Chemosphere, Vol.16, Nos.2/3, pp 381-394, 1987
Printed in Great Britain

0045-6535/87 $3.00 + .00
Pergamon Journals Ltd.

LONG TERM IMPACT OF DISSOLVED DISPERSED PETROLEUM HYDROCARBONS (DDPH) IN GULF OF ISKENDERUN

Ilkay SALIHOGLU, Cemal SAYDAM and Aysen YILMAZ

METU Institute of Marine Sciences

P.K.28 Erdemli,Içel-TURKEY

ABSTRACT

DDPH in sea water, polyaromatic hydrocarbons (PAH's) in sediment and in some marine biota were monitored for the period of August 1981 and April 1984. Maximum DDPH was measured in winter and minimum in summer. This phenomena showed an inverse relation with the sea water temperature. Increase in sea water DDPH concentration reflected itself immediately in fish liver but two months time lack between fish liver and flesh was observed.

GLC analysis results of sea water extracts and various crude oil showed that the petroleum hydrocarbons in the Gulf was mainly originated from Kirkuk crude oil.

INTRODUCTION

In recent years, petroleum pollution of the sea has become a global problem in the marine environment because of recovering, transportation and using oil. After a spill, petroleum and petroleum products enter the sea,it is subjected to changes. Physical, chemical and biochemical processes affect their dispersion and degradation. During the spill of oil on the sea,by sinking oil settle on the sea bed and pollute marine sediments. Hydrocarbon pollutants also, enter the marine food web and cause an increase in the long term toxicity 1. Investigation about the fate and effects of oil and measuring the quantity of petroleum hydrocarbons in the marine environment recently gain importance in the world 1.

Although, considerable work has been done in the NE Mediterranean, 2, in this work the Gulf of Iskenderun has been monitored in some detail, where in April 1982 about 8000 tons of crude oil entered the Gulf via Ceyhan River due to a crack in the pipeline carrying the oil from Iraq (Kirkuk) to the terminal in the Gulf.

MATERIAL AND METHODS

Instrumentation:

A Turner Model 430 Spectrofluorometer was used for the measurements of the concentration of DDPH in sea water and PAH's in sediment and in some marine biota. Samples were analyzed at 360 nm emission and excitation at 310 nm wavelength with a band width of 15 nm. Chrysene was used as a standard.

A Packard Model 428 and a Becker Packard Model 421 Gas Chromatography coupled with a Flame Ionization Detector (FID) was used for gas chromatographic measurements. Approximately 117 cm column coated with SE-30 (10% wt) was heated at 3-5^{o}C/minute from 60^{o}C to 270^{o}C with isothermal heating at the lower and upper temperatures. Nitrogen (~22 mls/min) was used as the carrier gas.

Reagents and Standards:

Analytical reagent grade n-Hexane ($C_{16}H_{14}$), Carbontetrachloride (CCl_4), Methanol (CH_3OH) and Benzene (C_6H_6) were used without any further purification for the preparation of samples and standards.

Sodium sulphate was activated at 600^{o}C overnight and it was used in order to homogenize the organisms samples.

Activated alumina (Al_2O_3) (90 Mesh size) was used for the removal of lipids from fish and sediment samples. Alumina activated at 120^{o}C for 6 hours.

Kirkuk Crude Oil (which had been obtained from Atas Refinery in Mersin) was used as the reference standard for the determination of the origin of petroleum.

Chrysene was used as a reference standard for the determination the amount of dissolved/dispersed petroleum hydrocarsons (by utilizing UV-Fluorescence spectrophotometer).

Sampling and Sample Preservation:

a) Sea Water: Samples were collected as far away as possible from the effect of the ship's exhaust and other contaminants. Samples were taken from a depth of 1 m from surface and transferred to dark glass bottles were analyzed as soon as possible. When they were not analyzed, then samples were stored with the addition of 50 ml carbontetrachloride at room temperature.

b) Marine Organisms: Some fish which died during petroleum pollution in April 1982 were collected by hand. A deep trawling net was used for collection of fish in the Gulf of Iskenderun. (Fish samples of the following species were chosen for analysis: Mullus barbatus, Solea solea, Epinephelus aeneus). Care was taken to have more or less the same size (thus the same age) of samples from each species. Flesh and liver of some samples were dissected and wrapped with aluminum foil and stored in a deep-freezer at -20°C until usage.

c) Sediment: Sediment samples were collected by using a Van Veen grap sampler and/or gravity corer and stored in a deep-freezer at -20°C in polyethylene container until usage.

Analysis of Sea Water:

2.8 l sea water samples were extracted with 100 ml carbontetrachloride by shaking them vigorously for 20 minutes. (Then samples were allowed 10 minutes to seperate into two phases). Then the organic phase was seperated and the solvent was removed by a slow rotary evaporation up to residue or to dryness at about 50-60°C.

The residue was dissolved in n-hexane and drawn into 5-10 ml volumetric flask. This solution was transferred to quartz cell for spectrofluorometric analysis and gas chromatographic analysis was performed later with the same extracts.

Analysis of Marine Organisms:

About 0.5-1 gram of fish liver and 2-3 grams of fish flesh were weighed (wet weight) and homogenized with sufficient amount of activated sodium sulphate in a mortar. The homogenate was extracted with 150-175 mls n-hexane in Soxhlet apparutus for 10 hours (for about 24 cycles). Then the extract was evaporated by rotary evaporator at 50-60°C up to dryness. The residue was collected with n-hexane into 5-10 ml volumetric flask and analyzed by spectrofluorometer.

Analysis of Sediment:

About 20-30 grams (wet weight) of sediment was weighed and Soxhlet extraction was performed for 10 hours with 1:1 (v/v) benzene:methanol mixture. The benzene phase was separated into a flask and the solvent was evaporated by using a rotary evaporator up to dryness. The residue was collected with n-hexane and this solution passed through the activated alumina column and analyzed by the aid of fluorescence spectropohometer.

RESULT AND DISCUSSION

Sea Water: The dissolved/dispersed petroleum hydrocarbons, DDPH, in the upper 1 meter of the Gulf of Iskenderun were monitored for the time period between August 1981-April 1984. During the monitoring period there has been a burst in the pipeline which carries Kirkuk crude oil to the Gulf. As a result considerable amount of (approximately 8000 tons) crude oil was introduced to the Gulf via Ceyhan River (Figure 1).

Since the monitoring has started before the incident, it was expected to see the immediate and after effects.

The measured DDPH concentrations in the Gulf is given in Table 1 and plotted in Figure 2. The feature of the Figure 2 is that the three minimum zones observed during 1981-1984 monitoring period all were in Aug-Nov period, (i.e. 1.40 ug/l in Aug.1981, 0.64 ug/l in Aug 1982). During winter and spring the measured DDPH concentrations increased to higher levels which were 3.79 ug/l in Feb. 1982, 3.88 ug/l in May. 1982.

This somewhat natural cycle has been disturbed by the pipeline accident and immediate effect can be seen by the existence of an average peak value of 25.2 ug/l DDPH concentration in surface

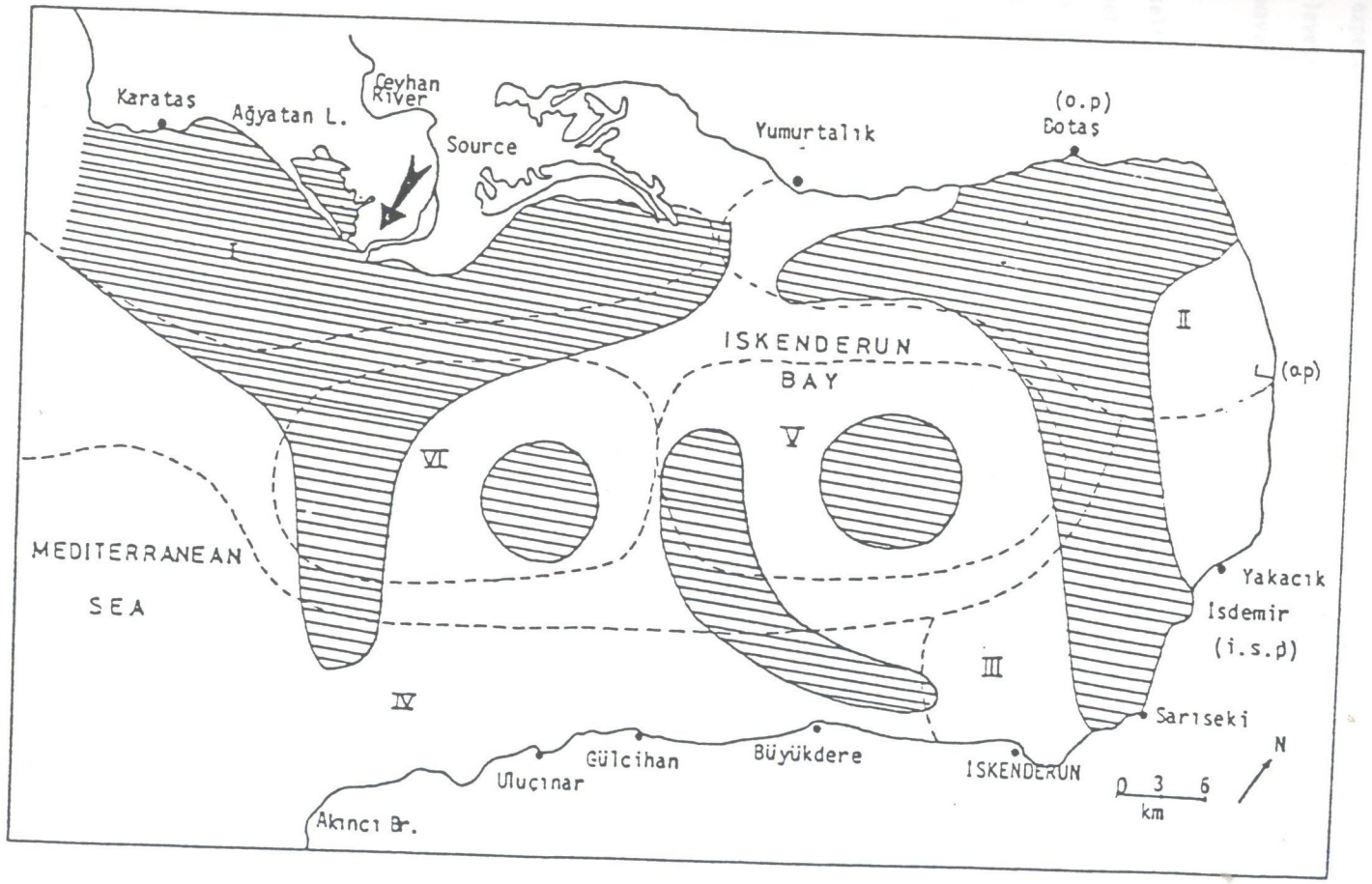

Figure 1: Observed Oil Slick Distribution in the Gulf of İskenderun (April, 27-May, 5, 1982)

o.p : Oil Pipeline Terminal

i.s.p: Iron-Stell Plant

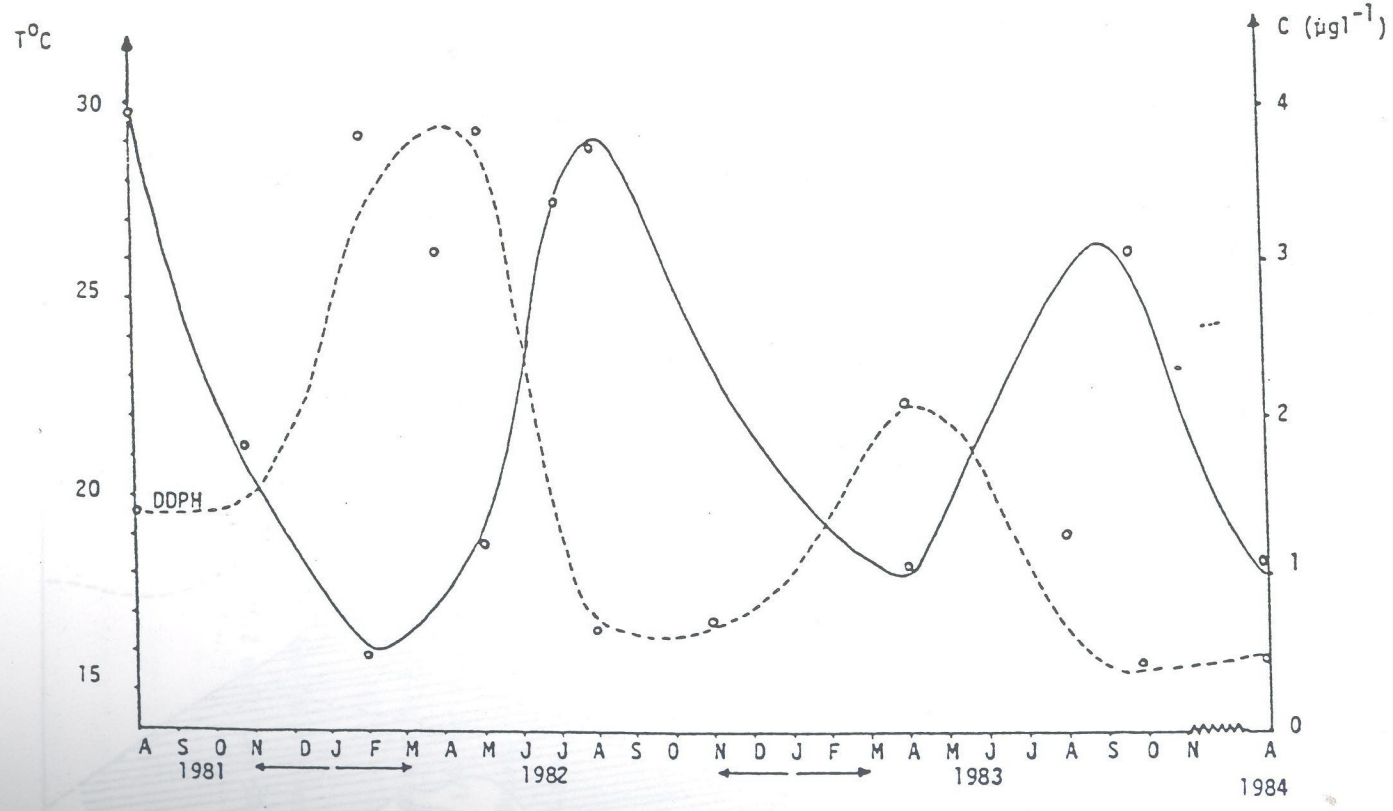

Figure 2: The Seasonal Variation of DDPH and Temperature in Sea Water in The Gulf of Iskenderun.

waters of the Gulf (Table 1). But still the average values did not increase well above the expected annual cycle. Even after this event the measured concentrations decreased to background levels again in Aug-Nov period (these variations in concentration depends on the fate of winds, waves, currents, water depth, temperature, salinity, organisms, nutrients and nature of oil).

It can clearly be seen from Figure 2 that temperature is the most critical factor in the self cleaning of the Gulf. It is known that evaporation is one of the most effective factor in petroleum spillages,3. There is an inverse relationship between temperature and DDPH concentration observed in sea water. This behaviour is due to the temperature effect on the weathering of the oil. A decrease in the temperature increases the solubility of the volatile components but decreases the solubility of the non-volatile components 4. Thus an increase in the temperature leads to a decrease in concentration of DDPH in the measured upper 1 meter column of sea water. Ofcourse, the exchange of water between the Gulf and the general Mediterranean currents also plays an important role during winter months.

Marine Organisms: Fish, living in petroleum contaminated environments, accumulates and excretes hydrocarbons. Thus fishing can be a problem in petroleum polluted areas since aromatic compounds tainting destroys the quality of edible fish. There is commercial fishing in the Gulf of Iskenderun.

Simultaneusly with DDPH in the Gulf of Iskenderun Mullus barbatus, Solea solea, and Epinephelus aeneus species were analyzed for petroleum hydrocarbons (Table 2). The monitoring period has started couple of months before the oil spillage to the Gulf. There was an increasing trend in the concentration of polyaromatic hydrocarbons, PAHs, both in liver and flesh samples of biological species during 1982 winter season.

The average concentration of PAH's in M.barbatus liver reached maximum values (Figure 3) in June and Aug. 1982, in S.solea liver concentration increased in July. 1982, in E.aeneus liver maximum concentrations observed in March and Oct. 1982.

The average PAH's concentration of M.barbatus flesh (Figure 4) had maximum value in March 1982 and S.solea and E.aeneus and maximum value in April, 1982, but concentrations decreased and then reached minimum value in October 1982 after the pipeline incident.

Table 1. The Mean Values of DDPH Concentrations and Their Range in Sea water in the Gulf of Iskenderun

Date	N	R	$\bar{x}$	: T°C (av)
Aug. 1981	8	0.7-1.9	1.40	29.84
Nov. 1981	7	0.7-3.7	1.44	21.36
Feb. 1982	22	1.1-11.8	3.79	15.90
Apr. 1982	14	0.8-11.2	3.14	-
May. 1982	22	0.8-25.2	3.88	18.85
July.1982	19	0.5-3.9	1.47	27.45
Aug. 1982	10	0.2-2.0	0.64	28.85
Nov., 1982	9	0.2-1.8	0.68	23.15
Apr. 1983	12	0.04-5.7	2.07	18.14
Aug. 1983	18	0.4-5.2	1.0	-
Oct. 1983	27	0.1-1.0	0.42	26.14
Apr. 1984	16	0.1-2.2	0.43	18.12

N; Number of samples analyzed R: Concentration Range (µg/l)

$\bar{x}$: Arithmethical Mean T°C: Temperature

Table 2. The Average Concentration of PAH's(µg/g) in Fish Samples in the Gulf of Iskenderun

Species	M. Barbatus		S. Solea		E.Aeneus	
Date	$\bar{x}$		$\bar{x}$		$\bar{x}$	
(1982)	L	F	L	F	L	F
Jan.	0.50	0.06	1.41	0.04	0.56	0.04
March	3.64	1.32	-	0.17	8.16	1.14
Apr	5.26	0.83	2.81	0.55	-	1.95
May	6.47	0.34	1.96	0.23	2.11	0.20
June	10.03	0.40	2.24	0.25	0.96	0.16
July	2.93	1.39	11.70	0.52	2.88	1.27
Aug.	14.86	0.52	9.41	0.51	2.48	1.22
Oct.	5.27	1.69	3.04	1.22	5.30	1.78
Nov.	1.87	0.20	1.44	0.14	2.40	0.59

$\bar{x}$: Arithmethical Mean L: Liver F: Flesh

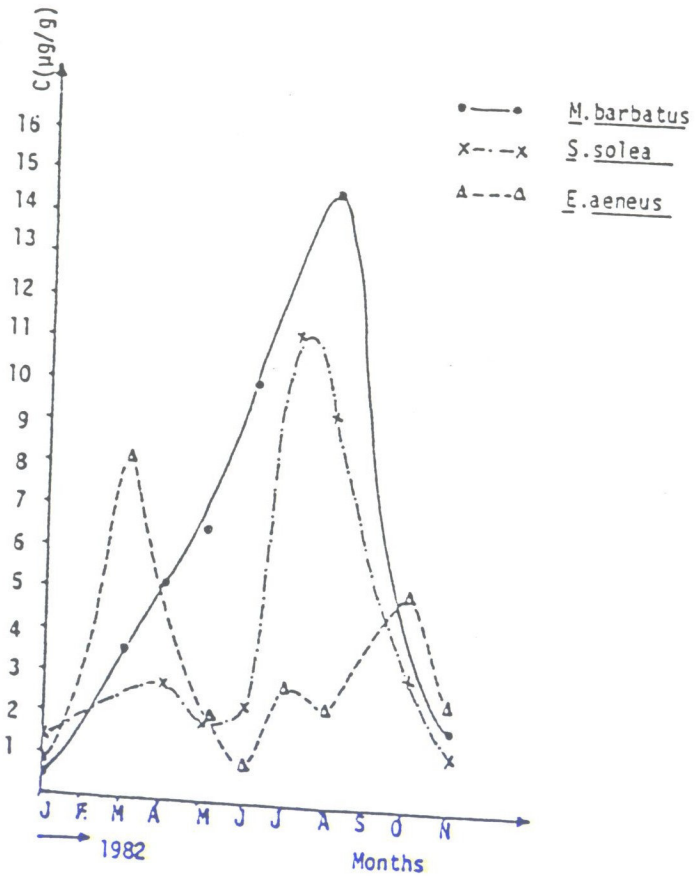

Figure 3: The Seasonal Variation of PAH's concentration in Fish Liver Extract

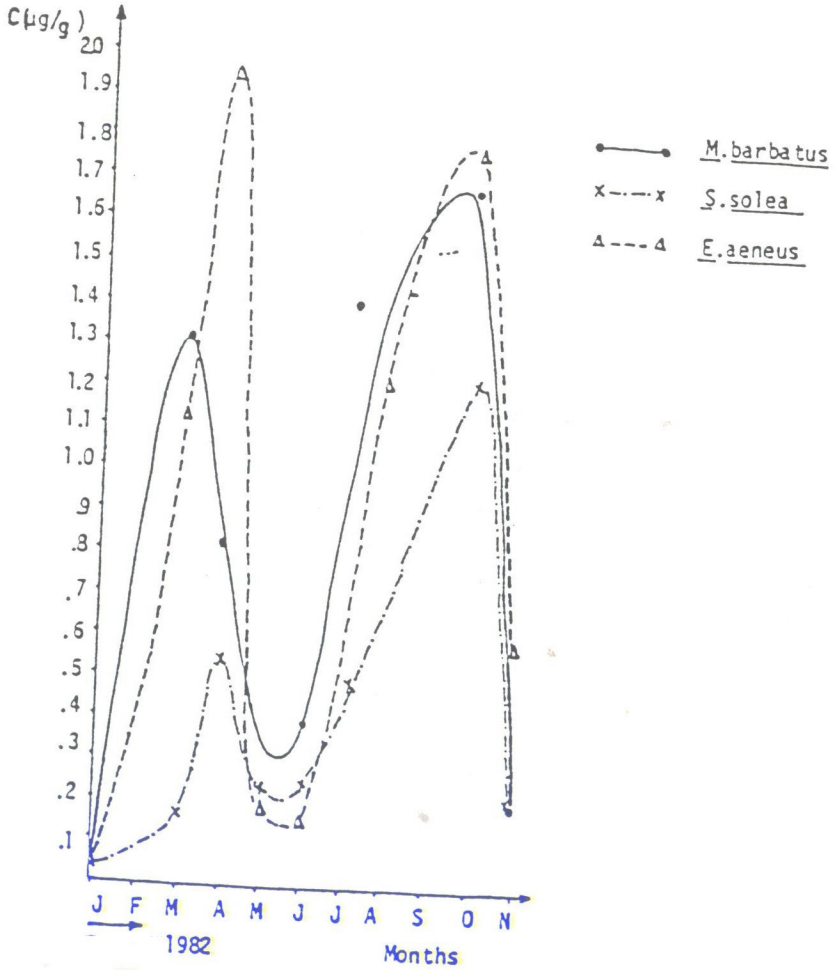

Figure 4: The Seasonal Variation of PAH's Concentration in Fish Flesh Extract

It is expected the increasing of the PAH's in liver observed before the increasing of PAH's concentration in flesh in marine organisms,5. Thus, the introduction of crude oil to sea water has shown its effect in liver samples after 3 months but approximately 5 months has elapsed before the maximum concentration has been reached (5 months passed after the accident fish flesh concentrations are affected). Rapid decrease in PAH's concentration in both liver and flesh samples shows that there must be some excretion mechanisms which becomes active to reduce the increased concentrations.

Sediment: The concentration levels of PAH's in sediments are given in Table 3 and the seasonal variations of PAH's concentration in sediments of Iskenderun Bay are shown in Figure 5. The PAH's concentration ranged in between 0.03 ug/g and 1.43 ug/g (wet wt) in the Gulf, the differences in concentration caused by the different locational effects, such as the presence of pipeline terminal, a huge iron and steel industry.

Limited number of sediment samples could shown the striking change of PAH's concentration after the pipeline incident in the Gulf, during 1982 sampling period the concentration of PAH's in sediments started to increase in April (Figure 5) and reached its maximum in June 1982. This abnormal increase in June, while the DDPH concentration in sea water were decreasing steadly, shows that after evaporation the crude oil residue sinks to the bottom and fraction of it clearly reached to the sediments. Some natural phenomena then decreases the levels to background again.

Gas Chromatographic Analysis: Typical gas chromatograms of sea water extracts are shown in Figure 6 and the gas chromatography results are given in Table 4.

The general pattern of n-paraffins between C_{10}-C_{35} was observed in almost all sea water samples. The paraffinic profile on most of gas chromatograms provides typical features of oil slicks 7.

The crude oil chromatograms usually start with n-C_9 or n-C_{10}; therefore in some locations samples were probably contaminated by oil slicks formed very recently because only low moleculer weight n-paraffins which are very volatile, were lost by evaporation and dissolution.

The n-C_{17} $Pr/_{n\text{-}C_{18}}$ Ph ratio of the samples changed between 1.0 and 1.4, averaging 1.2 which was the same value given by Kirkuk curde oil. Both the n-paraffinic patern and Pr/Ph values indicated a probable pollution from the pipeline terminals or tankers approaching the

Table 3. Average Concentrations of PAH's in Sediment Samples (µg/g, wet wt)

Date	$\bar{x}$
Nov. 1981	0.23
Dec. 1981	0.24
Feb. 1982	0.42
Apr. 1982	0.43
June 1982	1.12
July 1982	0.35
Sept. 1982	0.08
Apr. 1983	0.34

Table 4. Gas Chromatographic Analysis of Sea water Extract in the Gulf of Iskenderun

Regions	Date 1982	n-Paraffin Range	$n\text{-}C_{17}/n\text{-}C_{18}$ - / - Pr/Ph
I	Apr.27	C_{12}-C_{35}	1.1
I	July 5	C_{17}-C_{30}	1.4
II	Apr.27	C_{10}-C_{28}	1.3
II	Apr.27	C_{14}-C_{29}	0.9
II	July 5	C_{15}-C_{20} (T)	1.4
III	Apr.27	C_{13}-C_{35}	0.9
III	Apr.27	C_{15}-C_{33}	0.6
III	July 5	C_{16}-C_{30}	1.3
IV	Apr.27	C_{10}-C_{35}	1.0
V	Apr.27	C_{15}-C_{20}	1.0
VI	Apr.	C_{13}-C_{35}( )	1.2
Kirkuk C.O		C_{10}-C_{35}	1.2

N.D: Below the detection limit of the method (T): Small peaks

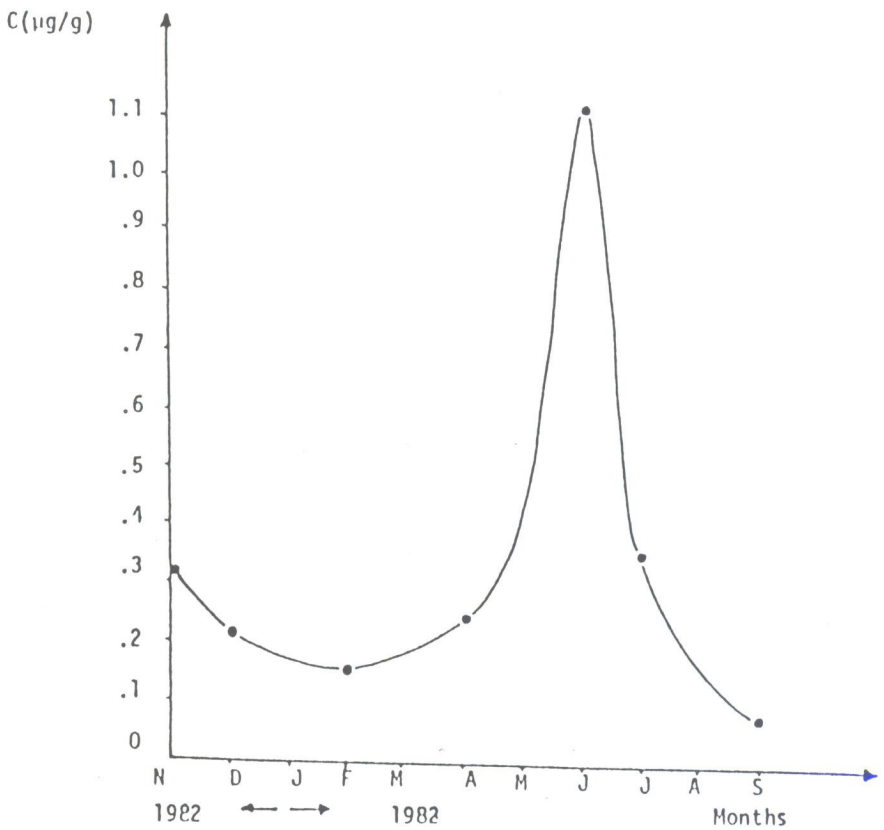

Figure 5: The Seasonal Variation of PAH's Concentration of Sediment in The Gulf of Iskenderun

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CONCLUSIONS

The three years monitoring of DDPH in sea water showed that the concentrations were at a minimum value in summer periods and reaches to maximum values in spring periods. A very sharp increase in concentration of DDPH in April 1982 was observed which is due to the pipeline accident, then a decay back to the background values in July-Aug. and Sept. 1982 was observed. Besides the effects of winds, waves, currents etc., especially the variation in temperature is the the main cause of the variation of DDPH concentrations in the sea water.

Petroleum hydrocarbon concentrations were found to increase in the fish liver 3 months after the pipeline incident and after 5 months in fish flesh.

Petroleum hydrocarbon concentrations of sediments from the Gulf of Iskenderun, first increased from April till June 1982 and then dropped down to the previous values measured in November 1981. Evaporation decreased the DDPH concentrations and caused sinking of the PAH's into the sediments.

The gas chromatographic analysis showed that petroleum pollution in sea water is originated from Kirkuk crude oil, when they were compared $n\text{-}C_{17}\,Pr/n\text{-}C_{18}\,Ph$ values.

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