

Riverine Field Oil Spill Experiment

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Abstract

This study concern the case of oil spill in the river Shatt al-Arab- site (Muftia) to understand the environmental conditions affecting during the case of oil spill accident.

It was found that there is privacy in such environment, during exposure to spilled oil, considering that such areas are characterized by high water temperature, long day light, And a special bacterial activity.

To understand such circumstances affecting the spilled oil. A gas liquid chromatography technique was used by selection the n-alkanes in this crude oil, the analysis of their n-alkanes reduced in concentration from 370-93 ug/g in crude oil before spill to 12.00 ug/g after 164 days of spill oil by 96.77% removal.

التجربة العراقية لدراسة التسربات النفطية في الانهار

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المستخلص

تم دراسة حالة التسربات النفطية في نهر شط العرب- موقع المفتية لفهم الظروف البيئية المؤثرة اثناء حالة تسرب النفط في حالة الحوادث حيث تبين ان هنالك خصوصية في مثل هذه البيئات اثناء تعرضها للنفط المتسرب باعتبار ان مثل هذه المناطق تتميز بفترات ضياء طويلة ودرجات حرارة عالية ونشاط بكتيري مميز .

لفهم مثل هذه الظروف المؤثرة على النفط المتسرب تم استخدام تقنية الغاز- سائل - كروماتوغرافي واختيار جزء الالكانات المتواجد في النفط حيث تناقصت تراكيزها من ٣٧٠,٩٣ ميكروجرام/جرام في النفط الخام قبل التسرب الى ١٢,٠٠ ميكروجرام/جرام بعد مرور ١٦٤ يوم على حالة التسرب النفطي .

Introduction

Oil production, transportation and uses are heavily in the coastal regions and pollution therefore predominately affects the surface waters of the rivers, Photo-oxidation and biodegradation are the two most important factors involved in the transformation of crude oil or its products that are released into the environment. Natural microbial populations in seawater biodegraded 28% of crude oil within 8 weeks at 20 C when sufficient nutrients were supplied to the sea water. It is concluded that susceptibility of crude oil to biodegradation is increased by its photo oxidation (Dutta and Harayama,2000)

The smaller day to day spills in the coastal waters and harbors produce chronic pollution that is much is larger in total volume and probably more severe in biological consequences.

Just after an oil spill on water, the major weathering factor acting on the oil is evaporation. Later, depending on the physical and chemical properties of the oil and on the environmental conditions (Regnier et.al., 1975).

The fate of oil in fresh water ecosystems in general and riverine oil Spills is scarcely investigated; the study by DouAbul and Al-Asadi (1990) was directed to understand the weathering of stranded oil deposited over river banks.

Local out door experiment study the changes of physico-chemical which alter the oil components was done by Al-Timari and Al-Imarah (1996).

Quantitative information on the weathering of spilled oil is essential to a fuller understanding of the fate and behavior of oil in the environment. Such data is also useful for spill modeling.

The composition and concentration changes of key components such as alkane were quantitatively correlated to evaporative loss.

Two opposing effects during evaporation-one is the loss of oil components due to evaporation, and another is build-up of oil components due to volume deduction-were examined.

So-called "pattern recognition" plots and these permitted deduction of a best of values for quantitation of exposure to evaporative weathering (Wang and Fingas, 1995)

But it Although the experimental spill in this study are small (2 barrels), its adequately represent for a chronic oil pollution in the region has dual objective for developing the methodology for investigating the fate of aliphatic hydrocarbons in a slick and for obtaining data on the rate of loss under natural environmental conditions.

Experimental Spills

It is interest to investigate the rates of disappearance of specific aliphatic components of crude oil slicks under natural conditions.

The site selected for the deployment booms is Al-Moftia oil Terminal pier. This area was chosen because it represents a possible source of oil spill and served as the base of operations for the experiment.

Two pieces of Covalca oil booms deployed in a chosen site, two barrels of Basra crude API (33.9) was spilled and field observation was done, weathering of crude oil through nC25 was determined by capillary gas chromatography following method described by DouAbul & Al-Asadi (1990).

Oil samples from surface were collected by immersing glass test tube to a depth of 5 cm below the surface slicks then removed slowly.

Comparison of chromatograms of the surface slicks with the original oil shows weathering and alternations that occur in the above carbon range. For this purpose a perkin-Elmer Sigma 300 capillary gas chromatography was equipped with flame ionization detector (FID) and a split-split less mode injection port.

Quantification of peaks and identification of hydrocarbons in chromatograms was achieved by a perkin-Elmer computing integrator (model LC 1-100).

The fused silica capillary column used was a wall coated open tubular (WCOT) 50X0.25 mm i.d.SE30 (methyl silicon).

Helium was employed as a carrier gas with a liner velocity of 75cm/s and a split ratio of 100/1, operating temperature for detector and injector was 350 C° and 300 C° respectively.

The column oven was operated under temperatures programmed conditions (2C/min) from 120 C° to 280 C° with an isothermal period (30 min) at the end.

Results & Discussion

Only few oil spill testing has been conducted out side of test tanks and realizing the limitation of such kind of experiments, a large scale oil spill experiment was done to understand the behavior of oil under natural circumstances.

GLC and capillary GLC using flame ionization detector (FID) have been used to investigate a multitude of naturally occurring and simulated oil spills depending primarily upon comparisons of n-alkane and isoprenoid (Van Vleet, 1984).

Although these approaches met with various degrees of success, more volatile components cast suspicion on the usefulness some of these techniques.

Fig.(1) illustrate losses of lower boiling components in Basra crude oil analyzed by capillary GLC which represent weathering processes that have take place after the spill.

Table (1) shows the results of n-alkane in crude oil from nC9 to nC25 with total 370.93 ug/g. This concentration was reduced by weathering through the experiment to 14.44 ug/g after only 30 minutes with a minimum value of 12.004 ug/g was observed after 82 days of exposure, then after 164 days of exposure the alkane level of 20.979 ug/g.

The loss represents 96.10% of the initial crude oil concentration once spilled and reduced to 94.34% after 164 days of the experiment, this removal in agreement which obtained from out door experiment in which the loss removal reached to 85.24% (Al-Asadi, 1996). The relative importance of the numerous weathering processes is influenced greatly by composition of spilled oil and the environmental factors such as turbulence and temperature (Gordon et.al., 1976).

The degradation pattern and rate of biodegradation were found to be dependent on the oil concentration and on the presence of nutrients. Faster rates were observed at lower oil

concentrations, while the addition of nutrients greatly slowed the degradation of PAHs and enhanced the degradation of the saturates (Fayad & Overton, 1995) and this study had also shown that the use of C17/pristine and C18/phytane ratios may underestimate the magnitude of oil biodegradation in the presence of micro-organisms. There is a need to monitor the changes in both saturates and aromatics hydrocarbons in order to assess the biodegradation of spilled oil. If changes in in one fraction were monitored, perdition of the effect on the other fractions of oil could not be made.

Prisatne/Phytane ratio (Pr/Ph) range from 1.333 to 0.576 after 82 days which is a good indicator for the high rate weathering for the spilled oil.

It is important to distinguish between patterns of distinct oil composition due to biodegradation, which is significantly different

From the pattern due to physical or short-term weathering, the oil composition changes due to biodegradation can be readily differentiated from those due to physical weathering (wang et.al.,1998).

The observation of individual boom performance in this experiment is within the requirement which needed for oil-holding capacity to protect water intakes in the Shatt Al-Arab River which meet some problems from oil transport activities.

Also, these field data can be used to calibrate verification of laboratory experiment. The parameters used in identification of oil spill have to be independent of weathering (Grimalt & albaiges,1982). The analysis of crude oil under field conditions for this long period (more than 5 months) show the weathering mechanism which modify the distribution of alkane of the spilled oil in the aquatic environment.

Although alkanes are not particularly useful for determining the sources of the spill, they can give some information on the degree of weathering (wang et al., 2011)

This paper described an analytical approach using hydrocarbon distribution pattern recognition and diagnostic ratios of source-specific marker

compounds for the characterization of chemical composition and source identification of the spilled oil in the shatt Al-Arab river environment.

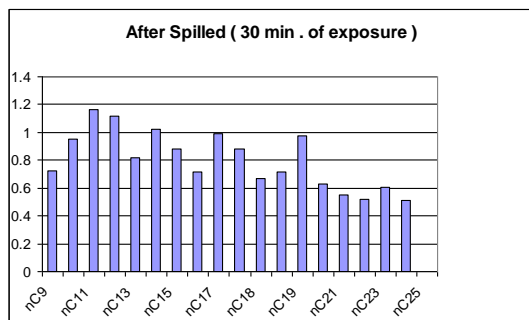
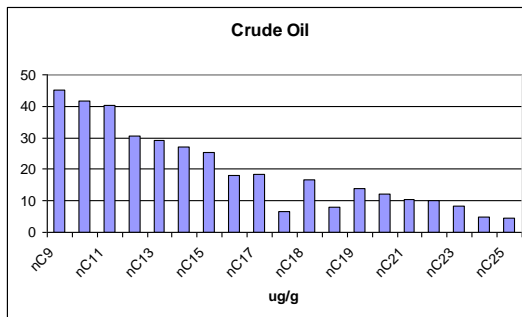
So, these data play an important role for preparing the oil print tool for this unique environment to

assess the degree of oil pollution which reached and it is possible to modulate these data to predict the fate of spilled oil.

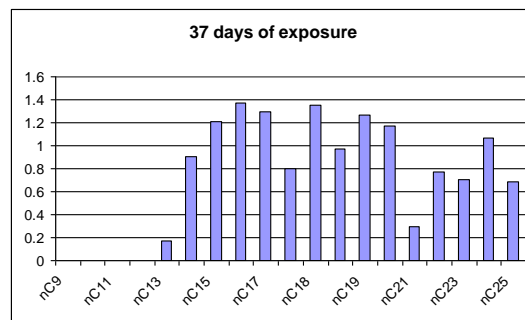
Table (1) variation of normal alkane –relative concentration for crude oil during field experiment

| Normal alkanes + isoprenoids | Regular Basra crude oil (ug/g) | After spilled (30 min Exposure) | 37 days of Exposure | 82 days of Exposure | 164 days of Exposure |
|------------------------------|--------------------------------|---------------------------------|---------------------|---------------------|----------------------|
| nC ₉ | 45.025 | 0.723 | N.D | N.D | N.D |
| nC ₁₀ | 41.511 | 0.954 | N.D | N.D | N.D |
| nC ₁₁ | 40.230 | 1.163 | N.D | N.D | N.D |
| nC ₁₂ | 30.505 | 1.113 | N.D | N.D | N.D |
| nC ₁₃ | 29.112 | 0.819 | 0.167 | N.D | N.D |
| nC ₁₄ | 27.252 | 1.020 | 0.908 | N.D | N.D |
| nC ₁₅ | 25.230 | 0.881 | 1.214 | 0.504 | 0.309 |
| nC ₁₆ | 18.190 | 0.718 | 1.370 | 0.951 | 0.649 |
| nC ₁₇ | 18.390 | 0.992 | 1.295 | 1.158 | 1.577 |
| Pristane (pr) | 6.717 | 0.881 | 0.801 | 0.603 | 1.132 |
| nC ₁₈ | 16.512 | 0.667 | 1.353 | 1.224 | 1.943 |
| Phytane (ph) | 7.822 | 0.714 | 0.970 | 1.046 | 0.956 |
| nC ₁₉ | 13.910 | 0.976 | 1.270 | 1.69 | 2.002 |
| nC ₂₀ | 12.112 | 0.630 | 1.175 | 1.140 | 1.211 |
| nC ₂₁ | 10.501 | 0.549 | 0.298 | 0.978 | 2.791 |
| nC ₂₂ | 10.151 | 0.522 | 0.772 | 0.793 | 2.537 |
| nC ₂₃ | 8.205 | 0.609 | 0.703 | 1.014 | 4.757 |
| nC ₂₄ | 4.990 | 0.511 | 1.065 | 0.865 | 0.713 |
| nC ₂₅ | 4.565 | - | 0.685 | 0.559 | 0.402 |
| Total | 370.93 | 14.444 | 14.046 | 12.004 | 20.979 |
| Pr./Ph.ratio | 2.351 | 1.333 | 0.825 | 0.576 | 1.184 |
| ∑nC odd | 195.168 | 6.712 | 5.632 | 5.903 | 11.838 |
| ∑nC Even | 166.218 | 6.135 | 6.643 | 4.973 | 7.053 |

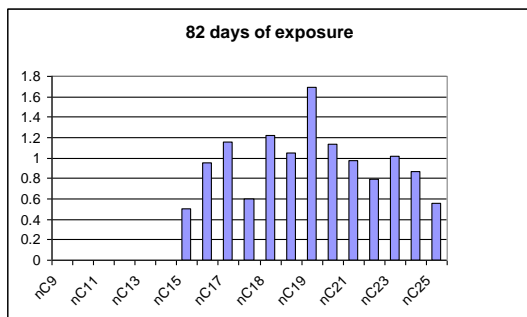
N.D. Below the detection limit



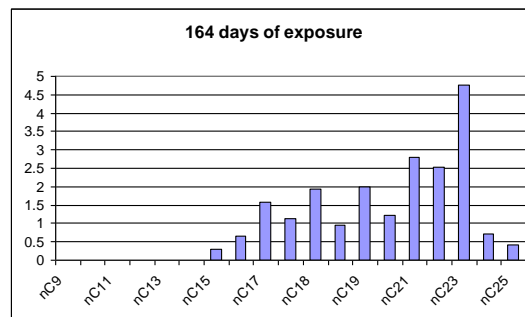
96.10 %Alkane removal



96.21 %Alkane removal



96.76 %Alkane removal



94.34 %Alkane removal

Fig.1 show weathering of crude oil during the field experiment

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