

## Study of Oil Pollution Levels in Sediment of the Umm- Qasr and khor Al-Zubair ports.

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### Abstract

The study area in this paper which represented by Umm-Qasr and Khor Al- Zubair ports are located in Southern Iraq could be effected by Various kinds of pollutants resulting from different sources. These may have severe impact on the water quality of these ports and eventually upon living aquatic organisms. Therefore, it is important to determine the total concentration of petroleum hydrocarbons TPHs. Oil concentration in the sediment collected, from July 2010 to April 2011at eight stations (3 sites within Umm Qasr Port and 5 sites within Khor Al- Zubair ports). Spectrofluorometric method has been adopted to measure the TPHs. The measured concentrations of oil in this study ranged between 10.12 - 20.5  $\mu\text{g/gm}$ .

It was suggested that 10  $\mu\text{g/l}$  indicate concentration of marine life with oil.

### الخلاصة

التلوث النفطي هي من اكثر المشاكل السائدة في البيئة. ولها تأثير شديد على نوعية مياه الموانئ وهي بنهاية المطاف لها تأثير على الكائنات المائية التي تعيش فيها, ولهذا السبب وجد من الضروري تقدير كميات النفط في الرواسب لكل موقع من مواقع الدراسة.

تمثل موقع الدراسة في هذا البحث بمينائي ام قصر وخور الزبير, وتم قياس تراكيز الهيدروكربونات في الرواسب لمواقع مختلفة ضمن منطقة البحث في اب من العام 2011م, وقد تم تحليلها بواسطة جهاز الفلوروفوتوميتر. تراوحت تراكيز النفط المقاسة في هذه الدراسة بين 10.12 و 20.5 مايكروغرام/غرام, وكانت ضمن النتائج التي نشرت لدراسات سابقه في نفس هذه المواقع والدراسات التي أجريت في مواقع عالمية اخرى.

## Introduction

The biggest spill occurred during the 1991 Arabian Gulf War, when about 240 million gallons of oil spilled from the oil terminals and tankers off the coast of Saudi Arabia. When oil is spilled into the sea it undergoes a number of physical and chemical changes, some of which lead to its removal from the sea surface, whilst others cause it to persist. Oil, when spilled at sea, will normally break up and be dissipated or scattered into the marine environment over time. This dissipation is a result of a number of chemical and physical processes that change the compounds that make up oil when it is spilled. The processes are collectively known as weathering. Oils weather in different ways. Some of the processes, like natural dispersion of the oil into the water, cause part of the oil to leave the sea surface, while others, like evaporation or the formation of water in oil emulsions, cause the oil that remains on the surface to become more persistent. The way in which an oil slick breaks up and dissipates depends largely on how persistent the oil is. Light products such as kerosene tend to evaporate and dissipate quickly and naturally and rarely need cleaning-up. These are called non-persistent oils. In contrast, persistent oils, such as many crude oils, break up and dissipate more slowly and usually require a cleanup response. Physical properties such as the density, viscosity and pour point of the oil all affect its behavior. The time this takes depends on a series of factors, including the amount and type of oil spilled, the weather conditions and whether the oil stays at sea or is washed ashore. Sometimes, the process is quick and on other occasions it can be slow, especially in sheltered and calm areas of water. Pollution of waterways of Umm Qasr and Khor Al- Zubair Channel by petroleum hydrocarbons are expected to occur through different operations: land based discharges, atmospheric and natural inputs

(GESAMP, 1993)., as well as activities of human beings which comprise discharged through municipal and industrial wastes, urban and river runoffs. Moreover, the area of Umm Qasr and Khor Az Zubair channel is affected by petroleum hydrocarbons pollutants from fixed installations like Al-Shuaibah refineries, offshore production facilities, loading terminals, etc. (GESAMP, 1993). Untreated municipal and industrial wastes discharged into the lagoons, along with inputs of petroleum from oil spills and motorboat traffic, have severely compromised the relative health of the Venice ecosystem (Al-Saad.,1995, 1997). Petroleum hydrocarbon inputs into the marine water were computed, based on various databases into four categories. These include a) natural seeps, b) extraction of petroleum, c) transportation of petroleum, and d) consumption of petroleum (Al-Saad, 1998). In order to further pinpoint the source of these discharges.

### The aim of study

Given the importance of the major ports of Umm Qasr and Khor Al-Zubair, who are among the most important waterways Iraqi and uses extensive in recent times to transport goods, navigation and fishing so it was important to study the quality of water and hydrocarbons, the impact of that spill forth.

### Description of Study Area

Umm Qasr and Khor Al- Zubair are the main targets of this project. The study area is located between (40° 51' – 47°53') East and (30°12' – 30°13') North as shown in Image (1). Khor Al- Zubair is an extension of the Arabian-Gulf waters in the lower reaches of Mesopotamia. It has an approximate length of 42 km, a wide of 1 km at low tide, and an average depth of 10-20 m. The lower (South) end is connected with Khor Abdullah .The topography of Khor Al- Zubair looks like a spindle with tapering ends, at the northern

and southern ends. The northern end receives freshwater influx of average 700 m<sup>3</sup>/sec throughout the tidal cycle. The current in the Khor is characterized by one directional throughout the tidal cycle towards the southern end (Arabian Gulf), with a 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<sup>3</sup>/sec with a velocity range of 0.8-5.78 m/sec. [4], with big tidal range at Umm-Qasr reaching 4.3m. Due to the low profile of the shore-line, the tidal floods penetrate the mudflats to a further distance, depending on the state of the tide, covering the halophytic vegetation.



**Image (1): Satellite Image of sampling Location.**

## Material and Methods

### 1-Sampling

The sampling area covers 3 sites within Umm Qasr Port and 5 sites within Khor Al- Zubair ports. Table (1) shows the geographical positions of the sampling sites. The samples were taken in July 2010 to April 2011, using 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 – 20 C°. Before analysis, sediment samples were freeze-dried, ground finely in agate mortar

and sieved through a 62µm metal (stainless- steel) sieve.

### 2- Extraction of oil

The extraction and clean-up procedure for the determination of petroleum hydrocarbons in the sediment was based upon that of UNESCO(1976). Sediment was placed in a pre-extracted cellulose thimble and soxhlet extracted with 150 ml methanol: benzene (1:1) mixture for 24 hours. 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

about 10 ml in a rotary evaporator. It was then saponified for 2 hours 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 by a stream of N<sub>2</sub> for UVF analysis.

### 3- Measurement of oil contents in sediments by Fluorescence method

The residue was dissolved in aromatic free n - hexane (checked by fluorescence analysis) and transferred quantitatively into 5 ml volumetric flask from the volumetric flask a sample of the extract dissolved in n-hexane. Aliquots of the hexane solution of the sample were pipettes to in a Teflon capped 1 cm silica fluorescence cell. The basic quantitative measurements were made by measuring emission intensity at 360nm with excitation set at 310nm and

monochromator slits of 10 nm .All blanks, standards and samples were run at identical instrumental conditions. For this work a Shimadzu RF-450 spectrofluorometer equipped with a DR-3 data recorder and Quartz cell 1 cm path length were used.

### 4- Background test (blank)

Strenuous efforts were made to minimize contamination of the samples, which would otherwise yield erroneous result. Throughout of the procedure great care was taken to ensure that samples were not being contaminated; for example avoiding unnecessarily exposure of the samples, the solvent or the final extract to the atmosphere or other potential sources of contamination. 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.

**Table (1) Sampling sites, Names and positions.**

<i>Sampling Point No.</i>	<i>Sampling Point Name</i>	<i>East (E)</i>	<i>North (n)</i>
S-01	Umm Qasr	47° 55' 47.65"	30° 03' 40.98"
S-02	Umm Qasr	47° 56' 22.08"	30° 03' 03.23"
S-03	Umm Qasr	47° 56' 45.06"	30° 02' 34.91"
S-04	Khor Al-Zubair	47° 57' 27.42"	30° 03' 00.95"
S-05	Khor Al-Zubair	47° 57' 07.99"	30° 04' 53.05"
S-06	Khor Al-Zubair	47° 54' 48.67"	30° 07' 19.78"
S-07	Khor Al-Zubair	47° 53' 56.82"	30° 09' 41.70"
S-08	Khor Al-Zubair	47° 52' 46.73"	30° 12' 21.82"

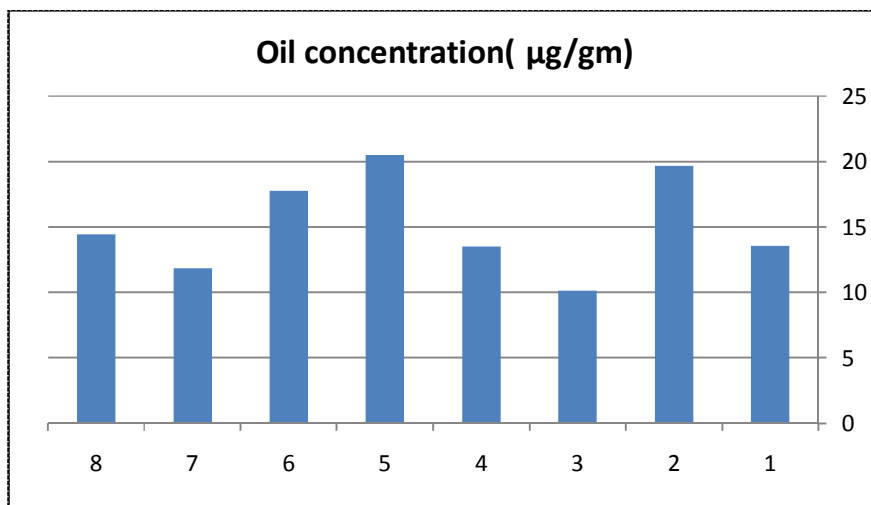
## Result and Discussion

where as the concentrations of the oil in these samples were determined using spectrofluorometer. The mean

concentrations of oil in the sediment ranged from 10.12( $\mu\text{g}/\text{gm}$ ) at station (3) to 20.50 ( $\mu\text{g}/\text{gm}$ ) dry weight at station (5) (Table 2, Fig.(1).

**Table (2): Oil concentrations for sediment in different stations**

<i>Station</i>	<i>Oil Concentration( <math>\mu\text{g}/\text{gm}</math>)</i>
1	13.53
2	19.66
3	10.12
4	13.48
5	20.5
6	17.76
7	11.84
8	14.44



**Fig. (2) Variation in Oil concentration ( $\mu\text{g}/\text{gm}$ ) in sediment**

Because petroleum is a mixture of hundreds of different hydrocarbon compounds, the composition of petroleum products released into the environment is variable. <sup>[6]</sup> Also the origin of hydrocarbons in sediments are biogenic, bio-synthesized by living organisms and anthropogenic due to oil pollution.

Exegetic hydrocarbon compounds may be released in environment during metabolism or death of the marine organism; these are calculated as 1-10 million tons per year. Moreover the area of Umm Qasr and Khor Al-Zubair channel is affected by petroleum hydrocarbons pollutants from fixed installations like Al-Shuaibah refineries,

offshore production facilities, loading terminals, etc [7]. Untreated municipal and industrial wastes discharged into the lagoons, along with inputs of petroleum from oil spills and motorboat traffic, have severely compromised the relative health of the Venice ecosystem [8&9]. Hydrocarbons in the water body could be associated with sediments and accumulated in 0-20 cm layer in the bottom soil along the water body. 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. Particulate material plus the adsorbed oil will be deposited it at the Khor bank or sink to the bottom as the water current is

reduced in speed. Such considerable movements of water masses have a great transport capacity, resulting in dilution oil with the speed from the source of spill to a negligible amount down the Khor. Hydrocarbons may be carried to the sediments adsorbed onto clay and silts which settle out of the water column [10&11]. Sediment containing 1 µg/g of oil residue is considered not polluted, that containing between 1 and 100 µg/g is moderately polluted, while that containing 100 µg/g dry weight is highly polluted. Khor sediment lies in the second category. The present data were within the ranged of 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 estimated by fluorescence spectroscopy in different area.**

Location	Concentration (µg/g)	References
Falmouth Bay (UK)	48.0	[11]
Carmarthen Bay (UK)	34.0	
Liverpool Bay (UK)	29.0	
Coast of Oman	0.8 - 19.0	[12]
Gulfe of Lion	3.0 - 420.0	[13]
Bay of Marseilles	132.0	
Saudia Arabia	13.0 - 540.0	[14]
Mediterranean	82.0 - 122.0	[15]
Saudia Arabia	62.0 - 1400.0	[16]
NW Arabian	0.4 - 40.0	[17]

Gulf		
Shatt Al-Arab river	2.6 - 44.0	
Khor Al-Zubair	3.5 - 5.0	
Shatt Al-Arab river	3.7 - 26.0	[18]
Shatt Al-Arab river	8.5 - 38.3	[19]
NW Arabian Gulf	2.5 - 10.7	
Shatt Al-Arab river	9.7 - 38.0	[20]
Khor Al-Zubair	21.0 - 178.0	[21]
Shatt Al-Arab river	28.8 - 275.4	[22]
Shatt Al-Arab river	59.5 - 148.4	[23]

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