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ABSTRACT

In 22 August 2006 the tanker BFC2 carried 4750 tons of Basrah Crude oil was crash in khor Al-Zubair area, this lead to make a crack with a length of 1.5 meter in bump room of the tanker and oil spilled about (10-15 tones) from the cargo pump tanker immediately making a large spill in this important area, To study oil spill in this area water, sediment and were taken. Also Composite samples of fish species (beyah) *Liza subviridis and* (Sheka) *Thryssa mystax* and two species of shrimps *Metapenaeus affinis* and *Exopalaemon styliferus* with plant samples *salicornia herbacea* were collected at different locations during the study period, High concentrations of total petroleum hydrocarbons (478.2 µg/ l and 38.5 µg/g) were recorded in water and sediments. Also, highest level of total petroleum hydrocarbons were showed in fish (59.46 µg/g in *Thryssa mystax*), shrimps (121.9 µg/g in *Metapenaeus affinis*) and plants (360.7 µg/g in *Salicornia herbacea*). The present data were higher than the early data in the same area, and higher in the range of concentrations in water in other site of the world.

INTRODUCTION

Pollutants (Substances that cause pollution) enter the ocean through accidents careless, and the deliberate dumping of wastes. The ocean can absorb some type of pollutants in certain quantities because of its great size and the natural chemical processes that occur within it. But people continue to introduce more pollutants into the sea. Pollutants that find their way to the marine environment will be either in solution or associated with suspended solids. In both cases pollutants will find their fate in bottom sediments after a period of time, which will differ according to the residence time. Pollutants in solution are more hazardous because they are more available to the marine organisms, and more dynamic, which means a rapid and wider spreading. However, chronologically, the water mass is not helpful to retrieve the history of an area. Sediments constitute a good record

if we want to know about the today's state and the history of a contaminated area they can provide an integrated picture about the events that occurred in the water column. For this reason, sediments have been widely used to identify sources of pollution, to evaluate its extent and to diagnose the environmental quality of aquatic system (Fowler *et al*.,1993).
During the last few decades the pollution of the world's oceans has become a matter of increasing international concern. A significant amount of pollution is caused by shipping and maritime activities. In tonnage terms, the most important pollutant resulting from shipping operations is oil. Every day about 100 million tonnes (31.5 billion gallons)of oil are being transported by sea (Sheppard *et al* ., 1992). The world uses about 9 million tonnes (2.73 billion gallon) per day. Vessels annually release about half million tones of oil into the marine environment. During the last decade of nineties, more than 3.4 million tones of oil were spilled worldwide .Oil pollution in the ocean has the capability to change the sea into a biological desert.

Study area

Khor Al-Zubair is an extension of the Gulf waters in the lower reaches of Mesopotamica Fig(1). It has an approximate length of 42 km, a wide of 1 km at low tide, and an average depth of 10-20 m, During 1983 this water body was connected to an oligohaline marsh (Hor Al-Hammar), changing the environment of the Khor from a hypersaline lagoon to an estuary one (Hussain and Ahmed, 1999). The topography of Khor Al-Zubair look like a spindle with tapering ends, at the northern and southern ends. The northern end receives fresh water influx of average 700 m^3/sec throughout the tidal cycle. The current in the Khor is characterized by one direction through out the tidal cycle towards the southern end (Arabian Gulf), with velocity exceeding 2m/sec during ebb tide and 0.66 m/sec in flood tide. At the Southern end, the water discharge reaches 10000 m^3/sec with velocity range 0.8-5.78 m/sec (Al-Badran *et al*. 1996). With big tidal range at Umm-Qasar reaching 4.3m. Due to the low profile of the shore-line, the tidal flood penetrate the mudflats to a further distance, depending on the state of the tide, covering the halophytic vegetation(e.g *Salicornia herbacea* and *Halocreamon strobilaceum*).

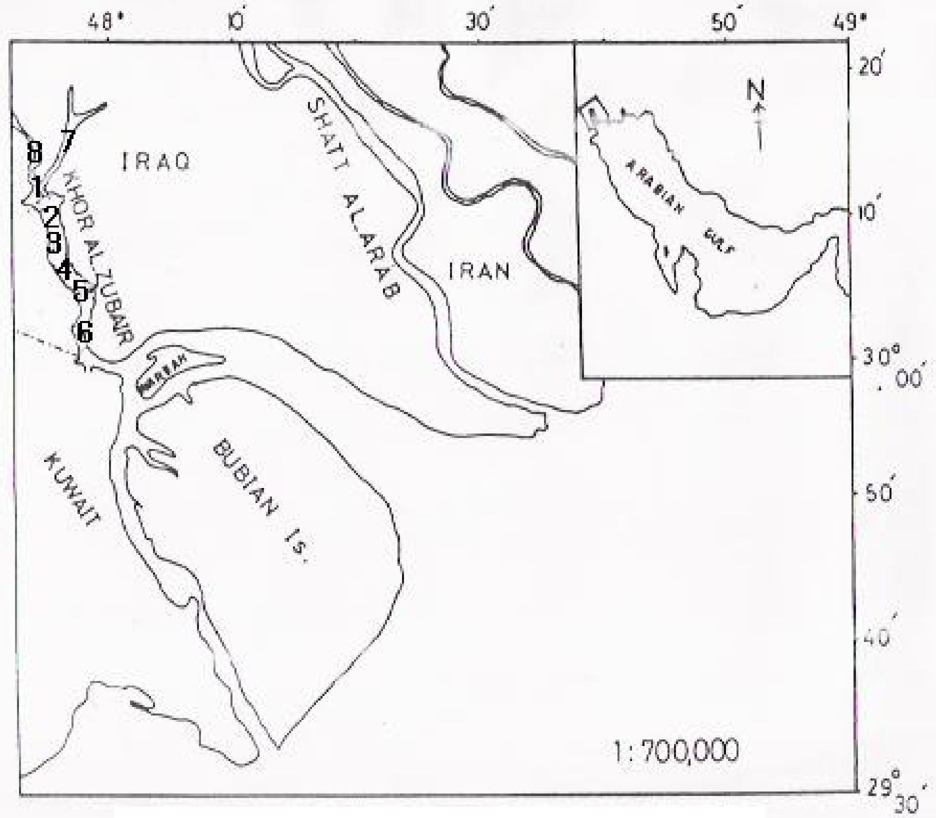

Figure 1. Sampling sations in Khor Al-Zubair

The Case of oil spill in Khor Al-Zubair

In 22 August 2006 the tanker BFC2 carried 4750 tons of Basrah Crude oil was crash in khor Al-Zubair area this lead to make a crack with a length of 1.5 meter in bump room of the tanker and oil spilled about (10-15 tones) from the cargo pump tanker immediately making a large spill in this important area, the spilt oil was transported by the fast moving current to reach inland water

MATERIAL AND METHODS

Eight sampling stations were chosen to represent different sectors of Khor Al-Zubair as shown in (Fig. 1) Sampling stations proximity to potential oil pollution sources were considered in selection these locations.

To study oil spill in this area water, sediment and biota samples were taken. Large samples of water (20 L) were collected at each station, with a clean amber-glass bottle of 5 liters capacity.

Hydrocarbons in water were solvent extracted following the procedure of UNESCO (1976). In this, 100 ml of Nan grade carbon tetrachloride (ccl_4) was used in two successive 50ml extractions and the extracts were combined. The mixture was vigorously shaken to disperse the ccl_4 thoroughly throughout the water samples The shaken is repeated several times before decanting the ccl_4. To these extract a small amount of anhydrous sodium sulfate was added to break any emulsion and to remove excess water. The ccl_4 extract were reduced in volume to less than 5ml by using a rotary evaporator .The reduce extract was carefully pipettes into a precleaned 10ml volumetric glass, making sure any residual particles of sodium sulfate were excluded and evaporated to dryness by a stream of pure nitrogen. Although ccl_4 is ideal solvent for the extraction process, it is not suitable for spectrofluorescence analysis, therefore ccl_4 must be replaced by a solvent, such as n-hexane which dose not absorb light in 300-400 nm range. The flask was then rinsed with fresh hexane and the rinsing used to make the samples volume up to exactly 5ml prior to ultraviolet fluorescence (UVF) analysis.

Sediment samples were also collected from the same locations in the study area by means of a Van Veen grab sampler. Undistributed, triplicate samples were taken. After retrieval of the sampler, the water was allowed to drain off, avoiding disturbing the surface layer of the samples. As soon as the samples were retrieved, they were wrapped in aluminum foil and immediately frozen – 20C°. Before analysis, sediment samples were freeze-dried, ground finely in agate mortar and sieved through a 62µm metal (stainless- steel) sieve.

The extraction and clean-up procedure for the determination of petroleum hydrocarbons in the sediment was based upon that of (AL-Saad, 1995). Sediment was placed in a pre-extracted cellulose thimble and soxhlet extracted with 150ml methanol: benzene (1:1) mixture for 24hours. At the end of this period, the extract was transferred to a storage flask and the samples were further extracted with a fresh solvent. The combined extracts were reduced in volume to ca 10ml in a rotary evaporator. It was then saponified for 2hours with a solution of 4N KOH in 1:1 methanol: benzene. After extracting the unsaponified matter with hexane, the extract was dried over anhydrous sodium sulfate, concentrated for UVF analysis.] For this work a Shimadzu RF-450 spectrofluorometer equipped with a DR-3 data record was used.

Heavy contamination of oil will, of course, cause the death of organism either directly or, more probably, indirectly by interference with food or oxygen supplies. A light contamination of soluble or emulsifiable oil may result in tainting of the flesh, rendering it, inedible. In this section fish, shrimp and plant samples were collected and analyzed in order to establish the levels of petroleum hydrocarbons which contaminated these organisms from the spilled oil.

Composite samples of fish species (beyah) *Liza subviridis and* (Sheka) *Thryssa mystax* and two species of shrimps *Metapenaeus affinis* and *Exopalaemon styliferus* with plant samples *salicornia herbacea* were collected at different locations during the study period, generally each composite consisted of at least 6 uniform size of adult fish and shrimp of the same species.

Fish samples and shrimp (edible tissues only) with plants were pooled and macerated in a food chopper from which at least 5 replicate of 50gm were freeze dried, grounded and sieved through a 1mm metal sieved. The extraction procedure employed in the present study was based upon that AL-Saad (1995). However, procedural blanks consisting of all reagents and glassware used during the analysis were periodically determined. It was preferred to eliminate sources of contamination rather than adjusting or correcting the data actually obtained according to the blank value.

RESULTS AND DISCUSSION:

Water column

The oil contents of the water particularly the toxic aromatic fraction were determined by fluorescence spectrophotometer. The level of petroleum residues, both in the solution or dispersed through the khor Al-Zubair (expressed in the term of Basrah crude oil equivalents) were found to vary between 36.8 µg/L to 478.2 µg/L. (Table 1).

However, great dial of variation in concentrations were absorbed between sample replicates, which my be partly due to the inhomogeneous nature of the water /oil solution. Our data indicates that the level of the oil residues encountered in the khor Al-Zubair were more than maximum permissible level of 30µg/L set by Word High Organization (WHO, 1971) for water utilized for domestic purposes. It is of interest to note that despite the fact that a considerable amount of highly weathered crude oil is lost to the north of Khor Al-Zubair yet still some concentration of oil residues were detected in the north of the khor Al- Zubair. This phenomenon may be attributed to self purification mechanisms, a natural mechanism, that enable natural water to keep its pristine natural .In the present case, both dilution and adsorption of the hydrocarbons to suspended particulate matter with the subsequent sinking or over bank deposition are the main factors.

Table (1): Mean Concentrations of petroleum hydrocarbons residues in water and sediments samples from Khor Al- Zubair

Station No.	Sediment hydrocarbons con. (µg/g)	Water hydrocarbons con. (µg/l)
1	5.38	297
2	5.33	242
3	3.15	169.2
4	38.5	478.2
5	11.4	246.1
6	27.7	324.3
7	2.28	36.8
8	2.07	45.9

The Khor has a large water discharge at the southern end, the water discharge reach 1000m^3/sec with velocity range 0.8-5.78 m/sec (Al-Badran *et al*,1996).

Such considerable movement of water masses have a great transport capacity, resulting in dilution oil speed from the source of spill to a negligible amount down the Khor.

It is postulated that petroleum hydrocarbons have a tendesy to adsorb on to suspended particulate matter (Al-Saad *et al*, 1998). since the Khor location carries a tremendous amounts of suspended particulate matter. Such huge amounts of this suspended particulate matter are capable of removing considerable amount of oil seeped to NW Arabian Gulf. Particulate material plus the adsorbed oil, will be deposed at the Khor bank or sink to the bottom as the water current is reduced in speed.

In case of the spill, the process of solution seems to be effected to a great extent by the following phenomena:

1-The rather fast water movement renew water layers underlying oil slick, thus resulting in a high solution rate.

2-The raped mixing might provide a greatest opportunity for hydrocarbons to dissolve in water.

3-Fluishing volume of a fast moving water is too big, thus dilution of the dissolved hydrocarbons to trace levels is evident.

4-Khor carry tremendous amount of suspended particulate matter which tend to absorb and /or adsorb hydrocarbons, thus depleting these contaminations in water.

The present data were higher than the early data in the same area, and higher than the range of concentrations in water in other site of the world (Table 2).

Table (2): Comparison of oil equivalent in coastal and open sea waters estimated by fluorescence spectroscopy

Location	Concentration (µg/l)	References
Southern Baltic sea	2.0 -130	Law & Anrulewicz (1983)
Qatar	1.2 - 428	El- Samra, *et al*., (1986)
Saudia Arabia	4.3 - 546	El- Samra, *et al*., (1986)
Kuwait	2.1 – 3.6	El- Samra, *et al*., (1986)
Winyah bay (USA)	0.23 – 25	Bidleman, *et al*., (1990)
Gulf of Thiland	1.9 – 72	Wattayakorn (1991)
River Humber (U.k)	9.3	MAFF (1993)
River Mersey (U.k)	11	MAFF (1993)
River Tees (U.k)	48	MAFF (1993)
River Tyne (U.k)	31	MAFF (1993)
River Wear (U.k)	13	MAFF (1993)
Cortiou (France)	104	Marchand, *et al*., (1988)
Gulf of Lion	18 – 23	Marchand, *et al*., (1988)
Arabian Sea	1.6 –11.1	Sen Gupt, *et al*., (1993)
Shatt Al–Arab & NW Arabian Guf	3.25-25.33	Al – Saad (1995)
Shatt Al – Arab & NW Arabian Gulf	2.7 – 86.7	DouAbul (1984)
Arabian Gulf	3.5	Ehrhardt & Burns (1993)
Khor Al-Zuabir	36.8-478.2	Present study

Sediment

In the light of the above discussion it my thus be concluded that oil residues introduced to the Khor as a result of oil spill reside in water column for a relatively short time and that the area of greatest concern is sediment (both bottom and bank sediments) where a major fraction of the released oil is deposited and my remain for many years. The oil contents of the sediment at Khor, particularly the toxic aromatic fraction, were determined by fluorescence spectrophotometer. The levels of petroleum resident range from 2.07 at station 8 to 38.5 ug/g at station 4 as a dry weight sediment respectively (Table 1). However ,a great variation in the concentrations were absorbed between replicated which may be mainly due to the uneven deposition of oil and /or the variation in sediment logical parameters. Sediment containing 1 µg/L of oil residue is considered not polluted, that containing between 1 and 100 µg/L as moderately polluted, while that containing 100 µg/l dry weight as highly polluted. Khor sediment lies in the second category. The present data were within the early data in the same area, and in the range of concentrations in sediment in other site of the world. (Table 3).

Table (3): Comparison of petroleum residues in polluted sediment measured spectrofluorometrically in different area

Location	Concentration µg/g	References
Bay of Cortiou (France)	480 – 9166	Marchand et al., (1988)
Gulfe of Lion	3.0 – 420	Marchand et al., (1988)
Bay of Marseilles	132	Marchand et al., (1988)
Tyne River (U.K)	53 – 750	MAFF(1992)
Mersey River (U.K)	1.1 – 240	MAFF(1992)
Shatt Al-Arab & NW Arabian Gulf	2.46-38.33	Al –Saad (1995)
Shatt Al- Arab & NW Arabian Gulf	0.4 – 40	DouAbul et al., (1984)
Kuwait*	1 – 291	Zerba (1985)
Bahrain*	20 – 103	Fowler *et al*., (1993)
UAE*	0.10 – 1.7	Fowler *et al*., (1993)
Oman*	0.2 – 30	Fowler *et al*., (1993)
Kuwait	13	Fowler *et al*., (1993)
Saudia Arabia	62 – 1400	Fowler *et al*., (1993)
Bahrain	6.0 – 14	Fowler *et al*., (1993)
UAE	5.7	Fowler *et al*., (1993)
Oman	1.0 – 12	Fowler *et al*., (1993)
Saudia Arabia	13 – 540	Ehrhardt & Burns (1993)
Mediterranean	82 – 122	Ehrhardt & petrick (1993)
Khor Al-Zubair	2.07-38.5	Present study

Biota

This aseptic is particularly complex in view of the great diversity of plant and animal life in inland water and the variation in the effects due to a large number of factors including the type and amount of oil, the degree of weathering, the climatic conditions prevailing, river hydrology, the clean up response and the time of the year. It should also be emphasized that the precise cause of observed effects may very difficult to identify and will in most cases be due to a combination of factors, not necessarily all related to the oil spill. The toxic effects of the spilled oil are associated mainly with low boiling components (light ends). The solubility of these components and there initial concentration in many oils is not very great. In addition, they tend to be the component lost most rabidly from spilled. Petroleum hydrocarbons are characterized by their very low water solubility, high lipid solubility and high lipid/water partition coefficient; thus, aquatic organism can accumulate in these contaminants. The oil spill incident in Khor Al-Zubair had led us to suspect that there might be a risk of ecological effects on the dwelling in the Khor area. We have chosen beyah (*Liza subviridis*), and sheka *Thryssa mystax* which are the most common species of fish in this region, also two species of shrimp which are *Metapenaeus affinis and Exopalaemon styliferus* with plant samples *salicornia herbacea.* The concentrations of petroleum hydrocarbons in fish tissues range from 17.5 ug/g dry weight in *Liza subviridis* to 59.46 in *Thryssa mystax* , while in shrimp the concentration range from 55.66 ug/g dry weight in *Metapenaeus affinis* to 121.90 in *Exopalaemon styliferus* and in plant samples were 360 ug/g dry weight (Table 4).

Table(4): Concentrations mean of petroleum hydrocarbons (ug/g) residues in fish, shrimps and plants samples from Khor Al-Zubair

Organisms	Species	Hydrocarbons con. (ug/g)
Fish	*Liza subviridis*	17.5
	Thryssa mystax	59.46
Shrimps	*Metapenaeus affinis*	121.9
	Exopalaemon styliferus	55.66
Plants	*Salicornia herbacea*	360.7

The variations in concentration in fish and shrimp samples may be due to the huge flushing volume of Khor Al-Zubair, and due to rapid metabolism of petroleum hydrocarbons (detoxification mechanism) which allows effectives removal of these compound from the tissues.

In the light of the analysis of oil spill samples of Khor Al-Zubair we can conclude that this spill may be affected by many factors, and we can summaries these factors as fellows:

1-Physical movement, including oil drift by currents and spreading of an oil slick is the principle process determines the fate (over bank deposition) of oil spilled to Khor at the first few hours.

2-Evaporation is responsible for the removal of the low molecular weight component. This process is though to be an important weathering mechanism in the rather arid climate of Iraq. However, evaporation was not effective in the case of medium to high molecular weight hydrocarbons which survived the hot summer season.

3-Another significant process governing the fate of the spill is dispersion .It is important may be comprehended in the view of the fact that the fast moving of water carries tremendous amounts of suspended particulate matter. Dispersion is further enhanced by the prevailing winds.

4- Emulsification is also effected by turbulence, thus it must be an important weathering process of a khor spill. This process is temperature depended and thus it particularly important in Iraq.

5-Sedimentation via over bank deposition and /or Khor settlement is one of the principle processes responsible for moving of oil from khor water.

6- Due to intensive solar radiation, it was anticipated that photo-oxidation is an important process in studying the fate of spilt oil to Iraq waters.

7-Although, favorable conditions are available for bacteria to degrade oil in khor,

8-Tar lump formation is another process that require sufficient time span that is not warranted. it should be kept in mind, however, that environmental conditions favorable for such a process are available in Iraq.

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دراسة حالة بقعة الزيت الطافية في خور الزبير

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المستخلص

في الثاني والعشرين من أب لعام 2006 حدث اصطدام للناقلة بي اف سي 2 في منطقة خور الزبير حيث كانت تحمل مايقارب 4200 طن من نفط خام البصرة مما أدى إلى حدوث شق بطول 1.5 متر في غرفة المضخات للناقلة وانطلاق من 10- 15 طن من النفط الخام مكونة بقعة نفطية كبيرة في المنطقة. قدرت التراكيز الكلية للهيدروكربونات النفطية في عينات من المياه والرواسب وبعض الأنواع من الأحياء (أسماك وروبيان ونباتات). سجل أعلى تركيز للهيدروكربونات النفطية الكلية في المياه (478.2 مايكروغرام/ لتر) وفي الرواسب (38.5 مايكروغرام/غرام). كما ارتفعت هذه التراكيز ليصل أعلاها في الأسماك (59.46 مايكروغرام/غرام في Thryssa mystax) والروبيان (121.9 مايكروغرام/غرام في Metapenaeus affinis) والنباتات (360.7 مايكروغرام/ غرام في Salicornia herbacea). أظهرت نتائج الدراسة الحالية ارتفاعاً في تراكيز الهيدروكربونات النفطية الكلية أعلى من تلك التي سجلت في نفس منطقة ومناطق أخرى من العالم.