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Temporal and spatial variations of petroleum hydrocarbons in water and sediments from Northern parts of Shatt Al-Arab River, Iraq

F.J.M. Al-Imarah[1*], S.A. Ali[2] and A.A. Ali[2]
[1] Marine Science Centre, [2] College of Education, Basrah University, Basrah-Iraq
*e-mail:farisalimarah@yahoo.com

Abstract - Regional and temporal distribution of Total Petroleum Hydrocarbons (TPH's) and percent Total Organic Carbon (TOC %) were investigated in water and sediments from 5 stations along Shatt Al-Arab river (1-Qurnah, 2-Shafi, 3-Deer, 4-Nihran Omer and 5-Sinbad close to expected sources of pollution by petroleum hydrocarbons. Measured TPH's in the dissolved phase of water were ranged between 5.10 ng/l in station 3 and 9.48 ng/l in station 5 comparable to Basrah light crude oil. In the sediments levels of PHC's ranged between 7.37 mg/l in station 3 and 24.41 mg/l in station 5.Seasonal variations in TPH's in waters and sediments were found as lower concentrations 2.65–4.20 and 3.15–10.36 mg/l respectively during summer, while higher concentration recorded during winter were found to be 7.86–15.60 µg/l in water and 13.52–45.21 mg/g in sediments. % TOC measured in the sediments were ranged from 0.50 % to 0.81 % in stations 2 and 5 respectively. Strong positive correlations were found between TPH's and TOC for all stations with correlation coefficient (r = 0.93).

Key wards: Petroleum hydrocarbons, TOC %, Northern, Shatt Al-Arab river, water, sediments.

Introduction

Pollution of water is a great problem which increased in complexity after the release of pollutants end exposure to weather conditions. The main sources of pollution are sewage and domestic wastes, industrial, agricultural discharges, production, refinery and transportation of crude oil.

One of the most dangerous pollutant for water environment is petroleum and it's derivatives. They could reach the water environment from different sources among which are natural seepage, petroleum exploration, transportation and accidents and consumption (Walker, 2002).

Petroleum and it's derivatives in the aquatic media are exposed to different processes among which are evaporation for surface layers (Grimalt *et al.*, 1985), settlements to the bottom of the river by adsorption (Wade and Qunin, 1980), dissolution in the water column (Harrison *et al.*, 1975), photo-oxidation for floating slicks(Larson *et al.*, 1976) and biodegradation by micro-organisms(Gerlach, 1981). The last two processes playing a great role in Shatt Al-Arab river and NW Arabian Gulf due to high temperature which enhance photo-oxidation and activate biological communities like bacteria and fungi for biodegradation.

Study area:

Shatt Al-Arab is the main source for fresh water in south of Iraq. The length of Shatt Al-Arab river from Qurnah to it's estuary is 175 km with width of 0.4 km at Basrah and 1.5 km at it's estuary, it is effected by the tides from Arabian Gulf. The water of Shatt Al-Arab river receives pollutants from different sources such as, waste discharges from Basrah city, industrial waste from different industries along Shatt Al-Arab banks, the paper and mill factory, power stations, petroleum fields and transportations, A certain studies were conducted to investigate presence of petroleum hydrocarbons in water of Shatt Al-Arab, all reported presence of TPH's from different sources in waters of Shatt Al-Arab (Al-Saad,1983; DouAbul and Al-Saad, 1985; Al-Saad, 1995). Low value was recorded at Qurnah 5.6 µg/l and high value was recorded at Basrah city, 14.2 µg/l. In sediments of the same area, levels of TPH's were of the same trend 0.4- 44 µg/g at Qurnah and Basrah city respectively. For organic pollution in the sediments of Shatt Al-Arab river recorded values reported were averaged as 0.62 % (Al-Saad, 1983; DouAbul, 1984; Al-Saad, 1995).

Materials and Methods

This study was conducted during the period Jan-Dec. 2004, the studied sites represented by 5 stations along the northern part of Shatt Al-Arab river from Qurnah (st.1), Al-Shafi (st.2), 15 km from st.1, Al-Deer (st.3), Nihran Omar (st.4), close to petroleum fields and Sinbad island (st.5) as shown in Figure 1.

Fig. 1. Location map of Shatt Al-Arab River showing the sampling stations.

PHC's in water and sediments from these 5 stations were measured. Subsurface water samples were collected from each station in 5 l bottles, while sediments were collected from the same stations by means of van veen grap sampler. Water and sediment samples were transferred to the lab in cool box and kept in fridge prior to analysis. Petroleum hydrocarbons were extracted from water and sediment samples by extraction with carbon tetrachloride solvent from water according to UNEP (1993), while the procedure of Goutx and Saliot (1980) was adopted for the extraction of PHC's from sediment samples. The extracts were dried by evaporation in rotary evaporator until dryness, then to each sample 3 ml of hexane solvent were added and the TPH's were estimated spectroflourometrically by UVF Shimadzu RF 540 spectroflurometer fitted with direct reading DR data base unit and 1 cm path length quartz cell, excitation was at 310 nm and emission at 360 nm (Al-Saad,1995). A calibration curve was done for Basrah light crude oil to calculate the concentrations of TPH's in each sample. % total organic carbon %TOC in sediments was measured according to El-Wakeel and Riley (1957).

Results and Discussion

Mean concentrations of TPH's for triplicate samples seasonally in the water from the selected fife stations were recorded and listed in Table 1.

Table 1. Seasonal variations in the mean concentrations of TPH's in the water from northern part of Shatt Al-Arab river.

Station No.	Seasonal variation in the mean conc. of TPH's, in water (µg/ml) (Jan-Dec.2004)				Temporal mean
	Winter	Spring	Summer	Autumn	
1	9.48	5.40	2.85	4.95	5.67
2	7.86	5.12	2.65	4.77	5.10
3	9.69	6.05	3.16	5.66	6.14
4	14.95	7.99	3.83	6.98	8.71
5	15.60	8.85	4.20	7.22	9.48

The mean concentrations of TPH's in the sediments from the same stations are listed in Table 2.

Table 2. Seasonal variations in the mean concentrations of TPH's in sediments from northern part of Shatt Al-Arab river.

Station No.	Seasonal variation in the mean conc. of TPH's, in the sediments (µg/gm) (Jan-Dec.2004)				Temporal mean
	Winter	Spring	Summer	Autumn	
1	14.275	9.025	3.575	5.575	8.113
2	13.520	8.110	3.150	4.715	7.373
3	15.705	9.460	4.415	6.585	9.290
4	40.020	21.645	9.775	17.320	22.190
5	45.210	23.620	10.36	18.470	24.415

The TOC % in the sediments were determined for the same periods of study, they are listed in Table 3.

Table 3. Seasonal variations in the mean of TOC % in the sediments from northern part of Shatt Al-Arab river.

Station No.	Seasonal variation in the mean TOC % (Jan-Dec.2004)				Temporal mean
	Winter	Spring	Summer	Autumn	
1	0.66	0.62	0.58	0.63	0.62
2	0.53	0.50	0.46	0.52	0.50
3	0.60	0.55	0.50	0.57	0.55
4	0.91	0.75	0.62	0.67	0.73
5	1.03	0.84	0.65	0.70	0.81

Shatt Al-Arab river was recorded in st. 2 which receives low domestic waste water and far away from any source of pollution by petroleum. It is reported that st. 1 is affected by domestic waste, human waste discharges as well as fishing boats (Al-Saad, 1983) which are represented among the most important sources of pollution by hydrocarbons (Eganhoyse *et al.*, 1981). The highest concentration recorded was at st. 5 which is affected by the discharges from power stations nearby which represented as the most important sources of pollution by hydrocarbons (Andelman and Suess, 1970). Water currents of Shatt Al-Arab river play a major role in transferring pollutants such as petroleum hydrocarbons from st. 4, which is close to oil fields of Nihran Omar, towards station 5 (Levy, 1975).

Seasonal variations in the concentrations of petroleum hydrocarbons in the dissolved phase of water from northern part of Shatt Al-Arab river were very clear in which higher levels were reported during winter which ranged between 7.86 and 15.6 µg/l in stations 2 and 5 respectively, while lower levels were reported during summer which ranged between 2.65 and 4.2 µg/l in stations 2 and 5 respectively. This variation is the nature of climate in the area which characterized by two extreme seasons with high differences in temperature, winter and summer. The same results were reported for the lower part of Shatt Al-Arab river (Ibaheem, 2004). These reasons lead to different effects of microbial degradation (Shamshoom *et al.*, 1990), photo-oxidation (Al-Saad and Al-Timari, 1993), turbidity of Shatt Al-Arab River during flood seasons (Al-Manssory, 1996).

This study didn't show a wide contrast in the levels of TPH's in the water of Shatt Al-Arab river compared to sites in Arabian Gulf where some sites contain high concentrations relative to adjacent areas (El-Samrah *et al.*, 1986), This is due to the absence of sources of pollution by petroleum in the northern part of Shatt Al-Arab, moreover the water current in Shatt Al-Arab is continuously running and the direction from north to south.

The reported levels of TPH's in water of Shatt Al-Arab are lay within the same range as for other places in the world as shown in table 4.

In the water column, it is estimated that 70% of petroleum hydrocarbons are precipitated to the bottom (Knap and Williams, 1982). The sediment layer of 1-5 cm will explain clearly the extent of area pollution

by petroleum hydrocarbons for a period of many years (Edgern, 1977). Concentration values listed in table 3, for TPH's in the sediments from Northern Shatt Al-Arab, revealed that TPH's in the sediments have the same trend as those for water in which lower values were at summer in the range 3.15 – 10.36 µg/g and in the range of 13.52 – 45.21 µg/g at winter, and during all seasons the lower vales were recorded in st. 2 and higher values were recorded in st. 5. The residue of PHC's in the sediments is effected by different factors among which is the rate of biodegradation (Lee *et al.*, 1978),which interfere with other factors such as temperature, photo-oxidation, nutrients and sediment texture (Gardner *et al.*, 1979). The seasonal variation of temperature affect the degradation rate of petroleum hydrocarbons present in the surface layer, moreover the fast degradation taking place in the surface layer contacting the water bottom which characterized with oxygen abundant (Hughes and Mckenzie, 1975). In addition to that the deposition of petroleum hydrocarbons toward the bottom lead to increase the bacterial aggregates which feed upon them, then the biodegradation will increase in the area following the increase of oxygen and nutrients like phosphate and nitrate (Zobell and Prokop, 1966). These observations were available in Shatt Al-Arab environment (Al-Saadi *et al.*, 1979). This is why petroleum hydrocarbons are high at winter and low at summer (Atlas, 1981).

Table 4. Comparison between the levels of dissolved TPH's (µg/l) in Shatt Al-Arab and other parts of the world.

Position	**TPH's in water (µg/l)**	**References**
Sao Sebasto coasts	2.5	Zanardi *et al.*, 1999
Victoria coastal	5.1 – 22.1	Burns & Smith,1980
Chedabucto Bay	1.0-90.0	Levy, 1979
Lyon Gulf	18.23	Marchand *et al.*, 1988
Malta Beach	14.9	Solnay, 1979
Lybian Beach	24.9	Solnay, 1979
Saudi Arabia Beach	4.3 – 546	El-Samrah *et al.*,1986
Qatari Beach	1.2 – 428	
Kuwaiti beach	2.1 – 3.6	
Shatt Al-Arab	5.2 – 14.2	Al-Saad, 1983
Shatt Al-Arab & NW Arabian Gulf	2.6 – 86.7	DouAbul, 1984
Shatt Al-Arab & NW Arabian Gulf	3.25 – 25.33	Al-Saad, 1995
Shatt Al-Basrah &Khor Al-Zubair	13.36	Al-Saadon, 2002
Shatt Al-Arab, Southern	3.97 – 11.72	Ibraheem, 2004
Shatt Al-Arab, Northern	5.67 – 9.48	Present study

Mean levels of TPH's in the sediments from northern Shatt Al-Arab river as listed in table 2 with high value in st. 5 and low value in st. 2 indicates that sediments are effected by the same sources of pollution in the same sites as those for water.

As usual, levels of TPH's in sediments are much higher than those dissolved in the water column above. On comparison of these levels with those reported in sediments from Arabian Gulf as well as other parts of the world, as shown in table 5, it is found that these levels are fallen within the recorded limits but higher than those studies previously in the same area (Al-Saad, 1983), which is explain on the basis of increased waste water from cities and industries

Table 5. Comparison between the levels of TPH's in sediments (µg/g) from Shatt Al-Arab and other parts of the world.

Position	TPH's in sediments (µg/g)	References
Lyon Gulf (France)	3 – 420	Marchand *et al.*,1988
Baffin Bay (Canada)	1.25-33.75	Levy, 1979
Lyon Gulf	18.23	Marchand *et al.*, 1988
Saudi Arabia Beach	17 – 671	Fowler *et al.*, 1993
Bahrani Beach	23 – 41	
Kuwaiti beach	28	
Oman beach	6 – 22	
Arabian Gulf	26.0- 342	Massoud et al.,1998
Arabian Gulf	5.4 – 92.2	Al-Lihabi & Al-Omran, 1996
Shatt Al-Arab	2.6 – 20.5	Al-Saad, 1983
Shatt Al-Arab & NW Arabian Gulf	0.4 – 44.0	DouAbul, 1984
Shatt Al-Arab & NW Arabian Gulf	2.46 – 38.33	Al-Saad, 1995
Shatt Al-Basrah &Khor Al-Zubair	0.10 – 7.74	Al-Saadon, 2002
Shatt Al-Arab, Southern	34.26 – 146.64	Ibraheem, 2004
Shatt Al-Arab, Northern	7.37 – 24.41	Present study

Sediments are the final place for degradable as well as non-degradable organic materials pollutant. The organic materials are investigated quantitatively through the determination of TOC which represents the measure of pollution degree (Khalaf *et al.*, 1986). This TOC is a result of different sources of pollution in the area (Literathy *et al.*, 1987). Seasonal and temporal variations in TOC % in the sediments from northern Shatt Al-Arab river are following the same trends as those for TPH's in water and sediments from the same sites as indicated in table 3. Higher values were recorded at winter; lower values were recorded at summer. Moreover, higher value was recorded in st. 5 while lower value was recorded in st. 2.

Statistical analyses for the results in this study revealed the presence of positive significant correlation between TPH's in the sediments and the TOC % with a correlation factor r = 0.980.

On comparison between TOC % in the sediments from northern Shatt Al-Arab river in this study and other studies in the same area as well as the Arabian Gulf, as shown in table 6, it is appear that the present results are higher than those previously reported in the same area (Al-Saad, 1983; DouAbul *et al.*, 1984; DouAbul and Bedair, 1986; Abaychi *et al.*, 1988) but they are lower than those recorded for other pats of Shatt Al-Arab river which are very close to sources of pollution by petroleum hydrocarbons (Abaychi and DouAbul, 1985; Ibraheem, 2004).

Table 6. Comparison between the levels of %TOC (w/w) in sediments from northern Shatt Al-Arab and other parts nearby.

Position	%TOC in sediments	References
Arabian Gulf	0.7	DouAbul and Bedair, 1986
Kuwaiti International Waters	0.67	
Arabian Gulf	0.33 – 1.92	Massoud *et al.*,1998
Shatt Al-Arab & NW Arabian Gulf	0.612	DouAbul, 1984
Shatt Al-Arab & NW Arabian Gulf	0.62	Al-Saad, 1987
Shatt Al-Arab	0.826	Abaychi & DouAbul, 1985
Shatt Al-Arab	0.51 – 0.75	Abaychi *et al.*, 1988
Shatt Al-Arab, Southern	0.57 -1.05	Ibraheem, 2004
Shatt Al-Arab, Northern	0.52 – 0.81	Present study

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التغيرات الموقعية والزمانية للهيدروكاربونات النفطية في مياه وترسبات الجزء الشمالي لنهر شط العرب.

فارس جاسم محمد الإمارة، ساهر عبد الرضا و أسعد عبود علي
مركز علوم البحار، كلية التربية، جامعة البصرة، البصرة - العراق

المستخلص في هذه الدراسة تم تقدييم التوزيع الموقعي والزماني في كل من المركبات الهيدروكاربونية الكلية والنسبة المئوية للكاربون العضوي الكلي في عينات مياه وترسبات من خمس مواقع منتخبة عند الجزء الشمالي لنهر شط العرب بالقرب من مواقع محتملة للتلوث بالهيدروكاربونات النفطية وهي 1- القرنة و 2- الشافي و 3- الدير و 4- نهران عمر و 5- جزيرة السندباد. سجلت الدراسة تغيراً في الهيدروكاربونات النفطية الكلية في الجزء الذائب للمياه بمقدار 5.1 مايكروغرام/ لتر عند المحطة رقم 3 و 9.48 مايكروغرام/ لتر في المحطة رقم 5 مقارنة بنفط خام خفيف البصرة. وفي الرواسب كان المدى بين 7.37 مايكروغرام/غرام في المحطة رقم 2 و 24.41 مايكروغرام/غرام في المحطة رقم 5. اما التغير الزماني في تراكيز الهيدروكاربونات النفطية الكلية في المياه والترسبات فقد كان بحدود اوطأ القيم 2.65 – 4.20 مايكروغرام/ لتر و 3.15 – 10.36 مايكروغرام/غرام على التوالي خلال فصل الصيف وبقيم عليا خلال فصل الشتاء قدرت ب 7.86 – 15.60 مايكروغرام /لتر و 13. 52 – 45.21 مايكروغرام/غرام في المياه والترسبات على التوالي. وكانت النسب المئوية للكربون العضوي المقاسة في الترسبات بحدود 0.50 – 0. 81 في محطتي الشافي (2) وجزيرة السندباد (5) على التوالي. ومن العلاقات الإحصائية فقد وجد ترابط موجب قوي بين تركيز الهيدروكاربونات النفطية الكلية والنسبة المئوية للكربون العضوي وبمعامل ارتباط قدره 0.93 .

كلمات دالة:هيدروكاربونات نفطية, النسبة المئوية للكربون العضوي, الجزء الشمالي لنهر شط العرب, مياه, ترسبات.