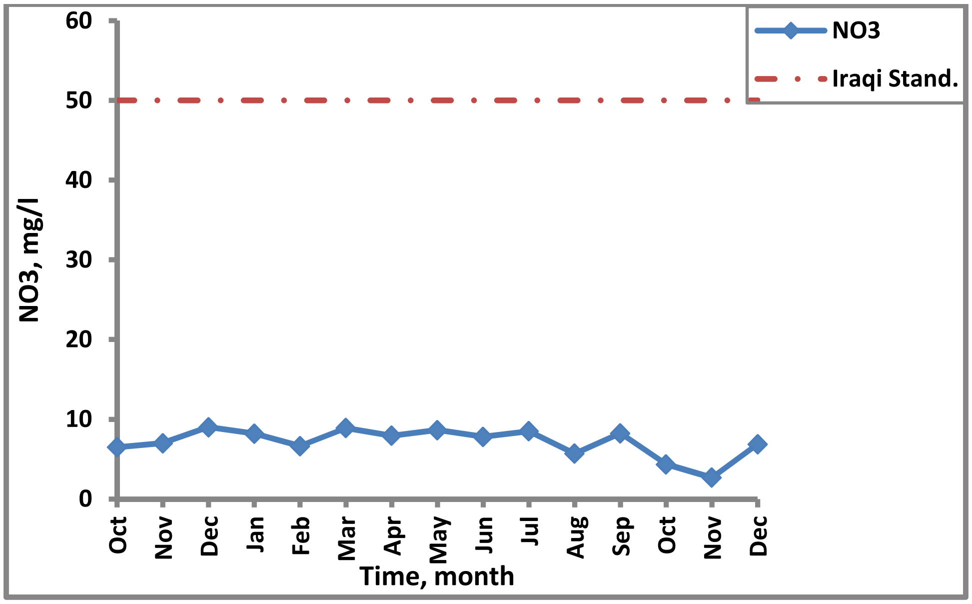

Figure (3): Variations of NO_3 with Time

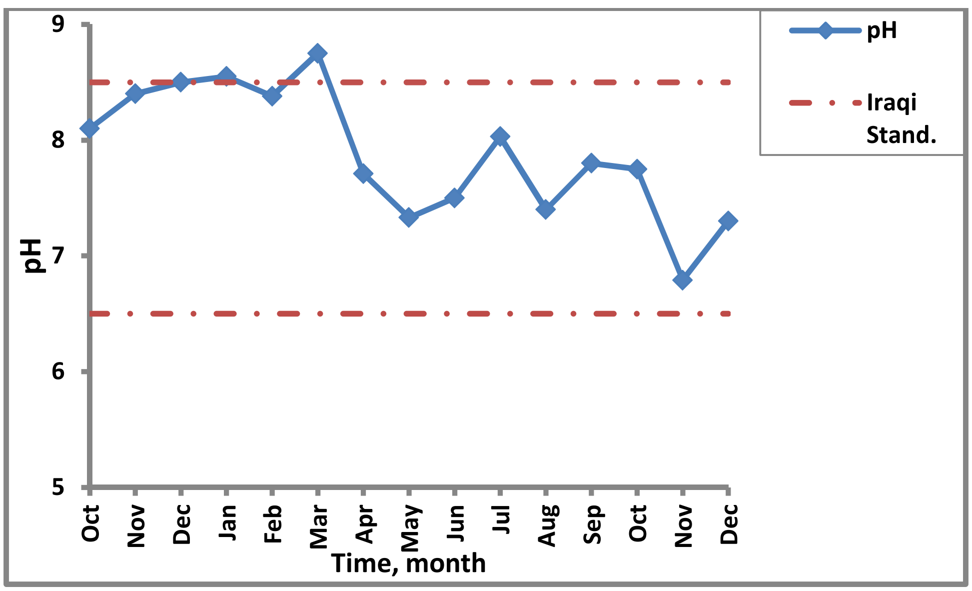

Figure (4): Variations of pH with Time

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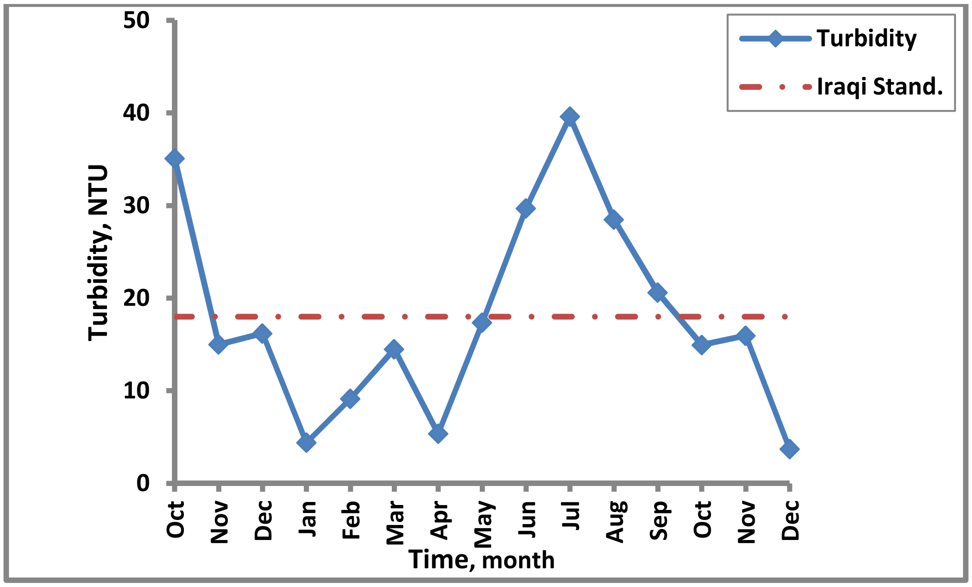

Figure (5): Variations of Turbidity with Time

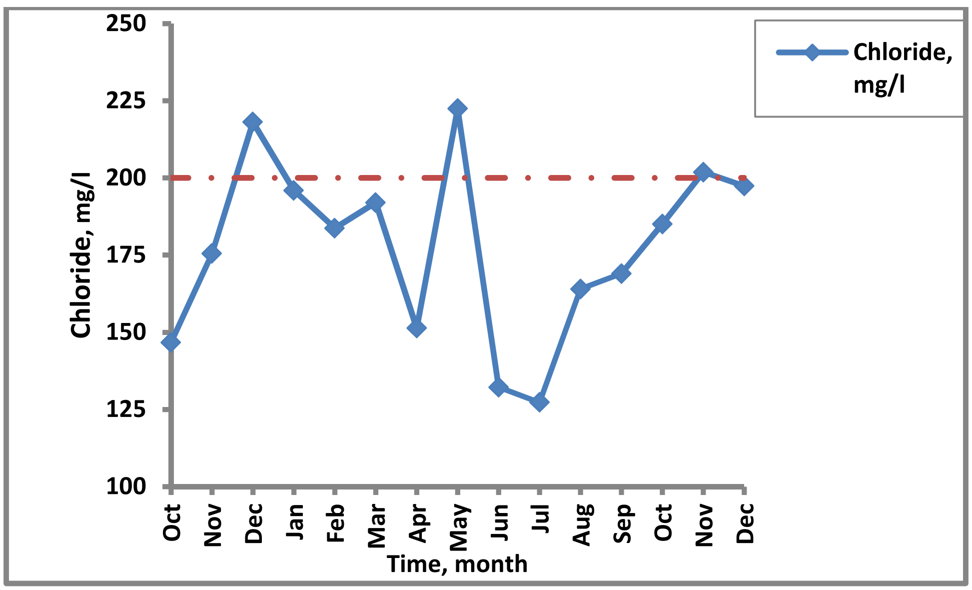

Figure (6): Variations of Chloride with Time

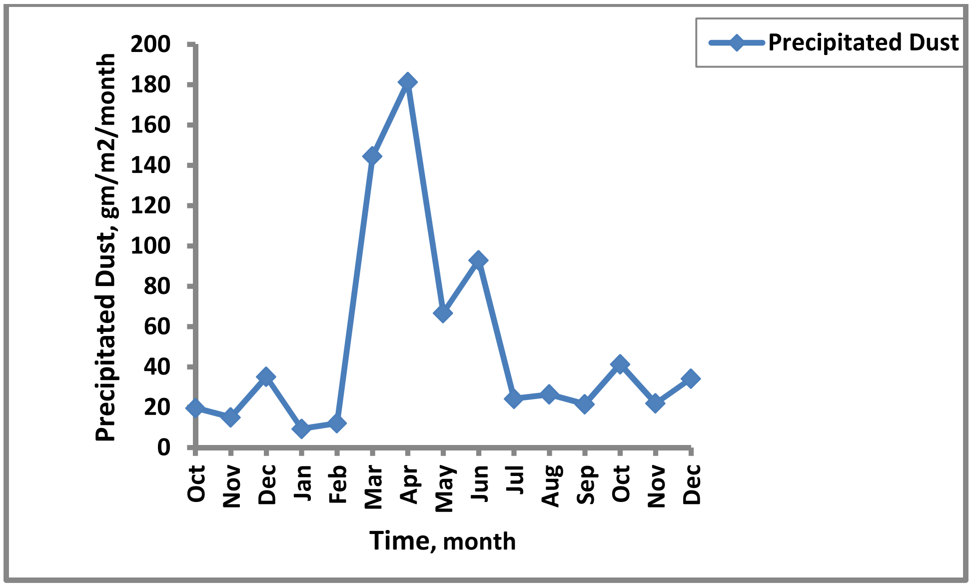

Figure (7): Variations of Precipitated Dust Particles with Time

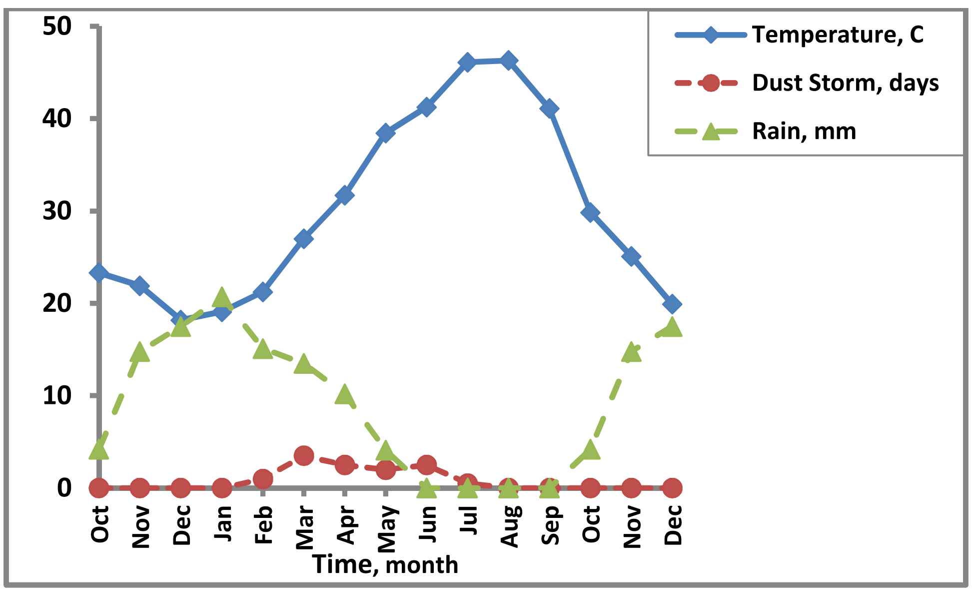

Figure (8): Variations of Temperature, Dust Storm and Rain with Time

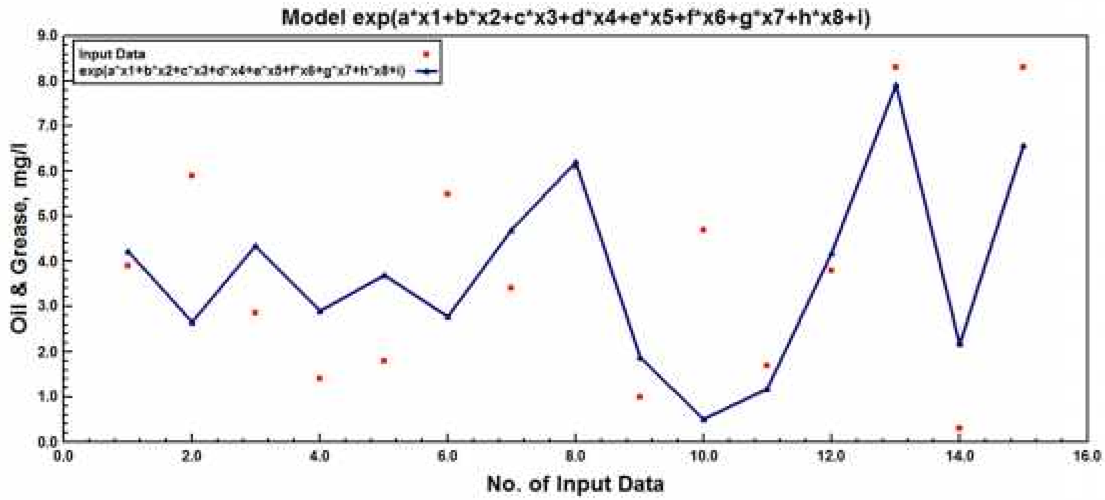

Figure (9): Plot model of parameters used in Al Manatherah river station

5. DISCUSSION

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). *Figure 2 shows oil* and grease concentrations between 0.3-8.3 mg/l in Al Manatherah river station throughout the study period, as Iraqi standard limits 0.1 mg/l, those concentrations range from 3 to 83 times greater than Iraqi standards. The highest values recorded were 8.3 mg/l in October and December (2011), but the lowest value was 0.3 mg/l in November (2011). The highest values 6.1, 8.3, 8.3 mg/l in May, October, and December, respectively. Value 6.1 mg/l recorded in May correlated with increased values of NO_3, T.U., Cl, T, and DS. Highest values of NO_3, T.U., and Cl, 8.65, 17.35, 222.5, respectively, registered in same month, increased as a result of wastewater discharged from drainage channel located at 750 meters north and a result of illegal sewage discharged to river containing grease and oil since the sewage from kitchens, slaughter houses and restaurants contains grease (Steel and McGhee, 1979l. Also, oil and grease increased with temperature as a result of oil product used for irrigation of rice crop, it 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 (residential, industrial and commercial zones) during working time especially through cooling processes by water and allow to water-oil mixture entering sewers to reach river. Moreover, oil and grease increased with dust storm 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.

Highest values of oil and grease 8.3 mg/l measured in October and December conjunction with T.U. and Cl in October through wastewater discharged to river, and with Cl and heavy monthly

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rain totals in December, this agreed well with result gained by Hunter et al., 1979 that presented a relationship between runoff and load.

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 5.9 mg/l in November (2010), increased according to high values of NO_3, pH, Cl, and Ra, as a result of sewage from northern drainage and raw waste water discharged to river affecting of chlorides, nitrates, and oil and grease increasing (Metcalf & Eddy, 2004). Consequently, oil and grease increased with rain since reasons mention above.

The variation of temperature, dust storm and rain with time during the period of the study is given in figure (8). The value of oil &grease reached (5.5 mg/l) in March, increased according to high values of NO_3, pH, T.U., Cl, PM, Ra, and high value of DS as a result of contaminants discharged to 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. Table (6) shows that the rain has high negative correlation with temperature and turbidity (-0.89 and -0.77) agreed very well Iraqi climatic conditions.

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.

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 Manatherah river station throughout the study period between 0.3-8.3 mg/l, those concentrations range from 3 to 83 times greater than Iraqi standard limits.
2. The highest values of oil and grease 8.3 mg/l measured in October and December related with T.U. and Cl in October through wastewater discharged to river, and with Cl and heavy monthly rain totals in December, caused oil washing into surface water in runoff from roads and parks.
3. The value of oil and grease 6.1 mg/l recorded in May interrelated with increased values of NO_3, T.U., Cl, T, and DS. Highest values of NO_3, T.U., and Cl, 8.65, 17.35, 222.5, respectively, registered in same month, increasing concentrations as a result of wastewater discharged from near drainage *channel and sewage discharged. Also, oil and grease increased with temperature as a result of oil product used for irrigation of rice crop.*
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.

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

Variance Analysis					
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	8	35.720	4.465	0.503	0.819
Error	6	53.250	8.876		
Total	14	88.979			

Table (4): Data statistics of variables in Al Manatherah river station

Statistics									
Variable	X1	X2	X3	X4	X5	X6	X7	X8	Y
No. of Pts	15	15	15	15	15	15	15	15	15
Miss Pts	0	0	0	0	0	0	0	0	0
Max. Value	9	8.75	39.6	222.5	181.29	46.3	3.5	20.7	8.3
Min.Value	2.68	6.79	3.7	127.3	9.31	18.2	0	0	0.3
Range	6.32	1.96	35.9	95.2	171.98	28.1	3.5	20.7	8
Average	7.132	7.886	18.004	177.499	49.745	30.033	0.8	9.107	3.93
Stad. Dev.	1.786	0.563	10.951	28.998	51.335	10.103	1.207	7.566	2.521

Table (5): Model selected of variables in Al Manatherah river station

Rank	Model	Std Error	Residual Sum	Residual Avg.	R^2
1	exp(a*x1+b*x2+c*x3+d*x4+e*x5+f*x6+g*x7+h*x8+i)	2.98	3.03	0.20	0.40
2	a*x1+b*x2+c*x3+d*x4+e*x5+f*x6+g*x7+h*x8+i	3.27	4.4	2.9	0.28

			E-15	E-16	
3	a*x1+b*x2+c*x3+d*x4+e*x5+f*x6+g*x7+h*x8	3.04	0.09	0.0	0.27

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

C. Ma.									
	X1,NO_3	X2,pH	X3,TU	X4,Cl	X5,PM	X6,T	X7,DS	X8,Ra	Y,O&G
X1,NO_3	1								
X2,pH	0.561	1							
X3,TU	0.019	-0.099	1						
X4,Cl	-0.054	0.013	-0.626	1					
X5,PM	0.327	0.011	-0.199	-0.146	1				
X6,T	0.112	-0.397	0.629	-0.530	0.163	1			
X7,DS	0.435	0.113	-0.076	-0.116	0.867	0.221	1		
X8,Ra	-0.006	0.352	-0.769	0.612	-0.061	-0.893	-0.103	1	
Y,O&G	0.107	0.051	-0.158	0.180	0.084	-0.083	-0.013	-0.032	1

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

Regression Variable Results				
Var.	Value	Standard Error	t-ratio	Prob(t)
a	0.109959435	0.184428327	0.59621771	0.57282
b	-0.281733672	0.518958156	-0.542883214	0.60677
c	-0.056259417	0.048498895	-1.160014428	0.29011
d	0.009213901	0.010342388	0.890887161	0.40729
e	0.002291032	0.009243516	0.247852859	0.81251
f	-0.117997699	0.091729839	-1.286361133	0.24572
g	-0.053879854	0.420470871	-0.128141704	0.90222
h	-0.187452108	0.125311655	-1.495887263	0.18532
i	7.124588788	6.372811697	1.117966312	0.30634

95% Confidence Intervals				
Var.	Value	95% (+/-)	Lower Limit	Upper Limit
a	0.109959435	0.451277674	-0.341318239	0.56123711
b	-0.281733672	1.269838713	-1.551572385	0.988105041
c	-0.056259417	0.118671945	-0.174931363	0.062412528
d	0.009213901	0.02530679	-0.016092889	0.03452069
e	0.002291032	0.02261796	-0.020326928	0.024908992
f	-0.117997699	0.224453742	-0.342451441	0.106456043
g	-0.053879854	1.028850173	-1.082730027	0.974970319
h	-0.187452108	0.306625088	-0.494077197	0.11917298
i	7.124588788	15.59363294	-8.469044155	22.71822173