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Assessment of Oil Wastes Residual in Water, Sediment of Tigris River within Baghdad City

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Abstract

This study conducted during 2013-2014 to investigated the effects of Oil Wastes and nutrients on the water /sediment quality of Tigris River in south of Baghdad, especially, the effluent that discharged from the Al-Doura oil refiner and the oil spills. Three station on the River were selected to be assessment point for the pollutions, the first one located at Al-Jaderria before Al-Doura oil refiner which represented the control area, the second station near Al-Doura oil refiner, while the third station located after Al-Doura oil refiner at Al-Zafrania , the result exhibit a series contamination of water/sediment samples by oil & grease and Total petroleum hydrocarbon, especially in station 2 where have the highest annual concentration levels of O/G and TPH, because its directly affected by the effluent discharge from the refiners. Moreover, the level of nutrient in sediment observed to be higher than that found in water sample.

Keywords: Oil, Grease, Wastes, TPH, Tigris River, Baghdad.

تقدير تراكيز المخلفات النفطية المتبقية في المياه والرواسب في نهر دجلة في مدينة بغداد

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مركز بحوث البيئة – الجامعة التكنولوجية

الخلاصة

اجريت الدراسة الحالية خلال 2013–2014 وتهدف الى الكشف عن تأثير المخلفات النفطية والمغذيات في نوعية المياه والرواسب لنهر دجلة جنوب مدينة بغداد, وبالتحديد المخلفات المطروحة من مصفى الدورة والبقع النفطية. تم اختيار ثلاث محطات على نهر دجلة لتكون محطات مراقبة، تقع المحطة الاولى في منطقة الجادرية وتمثل هذه المحطة منطقة السيطرة، والثانية بالقرب من مصفى الدروة، بينما تقع المحطة الثالثة بعد مصفى الدورة في منطقة الزعفرانية. وقد كشفت نتائج الدراسة الى وجود تلوث بالنفط والشحوم والهايدروكاربونات البترولية الكلية في كل من العينات المائية والرواسب وبالأخص في المحطة الثانية حيث سجلت اعلى تركيز سنوي، وتعود هذ الزيادة في تراكيز هذ الملوثات الى تأثر هذه المحطة بشكل مباشر بالمخلفات المطروحة من المصفى، بالاضافة الى ذلك فلقد وجد ان تراكيز المغذيات تكون اعلى في الرواسب منها في المياه.

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الكلمات المفتاحيه: النفط، الشحوم، المخلفات ،الهايدروكاربونات البترولية الكلية، نهر دجلة، بغداد.

1. Introduction

Iraqi Rivers faces a rapidly increasing deterioration due to the increasing discharge of oil wastes and industrial effluents into its water surface. The increasing of industrial development promotes serious environmental damage due to pollution of the environment. Regarding the petrochemical industry, contamination by oil and its derivatives causes the degradation of aquatic ecosystems.

Petroleum products are extensively widespread all over the world and their intensive use is strongly connected to the anthropogenesis discharge of hydrocarbons into the environment (Winkelmann *et al*.,2009). Environmental contamination by petrol derivatives has been a subject of study over the past four decades. The leakage of these derivative oils, such as oil and grease, is capable of harming the environment in many ways (Atlas, 1995).

Petroleum hydrocarbons can consider the major pollutants of aquatic environments as a result of terrestrial and freshwater run-off, refuse from coastal oil refineries, off shore oil production, shipping activities and accidental spills (Arulazhagan *et al*, 2010). The effects of oil spillages on the ecosystem have been very severe. These include damage to and loss of biodiversity, reduction of arable land, and reduction of available potable water and blockages of water ways (Nie *et al*, 2010) . Also Oil spill affect many species of plant, animal and human (Plohl *et al*, 2002). Long term effect on ecosystem may increase the concentration of toxicant in organism towards the top of the food chain increases (Samanta *et al*, 2002). the biodegradation of hydrocarbon in the natural environment is a slow process. The major factor responsible for this is the nutritional imbalance created by the oil spills and growth limiting nitrogen and phosphorus concentration (Eve Riser-Roberts, 1998). The addition of chemical fertilizer augment during biodegradation has been found effective (Margensin and Schinner,1999).

An oil and grease (O/G) contaminants can be defined as any materials recovered as a substance extracted in the form of organic solvent from a sample, and are composed primarily of fatty matter from animal and vegetable sources, petroleum of hydrocarbons origin, sulfur compounds, certain organic dyes, and chlorophyll (APHA,1995).Oil and grease in water may be free floating and form a sheen before dispersion and partitioning processes occur. The sheen observed in waterways and in parking lot or street runoff has often been the primary motivation to control oil and grease in stormwater runoff. Water quality criteria established by U.S. EPA pursuant to Section 304(a) of the Clean Water Act specify that oil and grease should not be present at levels that produce a visible oily sheen (U.S. EPA,2004).O/G concentrations less than 1 mg/l can create sheen on surface waters due to the reflection of sunlight (CDS Technologies, 2005).

The term total petroleum hydrocarbons (TPH) is used to describe a broad family of several hundred chemical compounds that originally come from crude oil. It is useful to measure the total amount of all hydrocarbons found together in a particular sample of water, soil, or air. TPH is defined as the measurable amount of petroleum based hydrocarbon in environmental media (Teresa, *et al*., 2010). TPH concentrations may provide a more representative measure of the amount of petroleum-based compounds in water than oil and grease concentrations (Sacramento County, 2004).

In such country like Iraq that depended on the oil industry the Oil pollution accidents are a common phenomenon and have caused ecological and social catastrophes. So this paper focus on the effluent that discharged from the Al-Doura oil refiner and the oil spills to provide baseline data to assess the level of contamination by the oil wastes as well as to alert the appropriate agencies that deal with protecting the environment on the need to regulate and enforce a comprehensive environmental action strategies towards protecting the Iraqi Rivers.

2. Material And Methods

2.1 .Study Area Description

The present study focus on the effects of effluents discharge of the Al-Doura oil refiner which is located at

south of Baghdad city and discharged their wastes directly to Tigris River, The study area include 3 stations on the river (Fig. 1.),the first one located at al-Jaderria before Al-Doura oil refiner, this Station considered the control area (between latitudes33° 17'3.83" N and longitudes44°22'31.06" E), and the second station near Al-Doura oil refiner (between latitudes 33°16' 56.85"N and longitudes44°24' 40.54"E), while the third station located after al-Doura oil refiner at Al-Zafrania(between latitudes33°16'51.59"N and longitudes44°27'14.75"E).

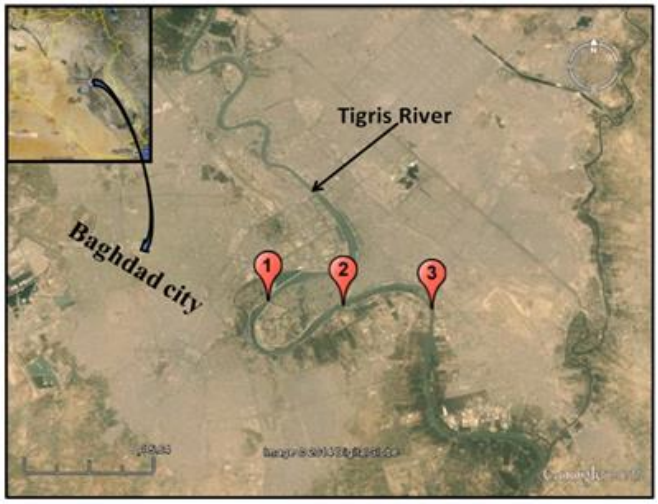

Fig. 1: Bagdad City Showing Sampling Station on Tigris River (google earth 2015).

2.2. Sampling

Subsurface water and sediment samples were collected from Tigris River during 2013-2014 from each station every two month. Water samples collected using clean polyethylene bottles for Nitrate, Nitrite, Phosphate and sulfate, while Nisken bottles used for collecting oil & grease and Total petroleum hydrocarbon TPH samples. Sediment samples collected by using van veen Grab Sampler. Samples were analyzed for chemical properties immediately after collection according to (APHA, 2005). The Oil & Grease in each water sample was estimated gravimetrically, one liter of each water sample was acidified to pH 2using HCl and poured into a separating funnel, Oil & Grease extracted with chloroform then gravimetrically estimated according to (5520 B. Partition-Gravimetric Method), for determination of Total petroleum hydrocarbon (TPH) the extraction of oil & grease was used (5520 F. Hydrocarbons),Nitrate (4500-NO_3^-F Colorimetric method), Nitrite (4500-NO_2^- F Colorimetric method), Phosphate (4500-P E Ascorbic Acid method), sulfate (4500-SO4-2 E Turbidimetric Method) measured according to (APHA,2005).

The oil & grease and Total petroleum hydrocarbon (TPH) was extracted from 10 g of sediment by sequentially extraction with of hexane (US EPA, 2002).

3. Results & Discussion

The mean ± standard deviations and Minimum-Maximum of all parameters measured in this study for the water and sediment samples are presented in Table 1. The higher annual mean concentration of oil/grease 0.5942 mg/l in water samples was observed in station 2 and the lowest value 0.1995 mg/l was in station 3, while in sediment samples the higher mean concentration of oil/grease was0.0757 mg/Kg in station 2 and the lowest value was 0.02045mg/Kg in station 1(Fig. 2,3). A similar trend was observed in total petroleum hydrocarbon (TPH) levels which in water samples the higher mean concentration was 0.3118 mg/l in station 2 and the lowest was 0.0451 mg/l in station 3. Hence, in sediment samples the higher mean concentration was 0.085 mg/Kg in station 2 and the lowest was 0.0145mg/Kg in station1 (Fig. 4,5).

Table 1: the mean ± standard deviations and Mini-Maxi of all parameters.

parameters	Station 1		Station 2		Station 3	
	Water (mg/l)	Sediment (mg/Kg)	Water(mg/l)	Sediment (mg/Kg)	Water(mg/l)	Sediment (mg/Kg)
	mean± SD mini-maxi	mean±SD mini-maxi	mean± SD mini-maxi	mean± SD mini-maxi	mean± SD mini-maxi	mean± SD mini-maxi
SO_4	387.7±308.4 146-840	1140±636.8 620-2050	610±551.54 220-1000	370±113.13 290-450	469±441.7 136-1120	2715±3070.9 920-7300
NO_3	0.886±1.25 0.00-2.658	7.124±13.0 0-26.58	0.2215±0.03 0.00-0.044	37.65±40.72 8.86-66.45	1.772±2.17 0.00-4.43	27.743±35.81 0-75.31
NO_2	0.037±0.019 0.02-0.0658	0.506±0.617 0-1.316	0.0329±0 0.03-0.0329	0.740±0.116 0.658-0.822	0.041±0.03 0.00-0.065	0.754±0.269 0.55-1.15
PO_4	0.095±0.036 0.05-0.14	0.625±0.342 0.3-1.05	0.27±0.353 0.02-0.52	0.6±0.7778 0.05-1.15	1.82±3.129 0.09-6.5	0.625±0.777 0.15-1.1
TPH	0.096±0.032 0.02-0.092	0.01±0.0003 0.002-0.002	0.311±0.386 0.04-0.584	0.085±0.071 0.034-0.135	0.045±0.13 0.01-0.289	0.052±0.071 0.0298-0.073
O/G	0.239±0.429 0.01-0.883	0.020±0.008 0.001-0.020	0.594±0.021 0.58-0.609	0.075±0.106 0.0005-0.15	0.199±0.34 0.00-0.722	0.028±0.1062 0.0026-0.035

SD= Standard deviations

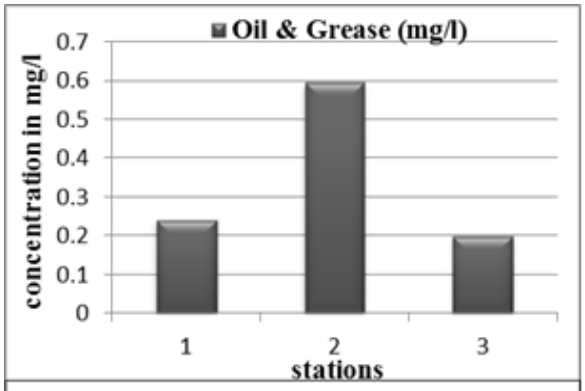

Fig. (2): The annual mean concentrations of oil/grease in water samples

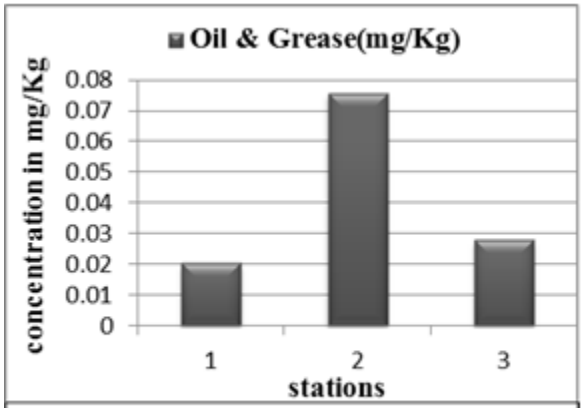

Fig. (3): The annual mean concentrations of oil/grease in sediment samples

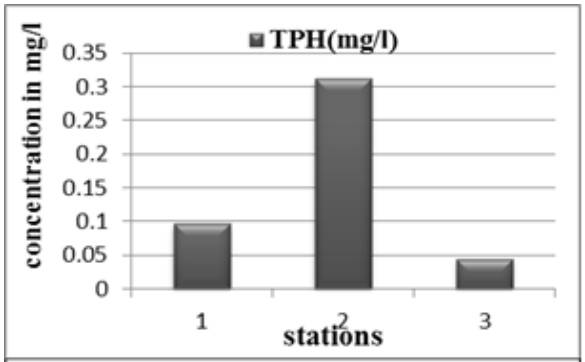

Fig. (4): The annual mean concentrations of TPH in water samples

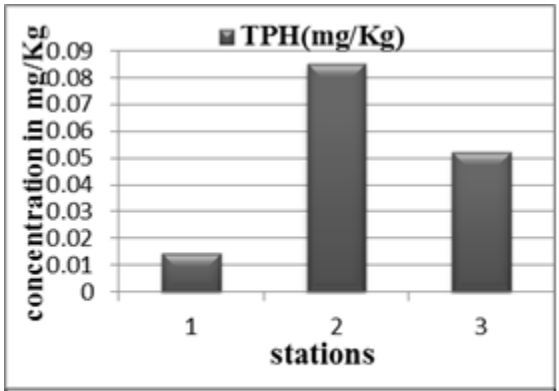

Fig. (5): The annual mean concentrations of TPH in sediment samples

From the Figs (2-3-4-5) its be clearly that al-Dura waste discharge have truly effect on the water of Tigris river, especially in station 2 where it's have the higher concentrations of oil & grease and TPH in both water and sediment samples which may return to its location near the refinery discharge. In general, almost all stations show high concentrations of oil & grease and TPH in both water and sediment samples including station 1 which supposed to be the control area where reveal a high concentrations of oil & grease and TPH, eventually lead to suggest Tigris River receive some oil wastes from other source that located in the north of Baghdad city. The U.S. EPA has set numeric water quality criteria for O/G for aquatic life protection, which specifies a level that is "0.01 mg/l of the lowest continuous flow 96-hour LC50to several important freshwater species, each having a demonstrated susceptibility to oils and petrochemicals"(The "LC50" is the concentration that is lethal for 50 percent of the test organisms.) U.S. EPA also specifies that surface waters be virtually free from floating oils "no visible sheen" for O/G or TPH (U.S. EPA, 1986).In water the concentration of TPHs relay on various factors including properties of TPHs as hydrophobic nature with low solubility, interaction of several processes such as biodegradation, bioconcentration, volatilization, sedimentation and solubilization (Maktoof,*et al*., 2014). So, the values that obtained for oil & grease in this study are much higher than the level that set by U.S. EPA which indicates of a real contamination of the surface water and sediment by petroleum. Moreover, these concentrations of oil & grease and TPH may pose a long-term risk to the aquatic ecosystem because of their tendency to accumulate in sediment over time (OEHHA,2006), so sediments considered excellent

indicators of historical pollution for many pollutants among which TPH &O/G (Calvin*et al*., 2004).

Fig. (6) Illustrated the annual mean concentration of sulfate SO_4in water sample, where station 2 have the highest value 610 mg/l and lowest value 387.75 was in station 1.Generally,all value of SO_4exceed the permissible level recommended by the Iraqi standards for rivers maintenance (limited value=200mg/l(Iraqi standards for Rivers Maintenance from pollution, 1967), while in sediment the value are differed where the station 3 have the highest annual mean concentration2715 mg/Kg and lowest concentration was observed in station 2 which reached to 370 mg/Kg (Fig. 7).

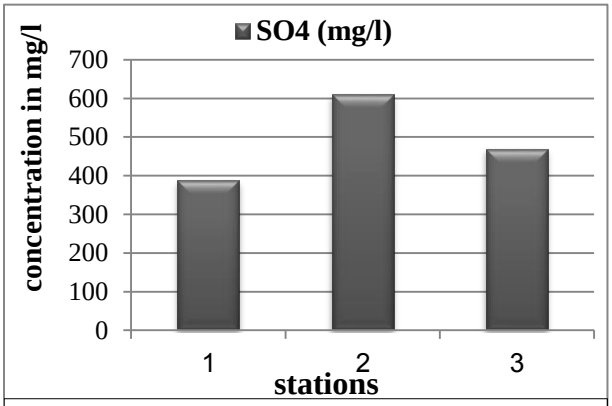

Figure (6): The annual mean concentrations of SO4 in water samples

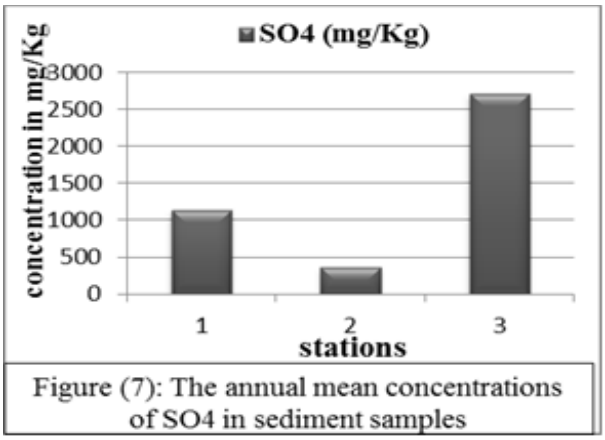

Figure (7): The annual mean concentrations of SO4 in sediment samples

For both NO_3 and NO_2concentrations the highest mean value were 1.772, 0.0411 mg/l which observed in station 3, and the lower mean were 0.2215, 0.0329 mg/l in station 2 in the water sample, respectively (Fig. 8-10).While in sediment sample their highest mean values were 37.655, 0.7543 mg/Kg in stations 2, 3and the lower mean were 7.1246, 0.506 mg/Kg in station 1, respectively (Fig. 9-11).

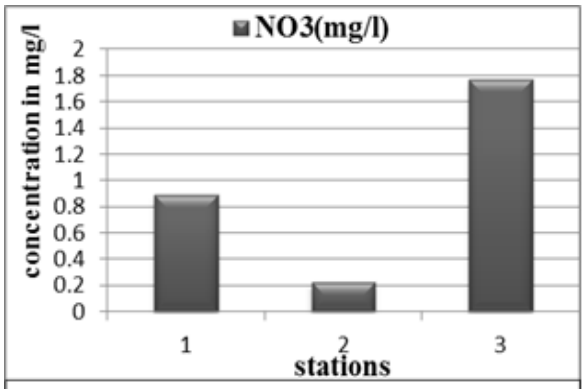

Fig. (8): The annual mean concentrations of NO3in water samples

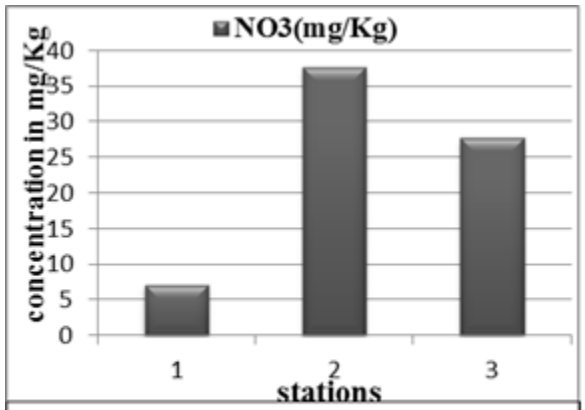

Fig. (9): The annual mean concentrations of in NO3 sediment samples

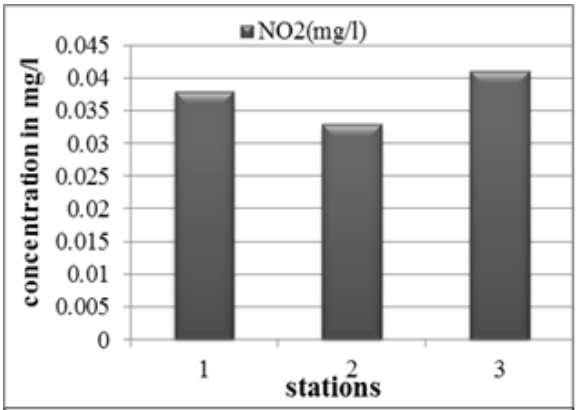

Fig. (10): The annual mean concentrations of NO_2 in water samples

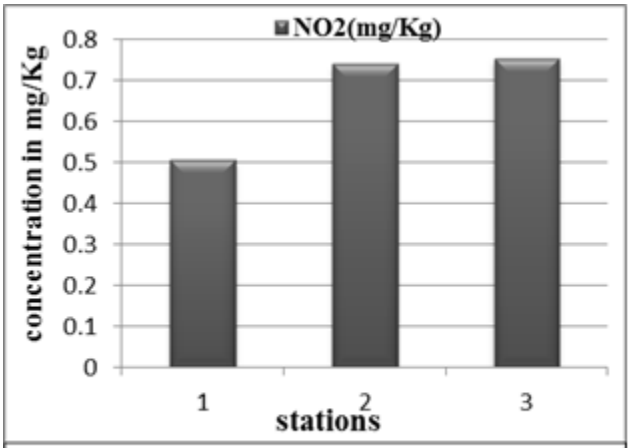

Fig. (11): The annual mean concentrations of NO_2in sediment samples

The mean annual concentration of PO_4 in water sample was found to be high in station 3 comp arable to the other stations which reached to 1.82mg/l and exceed the permissible level recommended by the Iraqi standards for maintenance rivers (1967) and lowest mean 0.095 mg/l found in station 1 (Fig. 12). However, the mean annual concentration of PO_4in sediment sample were almost the same in all station with minor change, station 1and 3 shared the same concentration 0.625, while in station 2 was 0.6 mg/Kg (Fig. 13).

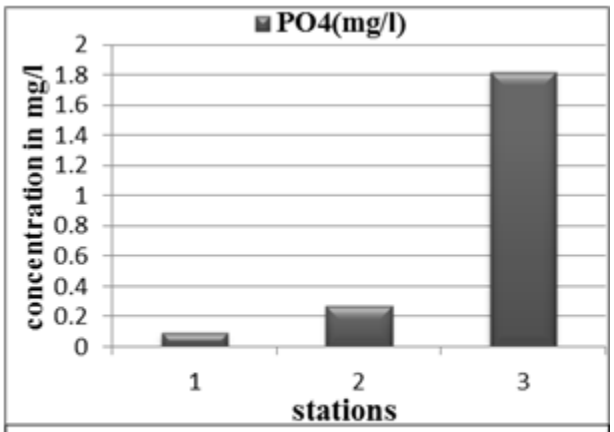

Fig. (12): The annual mean concentrations of PO_4 in water samples

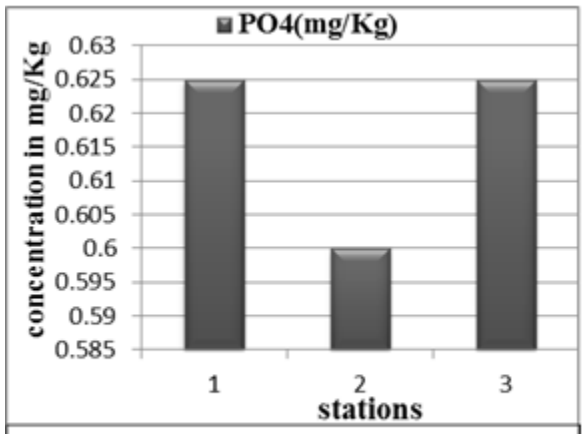

Fig. (13): The annual mean concentrations of PO_4 in sediment samples

Nutrient level (SO_4, NO_3, NO_2, PO_4) in the sediment was observed to be higher than that found in water sample due to accumulation of these nutrients, where reports indicate that phosphorus content in sediment can be approximately 1000 times higher than the concentration found in the water column (Rivas, 2000). The different profiles of phosphate under different DO concentration confirmed the theory that phosphorus is released from the sediment into the water column under anoxic conditions, while phosphorus is retained in sediment by the surface oxic layer under oxic conditions (Wetzel, 2001). The effect of oxygen also found in the nitrogen forms, whenNH^{4+}comes into contacted with oxygen, it immediately converted to NO_2(nitrite)which is then oxidized to NO_3(nitrate), this situation appear in the results of this study were the NO_2concentration is low in both water and sediment sample compellable to NO_3^-,So a possible explanation for this is that the Tigris river are in a highly oxic state which have been demonstrated by many Iraqi studies (Mauloo*det al.*, 1995 and Al- Kubaisi*et al.*, 2012) this oxic state due to the flood causing all nitrite present to be converted to nitrate.

Generally, the nutrient levels measured in the Tigris River are obvious in all stations, the possible sources of this pollution include run-off from human activities in urban, sewage leakage, as well as water discharged from industrial facilities, Crude oil pollution has also been associated with increase in nutritive levels of aquatic Ecosystem (Ward*et al.*, 1980 and Rhykered *et al.*, 1995).The results show a remarkable increase of PO_4 levels in water sample in stations 3 which may due to fertilizer pollution addition to other sources, because this area are subjected to agriculture works. However,

SO_4, NO_3, NO_2, PO_4 are essential nutrients to plants life, but when found in excess quantities, stimulates excessive plant growth such as algae bloom (Igbinosaand Oko, 2009).

4. Conclusion

This paper describes a case study in which three stations subjected to assess the water quality of Tigris river which including collecting and analyses water and sediment sample for set of parameter which are: oil & grease and Total petroleum hydrocarbon, SO^{4-}, NO^{3-}, NO^{2-}, $PO^{4}$the results and data interpretation clearly indicate that:

1. The contamination of water/sediment samples by oil & grease and Total petroleum hydrocarbon is real and evident.
2. The effluent discharge from Al-Dura refinery exhibit the higher concentrations for oil & grease and TPH in both water and sediment samples.

3-The activities of Al-Dura refinery should be of environmental concern, as adverse effects arising from oil and grease, TPH cannot be over-emphasized. Hence, it is pertinent that standard environmental management and appropriate environmental regulations should be established and enforced and primary treatment plant be improved in the refinery. Adequate remediation and clean-up measures should be carried out on the sites to save the environment of these chemical arising from TPH, oil and grease, in order to ensure the best environmental management practice.

References

Al- Kubaisi A. A.., Abdul-Hameed M. J. Al-Obaidy and Zahraa Z. Al-Janabi 2012. Study of Qualitative Composition of Phytoplankton For Tigris River Before Crossing Baghdad City and After Getting Out From It. Iraq 1st Conference of Biology Department, College of Science, University of Baghdad pp747-757.

APHA, American Public Health Association(1995). Standard methods for the examination of water and wastewater 19th edition,

APHA, American Public Health Association. 2005. Standard Methods for the Examination of Water and Wastewater, 21stEdition Washington, DC.22621pp.

Arulazhagan P., Vasudevan N. and Yeom I. T. 2010. Biodegradation of polycyclic aromatic hydrocarbon by a halotolerant bacteria l consortium isolated from marine environment. Int. J. Environ. Sci. Tech., 7 (4); 639-652.

Atlas R.M. 1995. Bioremediation of petroleum pollutants. International Biodeterioration and Biodegradation. 35(1-3):317-327.

Calvin C. Chien, Migual A. Medina jr, George F. Pinder, Danny D Reible,Bernt E. Sleep and Chumiao Z. 2004. Contaminated Ground Water And Sediment: Modeling for Management And Remedation. 1st edition LEWIS publisher A CRC press Company Boca Raton, London, New York, Washington D.C., 288 pp.

CDS Technologies. 2005. Oil and Grease in Stormwater Runoff. June 2005. Posted at: www.cdstech.com

Eve Riser-Roberts (1998). Remediation of Petroleum Contaminated Soils: Biological, Physical, and Chemical Processes .lewis publisher, CRC PressLLC, 576pp.

Igbinosa E.O. and Oko A.I. 2009. Impact of discharge wastewater effluents on the physisco-chemical qualities of a receiving watershed in a typical rural community. Int. J. Environ. Sci. Tech.6(2):175-182.

Iraqi standards for Rivers Maintenance from pollution 1967. Number 25, Ministry of health-environment.

Maktoof, A. A., Basim Y. Al-Khafaji and Zahraa Z. Al-janabi (2014). Evaluation of Total Hydrocarbons Levels and Traces Metals in Water and Sediment from Main Outfall Drain in Al-Nassiriya City/Southern Iraq, Natural Resources Vol.05 No.13795-803.

Margensin R. and Schinner F. 1999. A feasibility study for the in situ remediation of a former tank farm. World J. of Microbiology and Biotechnology. 15: 615-622.

Maulood, B.K.; Al-Azzawi, M.N. and Saadalla, H.A. 1994. An ecological Study on the Tigris River pre and after Crossing Baghdad. *J. College Educ. Women*. University of Baghdad, 5(1): 43-50.

Nie M., Xian N., Fu X., Chen, X. and Li B. 2010. The Interactive effect of petroleum-hydrocarbon spillage and plant rhizosphere on concentrations and distribution of heavy metals in sediments in

the Yellow River Delta, China. J. Hazard. Mater., 174 (1–3): 156 –161.

OEHHA. 2006. Assessment Characterization of Used Oil in Storm water Runoff in California. A report prepared by California Environmental Protection Agency Office of environmental health hazard Assessment (OEHHA) Integrated Risk Assessment Branch (IRAB) 42 p.

Plohl K., Leskovovsek H. and Briceilj M. (2002). Biological degradation of motor oil in water. ActaChimSlov 49:279-289.

Rhykered R.I., Weaver R.W. and Mclnnes, k.j. 1995. Influence of Salinity on Bioremediation of Oil in Soil. Environ. Pollut.,90, 127-130.

Rivas, Z. 2000. Nitrogen and Phosphorus Levels in Sediments from Tropical Catatumbo River (Venezuela). Water, Air, & Soil Pollution 117(1): 27-37.

Sacramento County. 2004. Discharge Monitoring Report 2003/204. Prepared for the acramen to Storm water Management Program by: Larry Walker Associates. Posted at:http://www.msa.saccounty.net/sactostormwater/documents/reports/0304-Joint-AR/Apx-E_DischargeMonRpt.pdf

Samanta K. S., Singh O.V. and Jain R. K. 2002. Polycyclic aromatic hydrocarbon: environmental pollution and bioremediation. Trends in Biotechnology 20(60): 243-248.

Teresa R., Sławomir Ż., Zenon P and Adekunle O. 2010 .Determination Of Oil And Grease, Total Petroleum Hydrocarbons And Volatile Aromatic Compounds In Soil And Sediment Samples / Journal Of Environmental Engineering And Landscape Management, 18(3): 163–169.

U.S. EPA. 1986. Quality Criteria for Water. EPA440/5-86-001. United States Environmental Protection Agency, Office of Water Regulations and Standards. Washington, D.C. May 1, 1986.

U.S. EPA. 2004. National Recommended Water Quality Criteria. Office of Water. Office of Science and Technology. United States Environmental Protection Agency. Posted at: http://www.epa.gov/waterscience/criteria/nrwqc-2004.pdf.

US EPA 2002. US EPA Method 1664. N-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons) Revision: September 1998; updated: December.

Ward D.M., Atlas R.M., Boehm P.D. and Calder, J.A. 1980. Microbial Biodegradation and The Chemical Evolution of Amoco Cadiz Oil Pollutants, Ambio, 9,277-283.

Wetzel, R. G. 2001. Limnology. 3nd. Edition. Academic Press, California. 431pp.

Winkelmann M., Hunger N., Hüttl R. and Wolf G. 2009. Calorimetric investigations on the degradation of water insoluble hydrocarbons by the bacterium Rhodococcusopacus 1CP. ThermochimicaActa. 482:12–16.