SEASONAL VARIATIONS OF OIL RESIDUES IN WATER OF SHATT AL-ARAB RIVER, IRAQ

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Abstract. The distribution and seasonal variations of petroleum residues in the Shatt al-Arab water column have been determined spectrofluorometrically. Their concentrations were found to vary between 1.7 to 35.4 $\mu g\ L^{-1}$ Kuwait crude oil equivalents. The results suggested that petroleum hydrocarbons present in this river originated from diverse sources. Hydrocarbon amounts tend to be highest in winter (averaged 17.4 $\mu g\ L^{-1}$) and lowest in summer (averaged 3.1 $\mu g\ L^{-1}$).

1. Introduction

The Shatt al-Arab River is the most important river and the only source of fresh-water in the arid surroundings of southern Iraq. It is the prime fresh-water source and pours about 5×10^9 m^3 nutrient rich water into the Arabian Gulf each year (Hartmann *et al.*, 1971). Shatt al-Arab waters are liable to contain petroleum origin wastes (Saad, 1976) because of numerous oil operations. The objectives of the present study are to:

(1) Determine the regional distributions of petroleum residues, both in solution or dispersed through the Shatt al-Arab water column, in an attempt to identify major sources;

(2) Estimate the seasonal variations of petroleum hydrocarbons in a warm millieu to study the main ecological factors acting upon the weathering of oil in Shatt al-Arab River waters; and

(3) Evaluate the role Shatt al-Arab River plays as a source of oil pollution for the Arabian Gulf.

In order to accomplish these aims, five sampling sites were selected to represent different regions of the north section of Shatt al-Arab River. Proximity to potential oil pollution sources was the criteria observed in selecting these locations. A reference station was chosen at the Euphrates River from Hor al-Hammar, north west of Basrah City. Areas included in the present survey and their positions are shown (Figure 1). The sampling programme was carried out seasonally over a period of 13 mo (November 1981 to December 1982).

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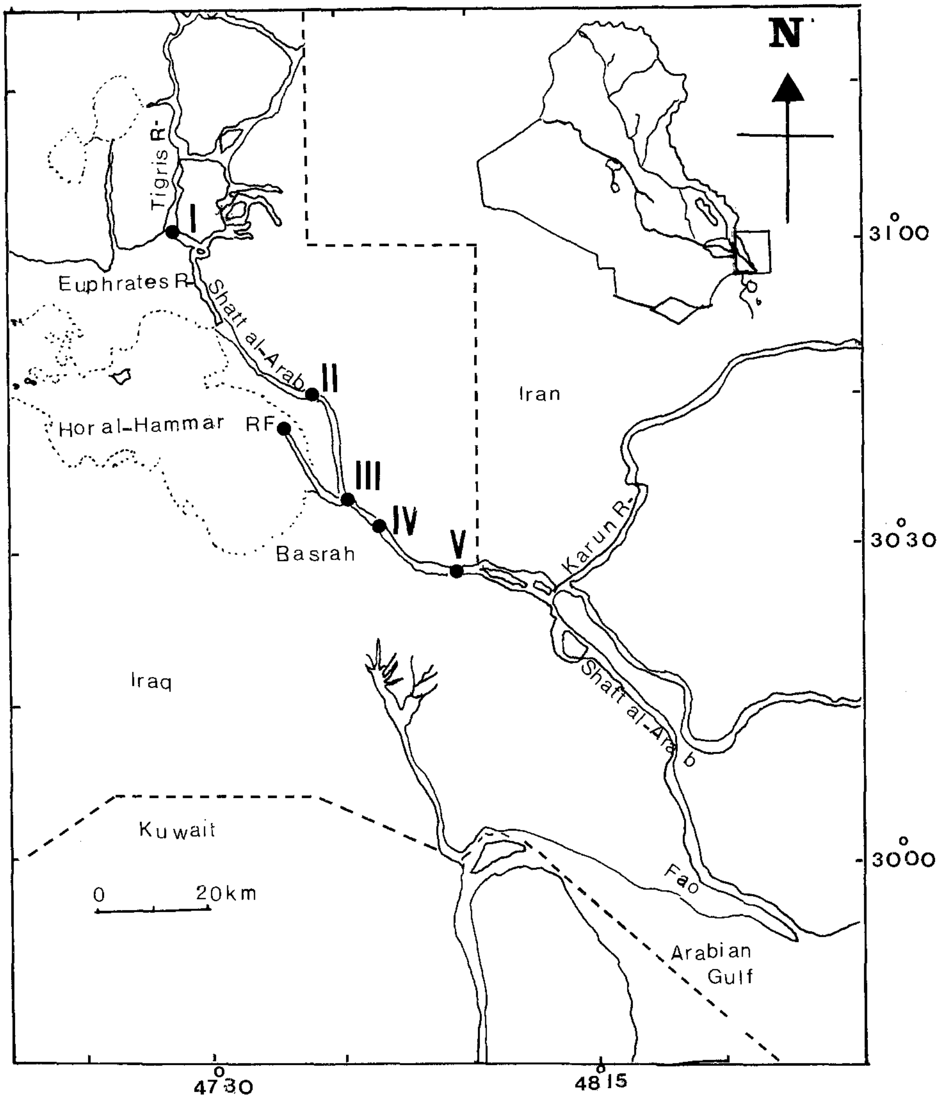

Fig. 1. Map of the Shatt al-Arab River showing the position of stations.

2. Description of Shatt al-Arab River

The Shatt al-Arab River originates from the confluence of the two major rivers of Iraq (Tigris and Euphrates) at Qurna. Karun River, the only tributary of the Shatt al-Arab River, joins its eastern bank south of Basrah City (Figure 1). The length of the Shatt al-Arab River from Qurna i.e. its place of origin, to its mouth in the Arabian Gulf, extends about 175 km. Its width varies at different points, ranging from 0.4 km at Basrah City to 1.5 km at its mouth. The water depth increases in general towards the Gulf with a maximum of 12.5 m. The water level is, however, affected by the high and low tides of the Arabian Gulf where the average tidal range is about 1.7 m. Shatt al-Arab waters are characterized as being well mixed with limited vertical stratifications of temperature (Saad and Kell, 1975) and chlorinities (Huq *et al.*, 1978). Although, Saad (1978) has reported that the water of Shatt al-Arab mouth may be traced as far as ca. 5 km into the Arabian Gulf, Brewer *et al.* (1978) indicated that the discharge of this river reaches the waters off Kuwait Bay during the flood season.

3. Materials and Methods

Subsurface (1 m) water samples have been collected at low tide from all stations utilizing the sampling device recommended by (IOC/WMO, 1976). After collecting water samples, the determination of petroleum residues was carried out without delay, following the spectrofluorometric method based upon that adopted for the IGOSS Project (IOC/WMO, 1976). Many research workers have employed such a technique to estimate oil residues in water (e.g. Zitko and Carson, 1970; Michalik and Gordon, 1971; Levy, 1971, 1972; Levy and Walton, 1973; Keizer and Gordon, 1973; Law, 1981). For the present study a Jobin Yvon JY3 spectrofluorometer was used. It has been reported that Shatt al-Arab waters are rather productive and contain high amounts of organic matter (both anthropogenic and biogenic) (Stefanson, 1975; Huq *et al.*, 1978). Hence, it was imperative to clean-up the extracts in order to remove non-petroleum materials fluoresars under the working conditions. Furthermore, materials that might cause quenching were eliminated simultaneously (Gordon and Keizer, 1974). All solvents used in the present study were spectrograde supplied by Merck, further redistilled in an all-glass still. Merck silica gel G60 was employed to clean-up the extracts according to the (IOC/WMO, 1976) procedure.

Blank determinations were carried out by repeating the procedure with pre-extracted water samples. The Kuwait crude oil which was chosen as an arbitrary standard for comparison has been supplied by the American Petroleum Institute (API). Chrysene standards were employed to calibrate the spectrofluorometer and check the quantification of the analytical results. In order to characterize the extracted hydrocarbons (Berlman, 1971; McKay and Latham, 1972), some of the samples were analyzed by Gas Liquid Chromatography. For this purpose a Hewlett Packard model 5710A with dual flame ionization detector and 1.5 m $\times$ 4 mm i.d. stainless steel column packed with 3% methyl silicon (OV-101) on chromosorb W was used.

4. Results

The level of petroleum residues, both in solution or dispersed through the Shatt al-Arab River water column (expressed in Kuwait crude oil equivalents) are listed in Table I. Regional average values of these data are presented in Table II and (Figure 2), while their average seasonal variations are indicated in Table III and (Figure 3). Water samples collected from the reference station (RF) throughout the study period have revealed the absence of any measurable amounts of petroleum hydrocarbons.

TABLE I

Concentration of petroleum residues observed in the Shatt al-Arab River waters

Date of sample collection	Site No.	Water temp. °C	No. of sample	Concentration range	($\mu g\ L^{-1}$) average	Standard error ($\mu g\ L^{-1}$)
1.11.1981	I	18	9	3.9–7.0	5.4	0.37
	II		9	5.4–7.1	6.8	0.32
	III		6	7.0–11.8	8.7	0.72
	IV		7	13.3–16.5	14.8	0.53
	V		7	8.6–11.8	9.6	0.50
	RF		9	Nd	–	–
19.12.1981	I	15	6	8.3–12.8	10.5	1.01
	II		8	9.8–12.8	11.1	0.56
	III		6	12.8–14.3	13.6	0.33
	IV		7	27.9–35.4	30.9(+)	1.23
	V		7	15.8–27.9	20.8(+)	1.42
	RF		8	Nd	–	–
24.3.1982	I	23	8	1.8–4.5	3.2	0.42
	II		9	2.7–4.5	3.4	0.25
	III		7	2.7–4.5	3.6	0.28
	IV		7	4.5–9.1	6.9	0.74
	V		7	3.6–5.5	4.5	0.28
	RF		7	Nd	–	–
10.8.1982	I	30	7	1.7–2.2	1.7(–)	0.14
	II		7	1.8–3.1	2.4(–)	0.16
	III		8	2.7–3.6	3.2	0.13
	IV		6	3.6–5.3	4.4	0.24
	V		7	2.7–4.4	3.6	0.24
	RF		8	Nd	–	–
20.12.1982	I	14	6	9.5–10.0	9.6	0.08
	II		6	10.9–11.2	11.1	0.04
	III		7	12.9–13.5	13.3	0.11
	IV		6	28.5–30.0	28.9(+)	0.23
	V		6	19.6–20.0	19.8(+)	0.06
	RF		6	Nd	–	–

RF = Reference station.
Nd = Not detected.
The minimum values are designated by (–) and the maximum by (+).

5. Discussion

5.1. Regional Distribution

The concentrations of petroleum residues present in the Shatt al-Arab River water samples were found to vary from 1.7 to 35.4 $\mu g\ L^{-1}$ Kuwait crude oil equivalents. A comparison of these values with those reported for some other world rivers and estuaries

TABLE II

Regional average values of petroleum residues in the water of the Shatt al-Arab River, November 1981–December 1982

Station No.	Average concentrations ($\mu g\ L^{-1}$)[a]
I	5.2
II	5.9
III	7.3
IV	14.2
V	9.6
RF	Nd

[a] Average concentrations calculated from the values of at least 25 determinations.
RF = Reference station.
Nd = Not detected.

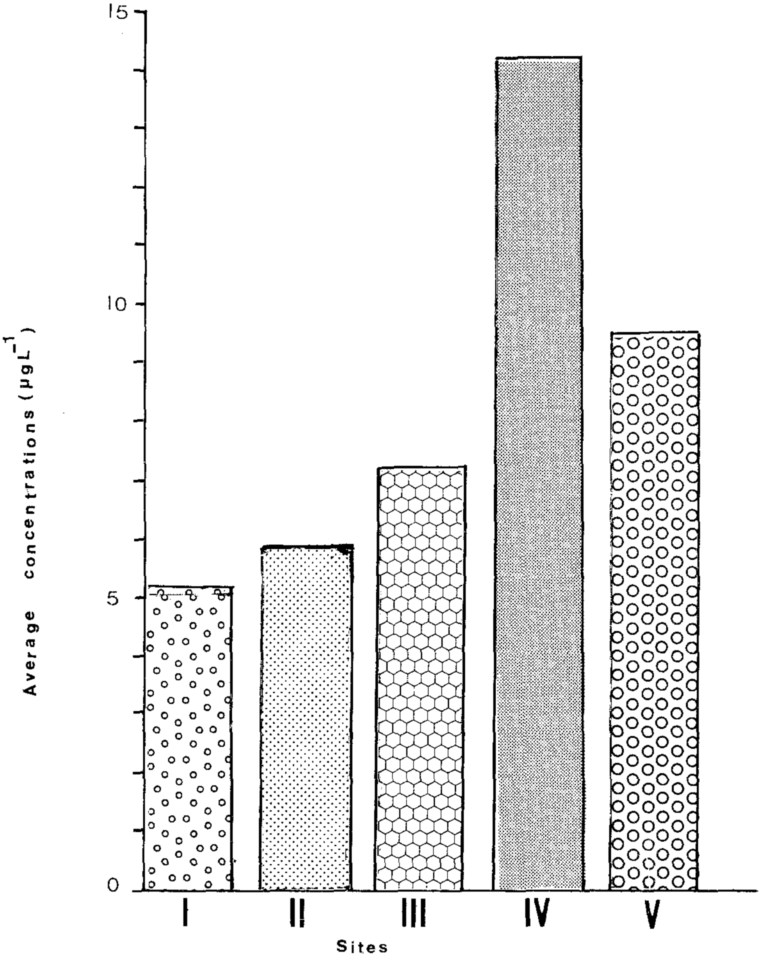

Fig. 2. Regional variations of petroleum residues in the waters of the Shatt al-Arab River during November 1981 to December 1982.

TABLE III

Seasonal average values of petroleum residues in the water of the Shatt al-Arab River, November 1981–August 1982

Station number	Average concentrations in ($\mu g\ L^{-1}$)[a]				
	Autumn (1981)	Winter	Spring (1982)	Summer	Winter
I	5.4	10.5	3.2	1.7	9.6
II	6.8	11.1	3.4	2.4	11.1
III	8.7	13.6	3.6	3.2	13.3
IV	14.8	30.9	6.9	4.4	28.9
V	9.6	20.8	4.5	3.6	19.8

[a] Average concentrations calculated from the values of at least 6 determinations.

is presented in Table IV. Our data indicate that the level of oil residues observed in the Shatt al-Arab River waters lie within the range of values reported for comparable areas. This study showed that, on average, the Shatt al-Arab River waters contain less petroleum residues than the Arabian Sea whose average value is 32.5 $\mu g\ L^{-1}$ (Sen Gupta and Kureishy, 1981).

From the results presented here, it is evident that, excluding the reference station, all the studied sites are contaminated to some extent with petroleum hydrocarbons. The highest concentrations were always observed at site IV, while the lowest were at site I. This indicates that Shatt al-Arab River oil pollution has possibly originated from diverse sources. Table V shows the suspected origin of oil as suggested by Al-Saad (1982). Evaluating our data in the light of this Table indicated that sewage discharge and urban run-off may be considered as the most significant sources of oil entering the Shatt al-Arab River. Connell (1982) has similarly identified sewage discharge and urban and rural run-off to be the most important oil-containing inputs to the Hudson Raritan Estuary-New York.

Assuming that there is no source or removal of oil residues from the Shatt al-Arab River waters further down site V, it is estimated that this river transports about 48 tonne of petroleum hydrocarbons to the Arabian Gulf annually. The significance of this figure is best appreciated by considering the input of oil into the waters of the Arabian Gulf through a variety of discharges, which has been estimated about 200 000 tonne during 1976 (Research Planning Institute, Kuwait, 1977).

5.2. Seasonal Variations

The Shatt al-Arab River water temperature undergoes seasonal variations. It has been reported that the seasonal range encountered at Basrah City (site IV in the present study) was 14.5 °C in January and 32 °C in August (Arndt and Al-Saadi, 1975). The water volume of the Shatt al-Arab River experiences variations at different seasons also. Thus the fresh-water flow maximum occurs in June, while the minimum flow is in December and January (Mohammad, 1982). However, the later phenomenon seems to

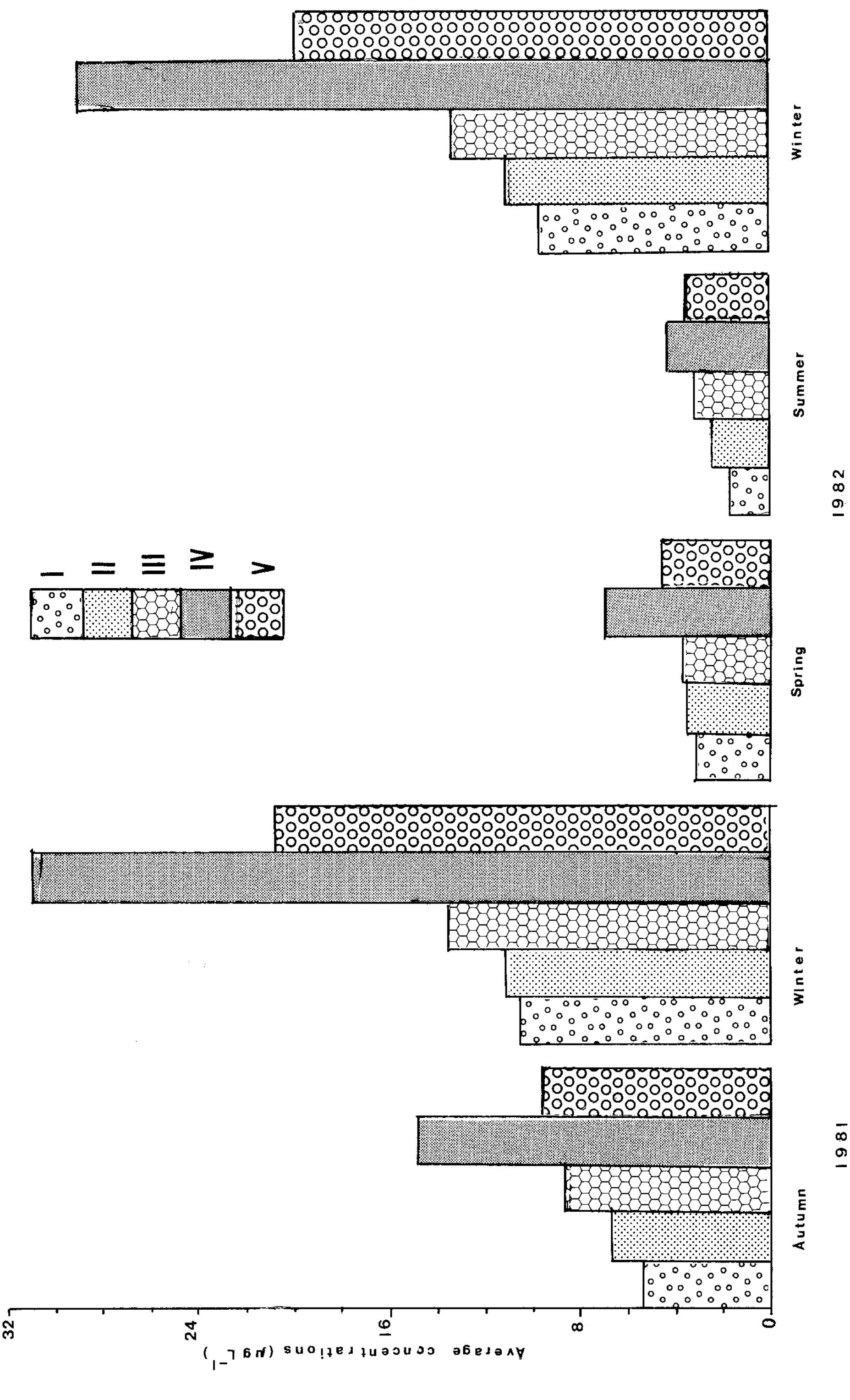

Fig. 3. Seasonal variations of petroleum residues in the waters of the Shatt al-Arab River during November 1981 to December 1982.

TABLE IV

Comparison of petroleum residues in polluted waters of different areas

Areas	Concentrations ($\mu g\,L^{-1}$)	Source
River Meresey	74	Law (1981)
Off Tees Bay	60	Law (1981)
Thames Estuary	43	Law (1981)
Off Blyth	28	Law (1981)
Off the River Tyne	24	Law (1981)
St. Lawrence River	2.6–4.4	Levy (1971)
St. Lawrence Estuary	1–5	Levy and Walton (1973)
Shatt al-Arab River	1.7–30.9	Present study

TABLE V

Sources of petroleum hydrocarbons (crude and refined products) influencing each of the studied stations along the north section of the Shatt al-Arab River[a]

Station number	Sources
I	Rural run-off
II	Oil refinery
III	Electricity generating station
IV	Sewage discharges, urban run-off and river transportation activities (e.g. boats, vessels, ships...)
V	Rural run-off and river run-off from station IV

[a] Adopted from Al-Saad (1982).

have relatively limited effect upon the concentration of petroleum residues recorded in this river compared to that of water temperature (Table III and Figure 3). Thus when the water temperature is higher than 20 °C (spring and summer) the estimated oil residues are lower than when the temperature is less than 20 °C (autumn and winter). It is well documented that temperature is the most important factor governing the removal of petroleum hydrocarbons from the water (Gordon *et al.*, 1978; Cheung *et al.*, 1979; Gearing and Gearing, 1982). Besides the direct effect of temperature on the evaporation of petroleum hydrocarbons from water, temperature increase favors processes of bacterial degradation (Cundell and Traxler, 1973; Mulkins-Philips and Stewart, 1974).

Photo-oxidation may also degrade components of oil in the waters (FAO, 1977; Lee, 1980). Thus, the intense solar radiation, which characterizes the climate of the subtropical region of Iraq will favor photo-oxidation of petroleum hydrocarbons present in the Shatt al-Arab River, particularly during summer.

It is also postulated that petroleum hydrocarbons have a tendency to adsorb onto particulate matter (Boehm and Quinn, 1974). Knap and Williams (1982) have concluded that adsorption of hydrocarbons to estuarine sediments is the principal mechanism for the removal of these hydrocarbons. Kell and Saad (1975) observed pronounced seasonal variations in the average values of suspended matter along the Shatt al-Arab stretch, being at minimum in summer. Therefore, the lower concentrations of petroleum residues observed in the waters of the Shatt al-Arab River during summer could be caused in part by the increased sedimentation of adsorbed hydrocarbons.

6. Conclusions

In the light of the above reasoning, the following conclusions may be drawn:

(1) It is evident that, with the exception of the reference station, all the sites that have been investigated are contaminated to some degree with petroleum hydrocarbons.

(2) The present data indicate that the levels of petroleum residues observed in the waters of the Shatt al-Arab River are comparable with those reported for other polluted rivers and estuaries.

(3) It is estimated that the Shatt al-Arab River transports about 48 tonne of oil residues to the Arabian Gulf annually.

(4) The present study indicates that the pollution of the Shatt al-Arab River waters by oil originated from diverse sources, the most significant of which are sewage discharge and urban run-off.

(5) Processes brought about by temperature variations, including evaporation, bacterial degradation and adsorption as well as photochemical oxidation, are postulated to produce a pronounced seasonal variations of petroleum residues in the Shatt al-Arab River waters. On the other hand variations in the water volume of this river seems to have limited effect in this respect.

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