# PETROLEUM HYDROCARBONS IN THE MARINE ENVIRONMENT

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MASTER OF SCIENCE
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TO MY MOTHER AND SISTER

# PETROLEUM HYDROCARBONS

# IN THE MARINE ENVIRONMENT

A THESIS PRESENTED
BY

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## ABSTRACT

Dissolved / Dispersed Petroleum Hydrocarbons (DDPH) concentration in surface (1m depth) sea water, petroleum hydrocarbons (PHs), particularly polycyclic aromatic hydrocarbons (PAHs), concentration in marine biota and sediment samples were measured by utilizing UV-Spectrofluorimetric technique.

Approximately 63% of the whole DDPH concetration remained below 1 ug/l. The highest average concentrations were measured in Izmit Bay (September 1983). The lowest concentrations were measured in the Mediterranean with an average value of 0.30 ug/l.

There is no relationship between the chrysene equivalent and gravimetric results for DDPH in seawater.

The investigation of seasonal variations and temperature dependence of oil resulted in an inverse relationship. Agyatan Lagoon was found to be polluted with Kirkuk crude oil after the pipeline incident. There is a trend between Kirkuk crude oil and chrysene equivalent concentrations in sediment samples in April 1983. But Kirkuk oil concentration was found to be much higher, near some sources and especially in Agyatan Lagoon sediment.

Approximately 3-5 months after the pipeline breakage an accumulation of oil first in fish liver and then two months later in fish flesh were observed.

Some samples such as tar ball, sea water, fish liver and sediment extracts were also analysed for source identification utilizing gas chromatographic technique. The tar balls were found to be a month old. The $n\text{-}C_{17}$ + Pristane (Pr)/$n\text{-}C_{18}$ + Phytane (Ph) ratios and unresolved complex mixture (UCM) of some tar ball, sea water and fish samples originated from Kirkuk oil.

Fluorene was observed in sea water, sediment and fish liver samples. Benz(a)pyrene, acenapthene and phenantrene also were found exist in fish liver extracts.

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# C H A P T E R I

## INTRODUCTION

In recent years, petroleum pollution of the sea has become a global problem in the marine environment because of recovering, transporting and using oil. After a spill, petroleum and petroleum products enter the sea and begin to change immediately. Physical, chemical and biochemical processes act effective roles on their environmental fates.In other words,these effects can be explained with dispersal and degradation processes.During the spill of oil on the sea naturally or by sinking agents,oil settle on the sea bed and pollute marine muds.So this hydrocarbon pollutants enter the marine food chain and cause an increase in the long term toxicity. Investigations about the fate and effects of oil and measuring the quantity of petroleum hydrocarbons become more important in the world and also in the seas around Turkey.

### 1- Nature of Petroleum

The original name of petroleum is petroleum,rock oil and it can be used of mineral oil,crude oil,oil or crude. Some properties of petroleum such as chemical composition,color,viscosity,specific gravity and physical properties depend on the source.

#### a) Composition of Petroleum

Mainly, petroleum contains carbon (82.2-87.1%), hydrogen (11.7-14.7%), sulphur (0.1-5.5%), nitrogen (0.1-1.5%), oxygen (0.1-4.5%) and inorganic substances (0.1-1.2%) (RANKAMA & SAHAMA,1968). Petroleum is divided into two categories according to its chemical properties.

##### i-Hydrocarbons

Hydrocarbon compounds are the major portion of any oil (60-97%)and consists of three subclasses,the aliphatics (25%),the alicyclics (35%) and the aromatics (20%) (TABLE I-1). n-Paraffins are the most abundant in oil, amount of iso-paraffins decreases while the number of branches increases and the aromatic portion of petroleum is usually less than the paraffinic portion.

##### ii- Non-Hydrocarbons

Besides the hydrocarbons, petroleum contains lesser quantities of non-hydrocarbon organic materials (TABLE I-2). These are particularly present in heavy crude oils. The oxygenated compounds, nitrogen compounds, sulphur containing compounds can be

TABLE I-1 Types of Hydrocarbons Found in Petroleum

| Type of Compound | Examples | |
|---|---|---|
| I- Aliphatics (Paraffins) | | |
| a) n-Alkanes | C-C-C-C-C-C (n-Hexane) | Straight chain alkane (saturated) |
| b) iso-Alkanes |  (iso-Butane) | Branched alkane |
| c) Alkenes | C-C=C-C-C (1-Butene) | Unsaturated aliphatic |
| II- Alicyclics (Cycloparaffins) |  (Cyclo_ hexane) | Cyclo, saturated rings |
| III- Aromatics | | |
| a) Aromatics |  (Benzene) | Unsaturated rings, all benzene ring structure |
| b) Naptheno_ aromatics |  (Fluorene) | Mixed Aromatic and Napthenic ring compounds |

TABLE I-2 Types of Non-Hydrocarbons Found in Petroleum

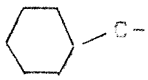
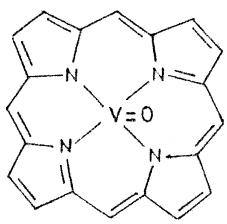
| Type of Compound | Examples | |
|---|---|---|
| 1- Oxygen Compounds |  | Napthenic acids |
| 2- Sulphur Compounds | C-C-C-C-SH | Alkylthiol |
| 3- Nitrogen Compounds |  (Pyridine) | |
| 4- Porphyrins |  | Metalloporphyrin |
| 5- Asphaltenes | ( C H N S O ) 79 92 2 2 3 | |

TABLE I-3 Major Groups of Compounds (Percentage Composition) In Crudes (WHITTLE et al;1982)

| | Light Crude | Heavy Crude |
|---|---|---|
| n-Alkanes | 23.3 | 0.9 |
| iso-Alkanes | 12.8 | 3.2 |
| cyclo-Alkanes | 41.0 | 19.2 |
| Aromatics | 6.4 | 9.2 |
| Naptheno-Aromatics | 8.1 | 27.9 (a) |
| Hetero cyclics (resins) | | 23.1 |
| Asphaltenes | 8.4 | 16.5 |

a: Include sulphur compounds

TABLE I-4 Estimate of Input of Petroleum into the Marine Environment (NAS,1975)

| Source | Input ($10^6$ t/yr) | % |
|---|---|---|
| Marine Transportation | 2.133 (a) | 35 |
| Offshore Production | 0.08 (a) | 1 |
| Land-based | | |
| -Coastal Refineries | 0.2 (a) | 3 |
| -Industrial Waste | 0.3 (b) | 5 |
| -Municipal Waste | 0.3 (b) | 5 |
| -Urban Run-off | 0.3 (b) | 5 |
| -River Run-off | 1.6 (b) | 26 |
| Natural Seepage | 0.6 (b) | 10 |
| Atmospheric | 0.6 (c) | 10 |
| TOTAL | 6.113 | 100 |

Confidence:a, high; b, medium; c, low

TABLE I-5 Input of Oil to the Oceans from Marine Transportation (NAS,1975)

| Source | Input($10^6$ t/yr) | % |
|---|---|---|
| LOT Tankers | 0.31 | 14.6 |
| Non-LOT Tankers | 0.77 | 36.1 |
| Dry Docking Operation | 0.25 | 11.7 |
| Terminal Operations | 0.03 | 0.1 |
| Bilges, bunkering | 0.50 | 25.5 |
| Tanker Accidents | 0.20 | 9.4 |
| Other Accidents | 0.10 | 4.6 |
| TOTAL | 2.13 | 100 |

found in petroleum. Porphyrins and asphaltenes have also been found in petroleum.

b) Fractions of Petroleum

Fractions of petroleum can be grouped according to their boiling points. They are petroleum ether (bp:20 to 60 °C), ligroin or light naptha (bp:60 to 120 °C), gasoline (bp:40 to 205 °C), kerosene (bp:175 to 325 °C), gas oil (bp:above 275 °C). Lubricating oil, vacuum distilled; and asphaltic or residual fuel oil (FIESER & FIESER 1961). As the boiling range of the fraction increases,the percentage content of normal paraffins, branched paraffins and monocycloparaffins decreases while the percentage content of polycycloparaffins and polynuclear aromatics increases.

c) Classification of Petroleum

Crude oil classification is based on physical properties or chemical composition. Crude oil can be subdivided into two categories according to specific gravity such as light crude which has specific gravity around 0.75 and heavy crude which has specific gravity near 1. Light oil contains higher percentage of low boiling fractions but heavy oil has a greater percentage of asphaltic and high boiling fractions. TABLE I-3 shows the percentage of compositions in crude oils.

Another classification depends on the relative amount of paraffinic, napthenic, aromatic and asphaltic compounds. In addition, the type of oil depends on its source and sulphur contents, as being high or low sulphur oil, but Kuwait oils are paraffinic-napthanic (GRUSE,1928) and high sulphur oil.

d) Sources and Inputs of Petroleum

There are many sources of hydrocarbons in environmental samples. These are;

1- Petroleum, petroleum products, coal,
2- Combustion products of fossil fuels,
3- Biosynthesis; terrestrial and marine,
4- Natural seeps,
5- Weathering and diagenetic processes.

TABLE I-4 gives a summary of the input of petroleum into the marine environment; the marine transportation input of oil to the ocean is shown in TABLE I-5.

e) Toxic Properties of Petroleum Hydrocarbons

Toxicity of petroleum is related to its composition, especially the degree of alkylation of the parent compounds benzene, napthalene and phenantrene. Four and five ring aromatic hydrocarbons such as chrysene and benz(a)pyrene is virtually insoluble in seawater and relatively non-toxic during the shortterm exposure.

Low boiling aromatics which are quite soluble in water are the most toxic and deadly. Higher boiling aromatics are effective as long term poisons and carcinogens.

Low boiling alkanes produce anasthesia and narcosis at low

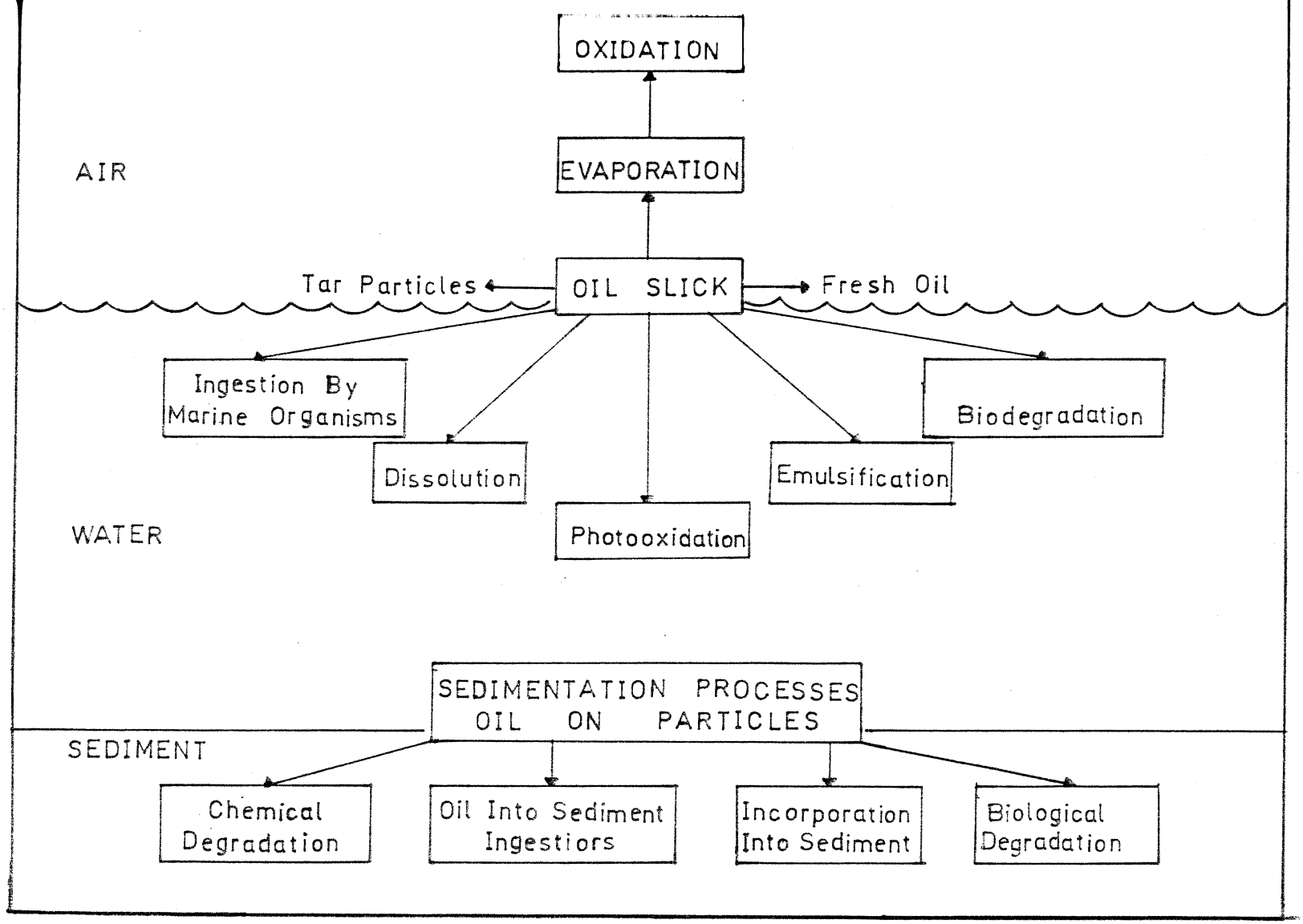



FIGURE I-1 Schematic Diagram Fate of Oil (LEE, 1977)

concentrations and cause cell damage and death at high concentrations. Alkenes are more toxic than alkanes but less toxic than aromatics.

## 2- Pathways and Fate Process of Petroleum in the Sea

When petroleum enters the sea, apart from the physical and chemical characteristic of an oil some other factors affect their spill. The general pathways and mechanisms are shown in FiGURE I-1. Evaporation, oxidation, solution and biological degradation processes are called "weathering process" (BOESCH et al;1974).

After petroleum is spilt on the sea surface, a slick forms and it is modified and dispersed by various processes. Winds, waves and currents effect the dispersion of the slick (LEE, 1977). The lighter fractions of the oil begin to evaporate immediately. The heavier fractions are affected by factors such as emulsification, dissolution, photooxidation, biodegradation, uptake by marine life, and adsorption to suspended particles.The composition of oil, especially its density and viscosity, and external factors such as temperature, light, oxygen, nutrients effect these processes. Eventually, a tarlike residue occurs and breaks up into the tar lumps or tarballs. TABLE I-6 shows the process of dispersion and degradation of oil as percentage and time scale.

### a) Spreading

Spreading is the first process after the spill of the product over the surface as a thin film. Initially, gravity provides the major spreading force and is opposed by inertia (FAY,1969; FAY & HAULT 1971).

For most spills, after the first hour or two , slick size is generally controlled by a surface tension-viscosity relationship which is independent of spill volume (GESAMP,1977). TABLE I-7 shows the surface tension of various crude oils and the interfacial tension of between these oils and water. Theoritically, the crudes spread until the formation a mono molecular layer. Viscosity acts as a retarding force, consequently; the rate of spreading decreases. The thickness of layer also decreases with time as shown in TABLE I-7. At the same time spreading is completed with emulsification. The effect of water in oil emulsification increases with time and so does the remaining slick, which reduces the tendencey of the slick to spread.

Thus, spreading is a self retarding process, it accelerates evaporation and leads to increased viscosity and increased pour point of the oil (BERRIDGE et al;1968).

### b) Evaporation

Evaporation is the most extensive and dispersive process. It effects low boiling compounds. The rate of evaporation depends on the vapor pressure of each component in the petroleum, the concentration of that component, the increased surface area and

TABLE I-6 Processes of Dispersion and Degradation of Oil (BUTLER et al; 1976)

| Pathway | Time Scale (days) | % |
|---|---|---|
| Evaporation | 1-10 | 25 |
| Solution | 1-10 | 5 |
| Photochemical | 10-100 | 5 |
| Microbial | 50-100 | 30 |
| Disintegration & Sinking | 100-1000 | 10 |
| Oil Residue | 100 | 20 |

TABLE I-7 Surface Tension and Theoritical Spreading Data for various Crude Oils (BERRIDGE et al; 1968)

| Crude Oil | a | b | c | d | | | |
|---|---|---|---|---|---|---|---|
| | | | | 2 10 s | 3 10 s | 4 10 s | 5 10 s |
| Libyan (Brega) | 23.1 | 13.9 | 27 | 2.28 | 0.49 | 0.11 | 0.02 |
| Iranian (Heavy) | 24.3 | 25.5 | 18 | 3.27 | 0.70 | 0.15 | 0.03 |
| Kuwait | 24.1 | 24.9 | 17 | 2.10 | 0.45 | 0.10 | 0.02 |
| Iraq (Kirkuk) | 23.7 | 16.9 | 21 | 2.57 | 0.50 | 0.12 | 0.03 |
| Venezuela (Tia Juana) | 24.1 | 19.2 | 17 | 2.55 | 0.55 | 0.12 | 0.03 |

a: Surface Tension (dynes/cm)
b: Interfacial Tension Seawater/Oil (dynes/cm)
c: Initial Spreading Pressure on Fresh Water (dynes/cm)
d: Thickness(mm) of Slick from Spillage of 100 $m^3$ of Oil after Spreading for
s: sec

thickness of the spill, wind, roughseas or size of waves, high sea temperature, irradiation (BOESCH et al; 1974).

Evaporation is most intense during the first few hours till weeks after the spill. Components in the oil are lost to the atmosphere in the gas phase or dispersed as aerosols. Some of them can diffuse as inputs of precipitation and dry fall out (WHITTLE et al; 1982).

Specific gravity and viscosities of the residues increase as the oil loses its volatile fraction. The evaporation processes contribute to the motion of thick residue oil sludges and tarballs. With the increase in the specific gravity of the residual oil, it may become denser than sea water and sink.

c) Solution

Solution is the physical process that effects lower molecular weight hydrocarbons. The rate of solution is governed by wind, seastate and the properties of the petroleum components (specific gravity, chemical composition, viscosity, surface tension, solubility).

Waters in equilibrium solution with crude oil can have 10-30 ppm dissolved hydrocarbon (MC AULIFFE, 1973). About one half of these are the more soluble aromatic compounds, the other half are primarly low molecular weight paraffins and the more polar compounds (NAS, 1975).

The photooxidation products such as phenols, ketones are more soluble than the original product. For the low molecular weight components, the aromatic compounds have higher solubility than alkanes of the same boiling point.

d) Emulsification

Much of the oil dispersed in the sea occurs as oil-in-water emulsions where the sea is the continous phase (PILPEL, 1968) or water-in-oil emulsions where the stable floating emulsion contains about 30 to 80 percent water. Water-in-oil emulsions are stable for periods ranging to greater than 100 days (GESAMP, 1977). Water-in-oil emulsions are very difficult to ignite, oil-in-water emulsions can break up or degrade. Refined products do not form water-in-oil emulsions and formation this depends on the amount of volatile residues (asphaltenes in crude oil).

e) Adsorbtion

Dispersed oil adsorbs onto particulate matter such as sand, silt, clays, shell fragments etc.in sea water and eventually this sediment with attached oil globules, settles on the bottom (POIRIER, and THIEL, 1941) when the seas become calmer. In estuarine areas that are characterized by fine sediments, salt marshes, the amount of suspended particles in the water is high and oil in this turbid area carries to the bottom.

Adsorbtion to suspended particles is an important process for high weight aromatic and aliphatic hydrocarbons which have low water particles (LEE, 1977). Lower weight hydrocarbons and more polar petroleum components remain in the water and show little adsorbtion to particles.

f) Sedimentation

This process is more important in estuarine and coastal areas where turbidity is high. The penetration of oil into sediments is related to sediment type and composition. Coarser sediments allow greater penetration than fine unconsolidated types. They also have higher rates of biodegradation than fine sediments, perhaps because of greater aeration and higher nutrient concentration in the subsurface. The highest concentrations of oil are associated generally with silt-sized sediments which have a larger surface area (LEE, 1980). After the oil attaches to particulate and settles on the bottom, masses of sunken oil roll along the bottom by wave and current action, accumulate larger particles of sand, shells and stones (NELSON-SMITH, 1970).

g) Aerosol

An oil which is spread out as a thin film may under turbulent sea conditions become transferred into the atmosphere as aerosol. The processes can be effective near the edges of a slick, but the residence time in the atmosphere is probably short (DUCE, 1973; NAS,1975).The nature and the extent of these reactions which occur as oxidation or photooxidative attack and adsorbtion on particulates are unclear (WHITTLE et al; 1982).

h) Oxidation

The chemical reaction in the petroleum occurs as oxidation in nature. Large amount of petroleum material floats on the surface and a major portion of the oxidation occurs here. Reaction also occurs in the water column. Reduction reactions occur when the material is carried to or released from the ocean bottom and the oxygen content in the overlying water column is extremely low (GESAMP, 1977).

There are two oxidation reactions in nature such as chemical or biological.

i- Chemical Oxidation

Chemical oxidation can be atmospheric oxidation or photooxidation type. Oxidation is catalyzed by materials present in the oil. Sunlight initiates free radical reactions and hydrocarbons content into hydroperoxide and these hydroperoxides transform to alcohols, acids, ketones and other oxygenated compounds (HANSEN, 1975; PILPEL, 1968).

Photochemical oxidation can sometimes produce dense and viscous polymers such as tars which are resistant to degradation (NIXON, 1972; FRIEDE et al;1972). Oxidation of these compounds is influenced by temperature, metal ions which act as a catalyst such as trace metals (i.e. Vanadium) and by sunlight especially by the intensity of the light in the UV ($\lambda$ = 250 nm) wavelength. Some compounds in petroleum such as sulphur act as antioxidants and inhibit autooxidation (BERRIDGE et al; 1968).

Little or no chemical oxidation occurs in the dark at temperatures below 30 °C (HANSEN, 1975). Some compounds such as nitrogen, sulphur, oxygen do absorb light in the visible spectrum

but the rates of oxidation at these wavelengths are much slower than in the UV. Some high molecular weight PAH also absorb light in the visible region and are oxidazed by sun light, thus benzo(a)pyrene is completely decomposed seawater within a few days after exposure to sunlight (ANDELMAN & SUESS, 1970).

ii- Microbial Oxidation

Microbes degrade the oil in the sea. Different hydrocarbon classes degrade at different rates tending to decrease as molecular mass and branching or substitution increase. The petroleum residues which include the asphaltenes are resistant to biodegradation for several years.

The rate of biodegradation depends on some conditions such as temperature, concentrations of nitrogen and phosphate sources, free oxygen and neutral pH conditions. Some hydrocarbon oxidizers can utilize nitrate or sulphate rather than oxygen as hydrogen acceptors, but they are a small minority. Thus, biodegradation is generally much slower in the absence of oxygen. The number of oil degrading microbes was very low during the winter in Raritan Bay (ATLAS & BARTHA,1973). Hydrocarbon utilizing bacteria occur in low concentrations in ocean water but are abundant in coastal waters and especially in the chronically polluted waters of harbours or ship channel (ANDERES, 1973).

3- Fate of Petroleum in Marine Biota

Petroleum can enter the marine food web by adsorbtion to particles, followed by ingestion of the particles, by filter feeding by active uptake of dissolved or dispersed petroleum and/or passage into the gut of animal that gulp or drink water (LEE & BENSON, 1973).

After petroleum hydrocarbons are taken up by an organism; they may be excreted unchanged, they may be metabolized or they may be stored with possible elimination at a future date. Oil from a slick can be grazed by plankton and the ingested oil precipitated in the faeces. Faecal matter is denser than sea water and sinks through the water column. It will be exposed to benthic organisms within the sediments. Faecal pellets can be ingested by marine organisms thus, providing a possible mechanisms for passage and/or concentration in the marine product.

The surface zooplankton in the Mediterranean take up large quantities of petroleum hydrocarbons from the heavily polluted surface film (MORRIS, 1974).

The grey mullet was observed to have a relatively high resistance to all pollution when exposed to an oil and bunkeroil concentration of 0.25 ul/l (MIRONOV, 1973). The grey mullet swallowed oil from the surface of the water. Later, when placed in clean water, the oil was found to be quickly released from the anal opening of the fish, coating the top surface of the aquarium with a film. The fish remained viable for several months after this.

Lee et.al; (1972) observed that the marine fish took up aromatic hydrocarbons via the gills. Metabolism occured in the liver which is high in lipids, followed by transfer of the hydrocar

bons and metabolites to the bile, and finally excretion.

The metabolism of hydrocarbons by marine organisms is not well understood. The pathways involving oxidases and other enzymes, important in the degradation of aromatic and paraffinic hydrocarbons by mammalian systems are documented (GESAMP, 1977). In the case of aromatic compounds, hydroxylation is followed by conjugation with sulphate or glucose and finally by excretion of the water soluble product.

Straight chain hydrocarbons are hydroxylated at the terminal end and further oxidized to the fatty acid which can be broken down by β-oxidation. Highly branched chain hydrocarbons such as pristane and phytane, are probably oxidized to an acid (e.g. phytanic acid) which can be further oxidized by a combination of α- and β-oxidation (MIZE et al; 1969).

## 4- Fate of Petroleum in Sediment

There are various sedimentation processes, such as adsorbtion to particles, that carry petroleum components of an oil slick to the bottom. After a spill, petroleum derived hydrocarbons persist in sediments for at least two years. The oil reaches a maximum concentration in coarse sediments one year after the spill, but the concentration reduces after there. In sediments microbial degradation of petroleum hydrocarbons is more rapid near the surface than in the lower layers since oxic conditions exist (WHITTLE, 1982).

The decrease in n-alkanes with depth in sediment cores is attributed to the greated degree of biodegradation. Hydrocarbons buried in the sediment can be remobilized to the surface by diffusion in the pore waters, which may account for the tendency of aromatics of low molecular mass not to survive long term accumulation.

Sediment microbes attack iso-alkanes, cycloalkanes and aromatic hydrocarbons slower than alkanes (ZOBELL, 1969; BLUMER, 1973). Different crude and refined oils show different rates of degradation because of variations in the relative amount of the different petroleum components (WALKER et al; 1976).

Temperature, water-sediment exchange processes, rates of bioperturbation and the physical characteristics of the sediments help to control the rate of degradation. In addition to the microbes, meiofauna and macrofauna also have an effect on the degradation of hydrocarbons in sediments. For example, polychaetes which are macrofaunas ingest sediment during their feeding and are able to metabolize petroleum hydrocarbons (ROSSI & ANDERSON, 1977; LEE et al; 1977).

## 5- Tar Balls

Tar balls are the most common form of residual oil after dispersion and degradation of low and medium molecular weight compounds in the sea. They can distribute throughout the water column according to their varying sizes and density and fall on the sea bottom. Some of them can reach the coastline (i.e on beaches and rocks).

Their physical appearance varies, for example their size may change from a few millimeters in diameter up to several centimeters (GESAMP, 1977), they can be soft, quite hard or almost brittle whilst many may incorporate sand and small particles.

Tarballs are the products of different degrees of physical, chemical and biological weathering. Evaporative weathering is effective on petroleum residues that contain the lighter molecules, i.e., $n\text{-}C_{14}$ diffuses through a 1 $cm^2$ tar ball over 250 days (EHRHART & DERENBACH, 1975). Higher weight n-alkanes take much longer.

## 6- Analytical Methods for Petroleum Hydrocarbons Quantities and Characterization

### a) Analytical Balance (Gravimetric Method)

Analytical balance procedure is simple and rapid for quantitative measurements of total hydrocarbons. After allowing the solvent to evaporate, the hydrocarbons which remain on the beaker can be weighed. The procedure is not as sensitive as gas chromatographic measurements but it is not necessary to have information on the chemical nature of components of the fraction.

The method has some disadvantages. One disadvantage is the loss of volatile fractions, which may include hydrocarbons up to n-tetradecane depending on the temperature used to evaporate the solvent (FARRINGTON et al., 1976). A second disadvantage of the weighing method is the lumping together of biogenic and petroleum hydrocarbons in one measurement.

### b) UV- Fluorescence Spectrometry

Aromatic hydrocarbons can be detected with the help of ultraviolet analytical techniques. The shape of the spectrum is useful for source characterization or identification and the intensity of fluorescence can be used for quantitation (FARRINGTON et al., 1976). Thus petroleum contamination can be detected with this technique. The most important advantage of this technique is the rapid scanning of samples to determine approximate upper limits for petroleum aromatic hydrocarbon concentrations in a marine sample. The detection limit of fluorometers is about 10 ng/l which is 100 times greater than the spectrophotometric method. Aromatic hydrocarbons can be found in complex mixtures within marine samples since their source varies, and may be of non petroleum origin. Determination of oil source is difficult if the origin of the sample is not known. The reliability of fluorescence spectroscopy is 0.911. Another advantage is that there is no interference from water. Although the technique gives no information for saturated hydrocarbons.

### c) Gas Chromatography

Gas chromatography can also be used to quantitative and qualitative measurement of hydrocharbons in a sample. Petroleum hydrocarbons or petroleum contamination can be detected using temperature programmed gas chromatography and choosing the proper

columns. One characteristic of the gas chromatograms of petroleum hydrocarbons on low and medium resolution columns is an unresolved complex mixture (UCM) signal. In the detector response, there are different shaped peaks for the resolved and for the UCM. The number of resolved peaks increases with increasing efficiency of gas chromatography columns.

Quantitatively, the hydrocarbons can be measured by comparing the detector response of the known fraction of a sample injected into the gas chromatograph and the response of a known amount of a standard compound injected into the gas chromatograph under identical conditions (FARRINGTON et al.,1976).

Analysis time of gas chromatography is between 10 minutes to 2 hours and the reliability is 0.911. Gas chromatography is very good for unweathered samples for producing finger prints but it is poor for biodegraded samples.

## 7- Aim of This Work

In the coordinated Mediterranean Pollution Monitoring and Research Programme (MED-POL) Phase I, a special emphasis was given to the petroleum hydrocarbon levels in the Mediterranean Sea. Within the framework of the programme a joint IOC/WMO/UNEP pilot project on "Baseline Studies and Monitoring of Oil and Petroleum Hydrocarbons in Marine Water (MED-POL I) " was initiated. In this programme the Mediterranean Sea was divided into 13 sections. The study also covered the Agean Sea, the Sea of Marmara and the Bosphorous region of the Black Sea.

Although, considerable work has been done in the North Levantine Basin during Phase I, no data exist for the Aegean Coast of Turkey, the Sea of Marmara and the Black Sea. Thus one of the aims was to determine the dissolved / dispersed petroleum hydrocarbon concentrations of these regions, so that a comparison could be made.

Another aim of the work was to follow the petroleum pollution and its effects on some biota in the Iskenderun Bay, where in April 1982 about 8000 tons of crude oil entered the bay via Ceyhan River due to a crack in the pipeline carrying the oil from Iraq (Kirkuk) to the terminal at the bay (FIGURE I-2).

Agyatan Lagoon which is located close to the Ceyhan River mouth and is used for fishery purposes received considerable quantities of Crude Oil. Due to the low salinity and shallownes of the lagoon some crude oil sank to the sediments within a relatively short period (a day after entering). One of the aims of this work was to assess the pollution level in the lagoon.

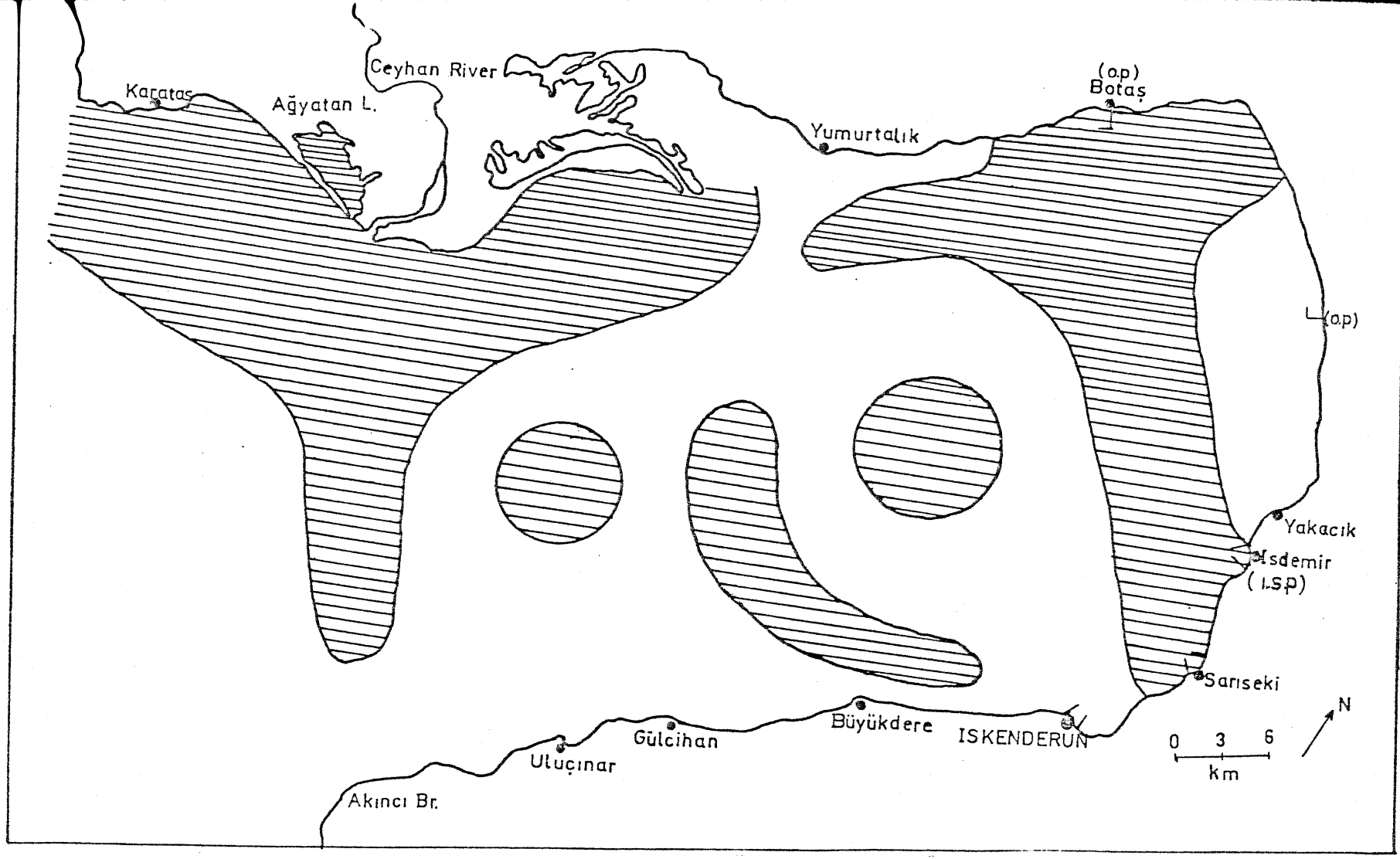



FIGURE I-2 Observed Oil Slick Distribution in Iskenderun Bay (April,27-May,5 1982).

o.p : Oil Pipeline Terminal
i.s.p : Iron-Steel Plant

# C H A P T E R II

## EXPERIMENTAL

### 1- Chemical Materials Used

#### a) Reagents

Analytical reagent grade n-Hexane ($C_6 H_{14}$), Carbontetra chloride ($CCl_4$), Methanol($CH_3OH$) as supplied by Merck and Benzene ($C_6 H_6$) as supplied by Riedel de Haen AG were used without any further purification for the preparation of samples and standards. Ethyl alcohol (technical), Acetone (99.5% technical and Merck), Sodium Hydroxide (NaOH,Merck) and chromic acid were used for the clean-up procedure.

#### b) Homogenization Materials

Sodium sulphate was activated at 600 °C overnight. This material after cooling down to room temperature was stored in a desicator until usage.

#### c) Open Column Chromatographic Material

Activated alumina $Al_2 O_3$ (90 Mesh size, Merck) was used for the removel of lipids from fish and sediment samples. Alumina activated at 120°C for 6 hours.

#### c) Standards

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

Chrysene was used as a reference standard material for determining the amount of dissolved/dispersed petroleum hydrocarbons (DDPH) by utilizing UV-Flourescence spectrometer. Some polycyclic aromatic hydrocarbons (PAH) such as; acenapthene, fluorene, phenantrene, pyrene, benz(a)pyrene and perylene were used as standard materials to determine the amount of PAH in gas chromatographic measurements.

### 2- Instrument Used

#### a) Field Instruments

i- Neuston Net; A Neuston Net as modified by MARMOPP was used for collection of pelagic tar. A deep trawling net was used for

collection of fish samples.

ii- Gravity Sampler and Gravity Corer; A Van Veen type grab sampler and a Phléger gravity corer were used for the collection of sediment samples.

b) Laboratory Instruments

For extraction of petroleum hydrocarbons from sediments and fish samples, soxhlet apparatus was used. Rotary evaporatory (Heidlph) system was used for drying and/or reducing sample volumes. All glassware used during the experiments were Pyrex.

Fluorescence spectrometer; A Turner Model 430 scanning spectrofluorometer was used for measuring the fluorescence intensity. Samples were analyzed at 360 nm emission and excitation at 310 nm wavelength with a band width of 15 nm to determine the concentration of DDPH relative to chrysene. Some samples were also measured for oil equivalent under the following conditions: $\lambda$em = 363 nm wavelength and $\lambda$exc = 402 nm wavelength for Kirkuk crude oil. Their fluorescence spectra were recorded with Varian A-25 Model. Full Scale Deflection (FSD) = 0.1 V

Chart Speed (CS ) = 5-10 cm/min
Scan Rate (SR ) = 10-30 nm/min

Gas chromatography (GC); 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.

Column Conditions:

| | |
|---|---|
| Column Length | : 117 cm |
| Outside Diameter | : 6 mm |
| Inside Diameter | : 2 mm |
| Liquid Phase | : SE-30 (10% wt) |
| Support | : Chromosorb WHP |
| Type of Column | : Pyrex glass column |
| Maximum Temperature | : 300°C |

Operation Conditions:

| | |
|---|---|
| Sample Size | : 3-5 ul |
| Column Temperature | : Programmed from 60°C to 270°C |
| | Programme rate 3-5°C/min |
| Injector Temperature | : 250°C |
| Detector Temperature | : 280°C |
| Carrier Gas | : $N_2$, 22 ml/sec |

Analytical Balance; Sartarious Model 2462 which had 0.1 mg weighing capacity and 2434 which had 0.01 mg weighing capacity were used for the gravimetric determination and preparation of samples and standards.

3- Sampling Locations

a) Sea Water

Sampling stations are in FIGURE II-1, FIGURE II-2 and FIGURE II-3. Stations were chosen out of petroleum polluted areas during petroleum spillage in 1982 in Iskenderun Bay, and the Mediterranean Sea stations were chosen from Mediterranean Action Plan (MED-POL II).

b) Marine Biota

Becase of the incident in 1982, some fishes were found dead and stations were chosen from polluted areas: Yumurtalik, Botas and Karatas in Iskenderun Bay and Agyatan Lagoon (FIGURE I-1).

c) Sediment

Sediment samples were taken from Iskenderun Bay and the Mediterranean Sea(FIGURE II-1 and 2).

d) Tar Ball

Tar balls were collected in some stations and beaches after the petroleum incident in Iskenderun Bay (FIGURE II-1).

4- Collection of Samples and Preservation

a) Sea Water

Samples were collected as far away as possible from the effect of the ship's exhaust and other contaminating matters,such as sewage water etc.. Samples were taken from a depth of 1 m from surface and transferred to 2.8 l dark glass bottles. Samples 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. Freezing was not necessary because carbontetrachloride is an effective bacteriostat.

b) Marine Biota

Some fish which died during petroleum pollution in 1982 were collected by hand and other fish were collected by using a fish scoope from Agyatan Lagoon. A deep trawling net was used for collection of fish in Iskenderun Bay. Fish samples of the following species were chosen for analysis: Mullus barbatus (Barbunya), Solea solea (Dil Baligi), Epinephelus aeneus (Lagos), Upeneus moluccensis (Nil Barbunyasi), Mugil cephalus (Kefal), Sparus aurata (Cupra), Diplodus annularis (Isparoz). Care was taken to have more or less the same size (thus age) of samles from each species. Flesh and liver of some samples were dissected and wrapped with aluminum foil and stored in deep-freeze at -25°C until usage.

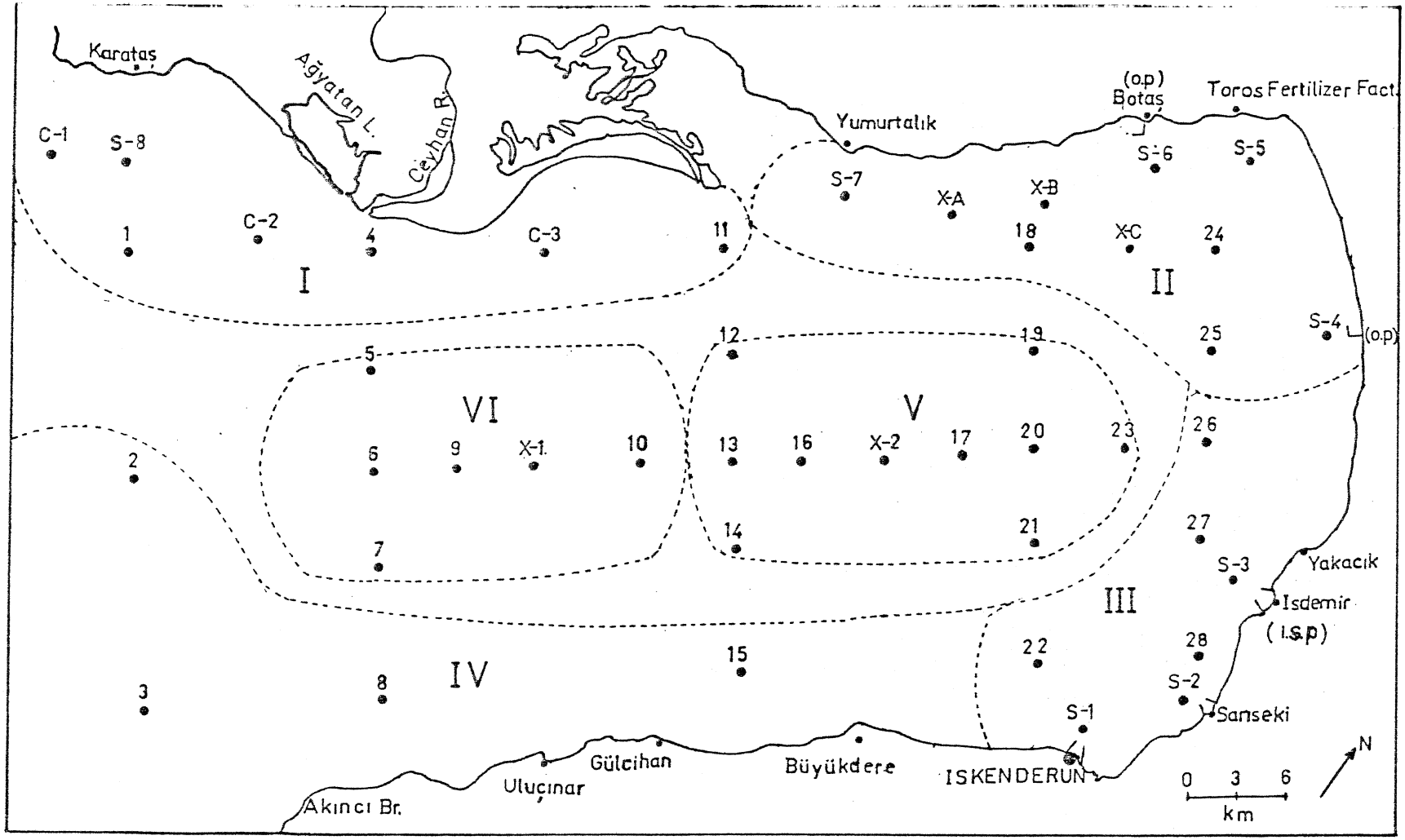
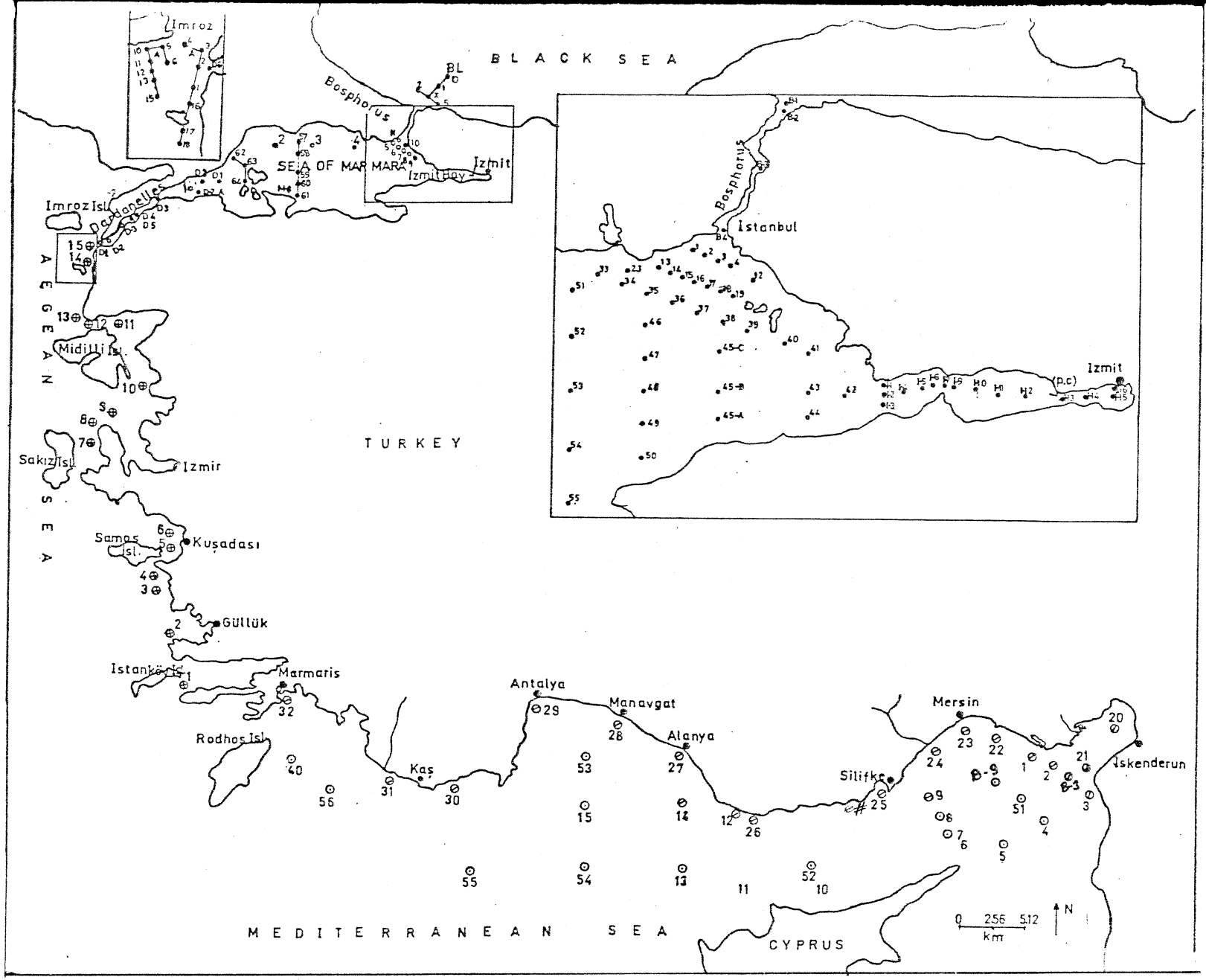



FIGURE II-1 Sampling Locations for the Tar Ball, Sea Water, Fish and Sediment Samples in Iskenderun Bay.

o.p : Oil Pipeline Terminal
i.s.p : Iron-Steel Plant




e Coastal Stations for the Medi.Sea

⊡ Reference Sta. for the Medi.Sea

⊕ Aegean Sea

• The Sea of Marmara (June 1982 Cruise)

. The Sea of Marmara and Aegean Sea

p.c : Petrochemical Complex

FIGURE II-2 Sampling Locations for the Sea Water in the Medi_ terranean Sea, Aegean Sea, The Sea of Marmara and Black Sea;and for Sediment in the Mediterranean Sea.

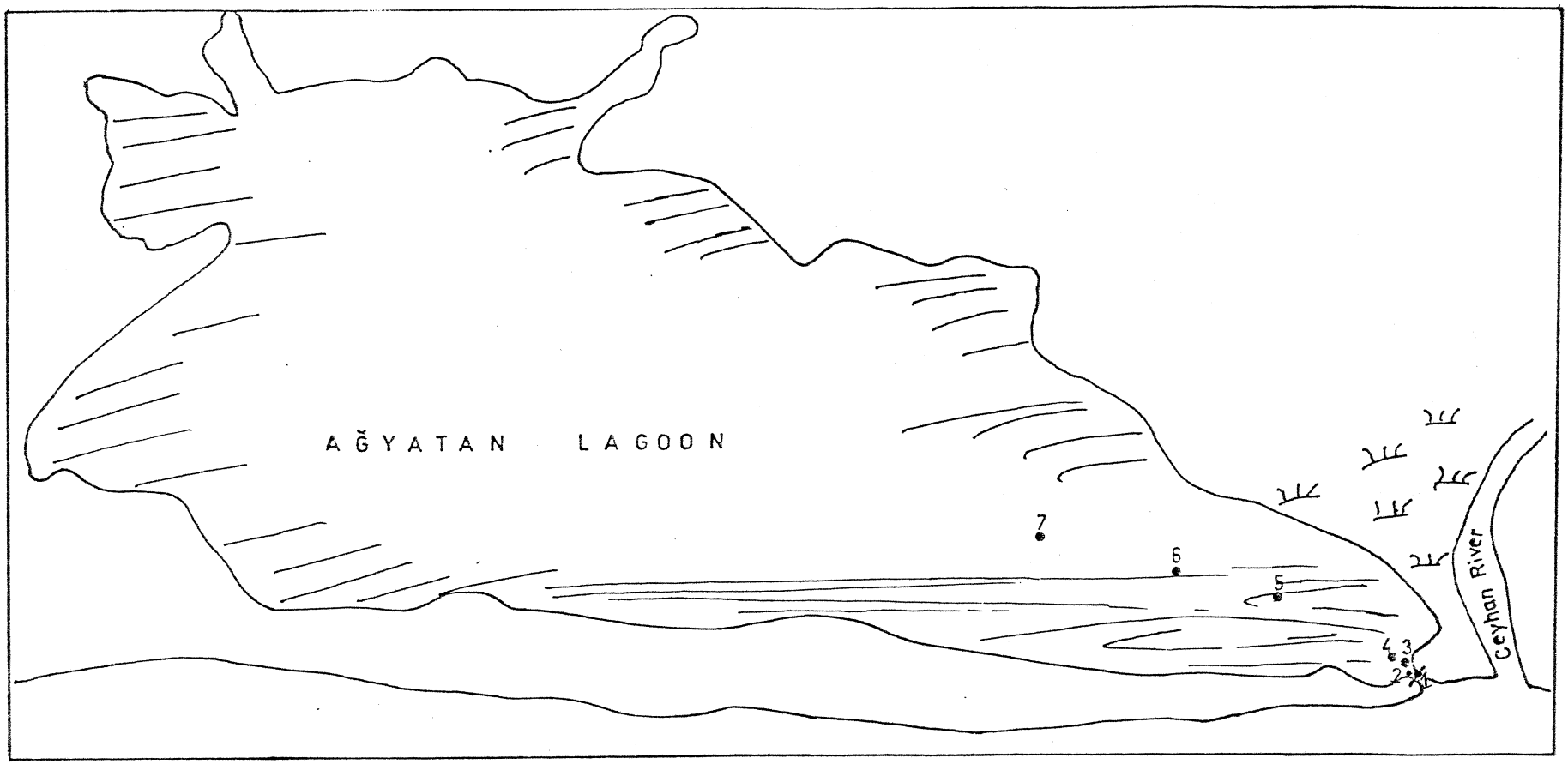



FIGURE II-3 Sampling Locations for Sea Water, Fish and Sediment Samplee in Agyatan Lagoon.

c) Sediment

Sediment samples were collected by using a Van Veen grab sampler and/or gravity corer and stored in a deep-freeze at -25°C in polyethylene container until usage.

d) Tar Ball

Tar balls were collected by hand from the beach and with Neuston Net from surface waters in Iskenderun Bay. The samples were stored in deep freeze in polyethylene bags.

## 5- Analytical Procedures

a) Clean-up Procedure

All glassware were cleaned as following:
- Washing with detergent,
- Removing the detergent with tap water,
- Washing with dichromate-sulphuric acid,
- Removing the dichromate-sulphuric acid by rinsing with tap water and distilled water,
- Removing the water with acetone,
- Rinsing with working solvent, such as n-hexane.

b) Preparation of Blanks

Blanks were prepared for sea water, fish and sediment samples to determine the contamination from solvent, reagents and the laboratory atmosphere.

i- Sea Water Blank

100 ml carbontetrachloride was drawn into a flask and solvent was evaporated by rotary evaporator till it dries. The residue was dissolved in n-hexane and, transferred to a 5 ml volumetric flask and then measured with the fluorescence spectrophotometer.

ii- Marine Biota Blank

Soxhlet extraction was done without any samples for 10-12 hours with 150-175 ml n-hexane for about 24 cycles. Then the solvent was evaporated with rotary evaporator at 50-60 °C by heating to dryness. The residue was dissolved with n-hexane and eluated through the activated alumina column. The eluation was collected into 5-10 ml volumetric flask and analyzed with spectrofluorometer.

iii- Sediment Blank

Only a cellulosic extraction thimble (without sample) was extracted for about 24 cycles. After this period the extract was transferred into a separatory funnel. Benzene phase was separated into a flask and evaporated with rotary evaporator to dryness.

n-Hexane was added to this residue and passed through the activated alumina column. The eluate collected into 5-10 ml volumetric flask and analysed with fluorescence spectrophotometer.

c) Preparation of Column

Alumina column; the lower part of a plastic tube (inner diameter 0.9 cm, length 14 cm) which was stoppered at the lower reduced end with some clean glass wool, was filled with activated alumina.

d) Preparation of Samples

i- Sea Water

2.8 l sea water samples were extracted with 100 ml carbon tetrachloride by shaking them vigorously for 20 minutes. Then samples were allowed 10 minutes to separate into the two phases. Afterwards, the carbontetrachloride phase was drawn into 250 ml flask with the aid of a glass pipette. The solvent was then removed from the extract in a slow rotary evaporator by mild heating up to residue or to dryness at about 50-60°C without boiling.

The residue was dissolved in n-hexane and drawn into 5-10 ml clean volumetric flask with the help of a medicine dropper. Finally, this solution was transferred to 0.1 cm quartz cell for fluorescence spectrophotometer. Some samples were measured using a gas chromatograph and some by the gravimetric method.

ii- Marine Biota

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 transferred into a cellulosic extraction thimble and extracted with 150-175 ml n-hexane in Soxhlet apparatus for 10 hours for about 24 cycles. Then the extract was evaporated by rotary evaporator at 50-60°C by heating to dryness.

This residue which was in 250 ml flask was collected into 5-10 ml volumetric flask. Lastly, eluated samples were analyzed with spectrofluorometer and gas chromatograph.

iii- Sediment

About 20-30 grams (wet weight) of sediments were weighed into a cellulosic extraction thimble and Soxhlet was extracted for 10 hours with 1:1 (v:v) benzene:methanol for about 24 cycles. At the end of this period, the extract was tranferred into a separatory funnel. Benzene and methanol phases were separated. Sometimes distilled water was added to this extract for better separation, because methanol dissolves in benzene but it is more soluble in water.

The benzene phase was collected into a flask and solvent was evaporated by using a rotary evaporator by mild heating to dryness. After evaporation n-hexane was added and passed through the activated alumina column. The eluate was collected into 5-10 ml

volumetric flask and analysed with fluorescence spectrophotometer and gas chromatograph.

iv- Tar Ball

After collection, tar was separated from other particles. If tar balls were not separated manually from extraneous material, then they were dissolved in carbontetrachloride and the carbon tetrachloride extract is recovered by filtration (CARPENTER, 1976).

The extract was evaporated to dryness and residue was weighed. Some tar balls had been separated manually; they were weighed directly after being air-dried at room temperature for few hours in order to remove the surface water. Finally, a few of them were analyzed with gas chromatograph.

## 6- Standard Solutions

100 ppm stock solution was prepared for chrysene and oil. This stock solution was diluted for 0.1; 0.25; 0.50; 0.75; 1 and 2 ppm solution. Acenapthene (20 ppm), fluorene (2 ppm), phenantrene (40 ppm), pyrene (5 ppm), benz(a)pyrene (5 ppm), perylene (5 ppm) and $C_{12}$ - $C_{20}$ were prepared as standard solution.

## 7- Quantification of Results

### a) Calibration Curve

The fluorescence intensity of the sample was compared with the fluorescence of a series of reference solutions. Chrysene and Kirkuk crude oil were used as reference solutions. 0.1; 0.25; 0.75; 1 and 2 ppm chrysene solutions were prepared and intensity of them were measured with spectrofluorometer. Concentrations of standards are given in X axis and intensities in Y axis (FIGURE II-4). The linear part of the curve is used calibrations.

### b) Calculations

The fluorescent intensity value obtained for the blank was substracted from the intensity value for the samples in order to elute contamination due to reagents, solvents and laboratory conditions. All the measured blanks did not affect the final results for the samples, because they were so low to be detected (i.e.zero). The unknown concentration of the sample was calculated using the calibration curve (FIGURE II-4). For sea water, the volume was measured and the concentration of fluorescing material was calculated as microgram (ug) of oil or chrysene equivalent per litre (l) of sea water.

The following equations were used for the calculations.

For sea water;

$$C_g \times V_f = C_s \times V_t$$

For fish and sediment;

$$C_g \times V_f = C_s \times W_s$$

Where;

$C_g$ : Petroleum hyrocarbon concentration of residue obtained from graph (ug/l and/or ug/ml)

$V_f$ : Final volume of the sample extract (l and/or ml)

$C_s$ : Concentration of sample which is dissolved/dispersed petroleum hydrocarbons in sea water (ug/l); petroleum hydrocarbons in fish and sediment (ug/g)

$V_t$ : Total volume of sample (l or ml)

$W_s$ : Weight of sample (g)

For the gravimetric method samples were weighed and total amount of petroleum hydrocarbons was calculated as micrograms per liter of sea water.

Gas chromatographic results were calculated from the following formula;

$$C_r = \frac{C_{st} \times V_{ist}}{H_{st} \times Att_{st}} \times \frac{H_s \times Att_{st}}{V_{is}} \times \frac{V_f}{W_s \text{ (or } V_t)}$$

$C_r$ : Concentration of residue in the sample (ug/g or ug/l)

$C_{st}$ : Concentration of residue in standard sample (ug/ml)

$V_{ist}$ : Injected volume of standard solution (ul)

$H_{st}$ : Peak height of the residue in standard chromatogram (cm)

$H_s$ : Peak height of the residue in sample chromatogram (cm)

$Att_{st}$ : Attenuation of standard chromatogram

$Att_s$ : Attenuation of sample chromatogram

$V_{is}$ : Injected volume of the sample (ug/l)

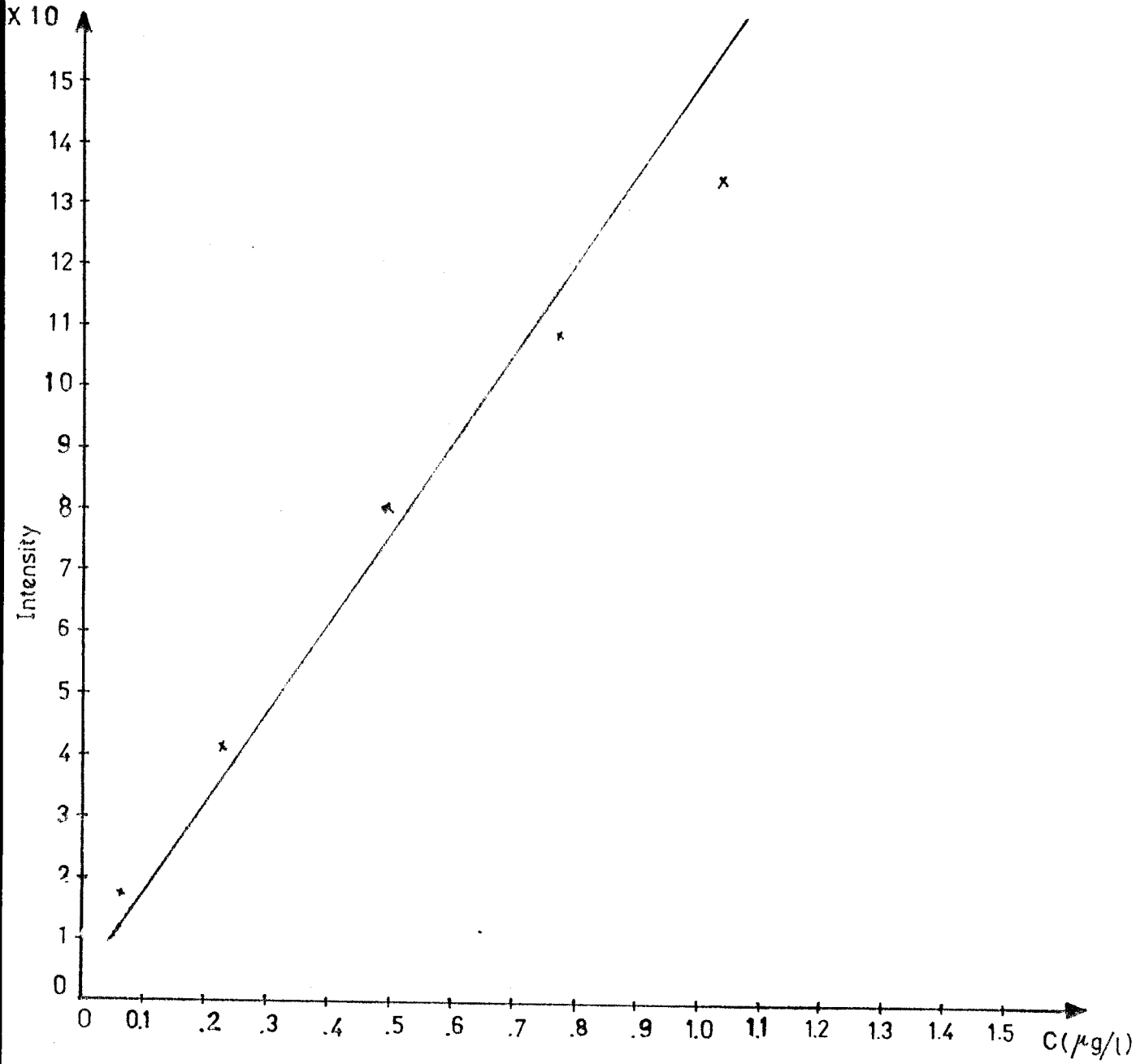



FIGURE II-4 Calibration Curve for Standards.

# C H A P T E R III

## RESULTS and DISCUSSION

### 1- Dissolved/Dispersed Petroleum Hydrocarbons (DDPH) in Surface Sea Water

#### a) General Distrubition of DDPH in Surface Water around Turkey

The distribution of DDPH in sea waters around Turkish coasts from Iskenderun Bay to the Black Sea was investigated. The locations of samples are shown in FIGURE II-1,2 and the results of the quantitative analysis with respect to chrysene are listed in TABLE III-1.

The overall frequency distribution of concentrations of all the analysed samples were calculated and plotted in FIGURE III.1. As can be seen from the FIGURE III-1 approximately 63.3% of DDPH values lie between the detection limits (including N.D) and 1 ug/l, 19.4% between 1 and 2 ug/l, about 10.3% between 2 and 4 ug/l and nearly 7% above 4.2 ug/l.

The 63.3% of DDPH which are below the 1 ug/l was distributed as follow: 21.8% for Iskenderun Bay (TABLE III-2), 18.2% for the Mediterranean Sea, 14.2% for the Sea of Marmara, 6.5% for the Aegean Sea, 1.4% for Izmit Bay. The distribution of the concentration values between 1-2 ug/l was found as 12.2% for Iskenderun Bay, 2.6% for the Mediterranean, 2.2% for the Sea of Marmara, 1.9% for Izmit Bay and 0.5% for the Aegean Sea. The frequency distribution for the concentration between 2-4 ug/l yielded 9.1% for Iskenderun Bay, 0.7% for the Sea of Marmara and 0.5% for the Mediterranean Sea. Finally, percentage distributions of the concentrations greater than 4.2 ug/l was found to be 6.4% for Iskenderun Bay, 0.2% for the Mediterranean Sea, 0.2% for Izmit Bay and 0.2% for the Sea of Marmara.

The highest percentage of the frequency distribution of DDPH concentration in sea water, i.e.; 63% which was obtained from the average of the whole data remains below 1 ug/l. The observation shows the distribution pattern of the petroleum hydrocarbon pollutants in surface waters around Turkey. According to data presented in the National Academy Report (1975), the concentration of hydrocarbons in marine waters varied from approximately 3 ug/l in open water, to 20-50 ug/l in inshore coastal waters, and to 100-1000 ug/l in oil spill and outfall areas.Then, most of seawater results can be considered to correspond to safe concentrations.

In addition, the average concentrations were also calculated by using TABLE III-1 for September 1983 cruise. As indicated in TABLE III-3 the average concentration of DDPH is found to be

TABLE III-1 Concentration of DDPH in Sea Water (ug/l)

ISK : Iskenderun Bay
ME : Mediterranean Sea
A : Aegean Sea
D : Dardanellas
M : The Sea of Marmara
B : Bosphorous
IZ : Izmit Bay
BL : Black Sea

| Regions & Stations | --1981-- 5 Aug | 21 Nov | ----------1982---------- 24 Feb | 27 Apr | 13 May | 5 July | 30 Aug | 3 Nov | -------1983------- 14 Apr | 15 June | 31 Aug | 5 Oct | 1984 17 Apr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I ISK C-1 | - | - | 1.4 | - | 4.2<br>2.3 | - | - | - | - | - | - | - | - |
| I ISK S-8 | - | - | 3.7 | 4.2<br>5.0 | - | - | - | - | - | - | - | - | - |
| I ISK 1 | - | - | 1.3 | 1.4 | 13.8<br>3.7 | 1.7 | - | - | - | - | 0.4 | 0.4 | 2.2 |
| I ISK C-2 | - | - | 11.5 | - | 1.0<br>1.4 | 1.3 | - | - | - | - | - | - | - |
| I ISK 4 | - | - | 4.9 | - | 7.7 | - | - | - | - | - | 2.4 | 0.5 | 0.2 |
| I Cey. R. | - | - | - | 5.7 | - | - | - | - | - | - | - | - | - |
| I ISK C-3 | - | - | 2.2 | 0.8 | 0.8<br>6.7 | - | - | - | - | - | - | - | - |
| I ISK 11 | - | - | 3.9 | - | 2.8<br>25.2 | - | 0.2 | 0.2 | - | - | - | 0.4 | 0.4 |
| II ISK S-7 | 1.4 | 1.8 | 2.0 | - | - | 0.8 | 0.6 | 0.4 | - | - | - | - | - |
| II ISK 18 | - | - | - | - | 2.4<br>3.4 | 0.8 | - | - | - | - | 0.6 | - | 0.1 |
| II ISK X-A | - | - | 1.1 | - | - | - | - | - | - | - | - | - | - |
| II ISK X-B | - | - | 3.0 | - | - | - | - | - | - | - | - | - | - |
| II ISK X-C | 6.5 | - | 2.3 | - | - | - | - | - | - | - | - | - | - |
| II ISK S-6 | 1.6 | 1.4 | 4.5<br>1.6 | 2.1 | - | 0.7 | 0.5 | 0.2 | - | - | 0.6 | 0.5 | 0.1 |
| II Botas | - | - | - | 260 | - | - | - | - | - | - | - | - | - |
| II ISK S-5 | - | - | 1.8 | - | - | 1.4 | - | - | - | - | - | 0.3 | 0.1 |
| II ISK 24 | - | - | 1.5 | - | 3.0 | 0.5 | - | - | - | - | - | - | - |
| II ISK 25 | - | - | - | - | - | 0.8 | - | - | - | - | - | - | 0.4 |
| II ISK S-4 | 85 | - | 2.2 | - | 2.0<br>4.3 | - | - | - | - | - | 0.5 | 0.2 | - |
| III ISK 26 | - | - | 3.0 | - | - | - | - | - | 3.1 | - | - | 0.2 | - |
| III ISK 27 | - | - | - | - | 3.0 | 1.4 | 0.3 | 1.3 | 0.04 | - | - | - | 0.2 |
| III ISK S-3 | 0.7<br>7.1 | 1.0 | 5.9 | 1.5 | 1.4 | 0.7 | 0.6 | 1.8 | 1.1 | - | 0.9 | 0.5 | 0.5 |
| III ISK 28 | - | - | - | - | - | - | 0.7 | 0.2 | - | - | - | - | - |
| III ISK S-2 | - | - | - | 1.8 | 1.0 | - | - | - | 2.0 | - | 0.6 | 0.8 | 0.7 |
| III ISK S-1 | - | 0.8 | 8.8 | - | - | - | - | - | - | - | - | - | - |
| III ISK 22 | 81 | - | - | - | - | 1.4 | 0.6 | 1.5 | 1.1 | - | 0.6 | - | - |
| IV ISK 15 | - | - | - | - | - | 1.3 | - | - | 2.5 | 0.1 | 0.6 | 0.2 | 0.1 |
| IV ISK 8 | - | 0.7 | - | 1.0 | - | 0.9 | 0.7 | - | - | - | 0.5 | 0.1 | 0.4 |
| IV ISK 3 | - | 0.7 | 2.2 | - | - | 2.0 | - | - | - | - | 1.5 | 0.4 | - |
| IV ISK 2 | - | - | - | 3.5 | - | 2.8 | - | - | 0.7 | - | 0.6 | 0.5 | - |
| V ISK 19 | - | - | - | - | - | - | - | - | - | - | 5.6 | 0.3 | - |
| V ISK 23 | - | - | - | - | 2.7 | - | - | - | - | - | - | 0.3 | - |

TABLE III-1 (Continuation)

| Regions & Stations | --1981-- 5 Aug | 21 Nov | ----------1982---------- 24 Feb | 27 Apr | 13 May | 5 July | 30 Aug | 3 Nov | -------1983------- 14 Apr | 15 June | 31 Aug | 5 Oct | 1984 17 Apr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V ISK 20 | - | - | - | - | 2.8 | 2.6 | - | - | 5.6 | 0.2 | 0.5 | 0.6 | 0.5 |
| V ISK 21 | - | - | - | - | 1.6 | - | - | - | 1.3 | - | - | - | - |
| V ISK 17 | 1.9 | - | 2.7 | 11.2 | 1.4 | 0.2 | - | - | - | - | - | 0.3 | - |
| V ISK X-1 | - | - | - | 1.2 | - | - | - | - | - | - | - | - | - |
| V ISK 16 | - | - | 11.8 | - | - | - | - | - | 1.1 | - | 0.6 | 0.1 | - |
| V ISK 12 | - | - | - | - | - | - | - | - | - | - | - | 0.6 | - |
| V ISK 13 | - | - | - | 1.6 | 1.3 | - | 2.0 | 0.2 | - | - | - | 0.1 | 0.7 |
| | | | | 1.8 | | | | | | | | | |
| V ISK 14 | - | - | - | - | - | 1.6 | - | - | - | - | - | - | - |
| VI ISK 10 | - | - | - | 3.3 | - | - | - | - | - | - | - | 0.1 | - |
| VI ISK X-2 | - | - | - | 1.3 | - | 3.9 | - | - | 5.7 | - | - | - | - |
| VI ISK 9 | - | - | - | - | - | - | - | - | - | - | 0.5 | 1.0 | - |
| VI ISK 5 | - | - | - | - | - | - | - | - | - | - | 0.8 | 0.6 | - |
| VI ISK 6 | - | 3.7 | - | - | 2.6 | - | - | - | - | - | 0.6 | 0.4 | 0.1 |
| | | | | | 2.1 | | | | | | | | |
| VI ISK 7 | - | - | - | - | - | - | - | - | - | - | - | 0.8 | 0.2 |

| Sta_tions | ------1983------ 16 Apr | 18 June | 22 Sept | 1984 17 Apr |
|---|---|---|---|---|
| ME 22 | 0.6 | 0.4 | 0.2 | 0.1 |
| ME 23 | 1.5 | 0.1 | 0.4 | N.D |
| ME 24 | 0.1 | - | 0.2 | N.D |
| ME 25 | 1.8 | - | 0.04 | 0.4 |
| ME 26 | 1.5 | 0.1 | 0.4 | N.D |
| ME 27 | 2.0 | 0.1 | 0.3 | 0.2 |
| ME 28 | 0.1 | 0.1 | 0.1 | 0.1 |
| ME 29 | 1.5 | 0.04 | 1.1 | 0.1 |
| ME 30 | 0.7 | 0.3 | 0.2 | 0.1 |
| ME 31 | - | 0.1 | 0.1 | 1.2 |
| ME 32 | 0.4 | 0.1 | 0.1 | 0.1 |
| ME 51 | 0.8 | 0.1 | 0.4 | 0.3 |
| ME 52 | 3.8 | 0.2 | 0.1 | 0.4 |
| ME 52A | 1.4 | - | - | - |
| ME 53 | 1.8 | - | 0.2 | 0.6 |
| ME 54 | 2.1 | - | 0.02 | 0.8 |
| ME 54X | - | N.D | - | - |
| ME 55 | 0.1 | - | 0.3 | 0.8 |
| ME 56 | 0.2 | 0.1 | 0.04 | 0.2 |
| ME 40 | 0.7 | - | - | - |
| ME 1 | - | - | 0.4 | - |
| ME 2 | - | - | 0.4 | - |
| ME 3 | - | - | 0.3 | - |
| ME 4 | - | - | 0.4 | - |
| ME 5 | - | - | 0.3 | - |

| Sta_tions | ---1983--- 25 June | 20 Sept |
|---|---|---|
| A 1 | N.D | - |
| A 2 | N.D | - |
| A 3 | N.D | - |
| A 4 | N.D | - |
| A 5 | 0.1 | - |
| A 6 | N.D | - |
| A 7 | 0.5 | - |
| A 8 | 0.2 | - |
| A 9 | 0.7 | - |
| A 10 | N.D | - |
| A 11 | 0.1 | - |
| A 12 | 0.2 | - |
| A 13 | 0.03 | - |
| A 14 | 0.1 | - |
| A 15 | N.D | - |
| A 16 | - | 0.5 |
| A 17 | - | 0.6 |
| A 18 | - | 0.1 |
| A 19 | - | 0.8 |
| A 20 | - | 1.33 |
| A 21 | - | 0.6 |
| A 22 | - | 0.5 |
| A 23 | - | 1.4 |
| A 24 | - | 0.8 |
| A 25 | - | 0.7 |

| Sta_tions | ---1983--- 26 June | 17 Sept |
|---|---|---|
| D 1 | 0.5 | - |
| D 2 | 0.03 | - |
| D 3 | N.D | - |
| M 1 | 0.1 | - |
| M 2 | 0.1 | - |
| M 3 | 0.1 | - |
| M 4 | 0.5 | - |
| M 5 | 0.1 | - |
| M 6 | 0.03 | - |
| M 7 | 0.1 | - |
| M 8 | N.D | - |
| M 9 | 0.2 | - |
| M 10 | 0.1 | - |
| M 11 | 0.5 | - |
| M 12 | 0.4 | - |
| M 13 | 0.2 | - |
| BL 0 | - | 0.5 |
| BL 1 | - | 0.4 |
| BL 2 | - | 0.8 |
| BL X | - | 0.6 |
| BL 5 | - | 0.4 |
| B 1 | - | 1.6 |
| B 2 | - | 0.4 |
| B 3 | - | 0.9 |
| B 4 | - | 0.3 |

TABLE III-1 (Continuation)

| Stations | 1983 22 Sept |
|---|---|
| ME 6 | 1.1 |
| ME 7 | 0.4 |
| ME 8 | 0.5 |
| ME 9 | 0.3 |
| ME 10 | 0.6 |
| ME 11 | 0.3 |
| ME 12 | 0.04 |
| ME 13 | 0.3 |
| ME 14 | 0.3 |
| ME 15 | 0.1 |

| Stations | 1983 22 Sept |
|---|---|
| A 26 | 0.6 |
| A 27 | 0.9 |
| A 28 | 0.2 |
| A 29 | 0.4 |

| Stations | 1983 19 Sept |
|---|---|
| IZ 1 | 1.0 |
| IZ 2 | 1.2 |
| IZ 3 | 1.2 |
| IZ 4 | 1.2 |
| IZ 5 | 1.4 |
| IZ 6 | 0.7 |
| IZ 7 | 1.0 |
| IZ 9 | 1.0 |
| IZ 10 | 0.9 |
| IZ 11 | 0.8 |
| IZ 12 | 1.6 |
| IZ 13 | 5.0 |
| IZ 14 | 1.0 |
| IZ 15 | 1.2 |
| IZ 16 | 0.8 |
| M 1 | 0.3 |
| M 2 | 1.4 |
| M 3 | 0.2 |
| M 4 | 0.3 |
| M 12 | 0.5 |
| M 13 | 0.6 |
| M 14 | 2.1 |

| Stations | 1983 19 Sept |
|---|---|
| M 15 | 1.0 |
| M 16 | 0.2 |
| M 17 | 8.1 |
| M 18 | 0.9 |
| M 19 | 0.3 |
| M 23 | 0.8 |
| M 33 | 0.3 |
| M 34 | 0.6 |
| M 35 | 0.9 |
| M 36 | 0.5 |
| M 37 | 3.5 |
| M 38 | 0.4 |
| M 39 | 1.1 |
| M 40 | 0.6 |
| M 41 | 3.0 |
| M 42 | 1.4 |
| M 43 | 1.1 |
| M 44 | 0.6 |
| M 45C | 0.5 |
| M 45B | 0.6 |
| M 45A | 0.5 |
| M 46 | 0.4 |

| Stations | 1983 20 Sept |
|---|---|
| M 47 | 0.3 |
| M 48 | 1.1 |
| M 49 | 0.4 |
| M 50 | 0.6 |
| M 51 | 0.5 |
| M 52 | 0.4 |
| M 53 | 0.8 |
| M 54 | 0.4 |
| M 55 | 0.4 |
| M 57 | 0.8 |
| M 58 | 0.4 |
| M 59 | 1.1 |
| M 61 | 0.6 |
| M 62 | 0.4 |
| M 63 | 0.5 |
| M 64 | 0.4 |
| D 1 | 0.3 |
| D 2 | 0.4 |
| D 2A | 0.3 |
| D 3 | 0.5 |
| D 4 | 0.4 |
| D 5 | 1.8 |
| D 6 | 0.8 |

N.D : Below the Detection Limit of the Method.

TABLE III-2 The Percentage of Frequency Distribution(f%) of DDPH in Sea Water (ug/l)

| Location | Number of Sample | Conc. Range (ug/l) | f% |
|---|---|---|---|
| Iskenderun Bay | 91 | N.D-1.0 | 21.8 |
| Mediterranean Sea | 76 | N.D-1.0 | 18.2 |
| The Sea of Marmara | 59 | N.D-1.0 | 14.2 |
| Aegean Sea | 27 | N.D-1.0 | 6.5 |
| Izmit Bay | 6 | 0.7-1.0 | 1.4 |
| Black Sea | 5 [a] | 0.3-0.8 | 1.2 |
| Total | 264 | N.D-1.0 | 63.3 |
| Iskenderun Bay | 51 | 1.0-2.0 | 12.2 |
| Mediterranean Sea | 11 | 1.0-2.0 | 2.6 |
| The Sea of Marmara | 9 | 1.0-2.0 | 2.2 |
| Izmit Bay | 8 | 1.0-2.0 | 1.9 |
| Aegean Sea | 2 | 1.0-2.0 | 0.5 |
| Total | 81 | 1.0-2.0 | 19.4 |
| Iskenderun Bay | 38 | 2.0-4.0 | 9.1 |
| The Sea of Marmara | 3 | 2.0-4.0 | 0.7 |
| Mediterranean Sea | 2 | 2.0-4.0 | 0.5 |
| Total | 43 | 2.0-4.0 | 10.3 |
| Iskenderun Bay | 27 | > 4.0 | 6.4 |
| Mediterranean Sea | 1 | > 4.0 | 0.2 |
| The Sea of Marmara | 1 | > 4.0 | 0.2 |
| Izmit Bay | 1 | > 4.0 | 0.2 |
| Total | 30 | > 4.0 | 7.0 |
| Overall Total | 418 | N.D->4.0 | 100 |

a : Insufficient Data

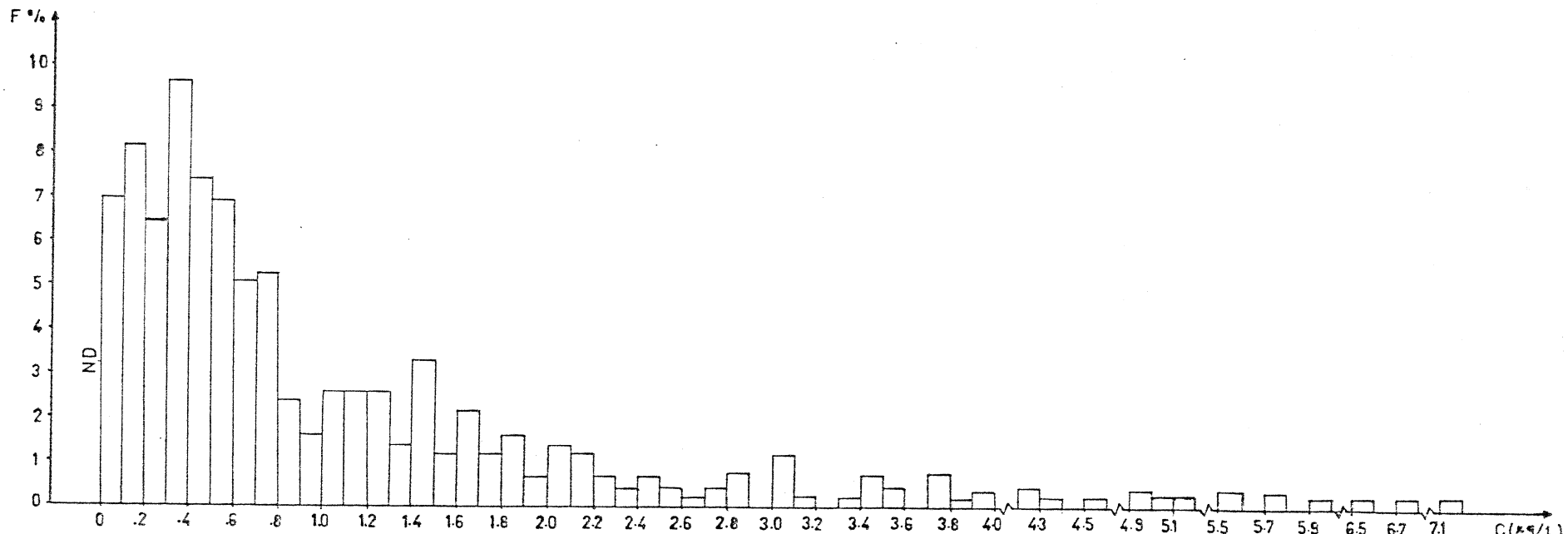



FIGURE III-1 The Average Frequency Distribution of DDPH in Sea Water Samples around Turkey.

TABLE III-3 The Mean Values of DDPH Concentrations and Their Ranges in Sea Water in the all Investigated Locations

| Date | Location | N | R | $\bar{X}$ | T °C (av) |
|---|---|---|---|---|---|
| Aug. 5,1981 | Iskenderun Bay | 4 | 0.7-1.9 | 1.40 [a] | 29.84 |
| Nov. 21,1981 | " | 7 | 0.7-3.7 | 1.44 | 21.36 |
| Feb. 24,1982 | " | 22 | 1.1-11.8 | 3.79 | 15.90 |
| Apr. 27,1982 | " | 14 | 0.8-11.2 | 3.14 | - |
| May. 13,1982 | " | 22 | 0.8-25.2 | 3.88 | 18.85 |
| July 5,1982 | " | 19 | 0.5-3.9 | 1.47 | 27.45 |
| Aug. 30,1982 | " | 10 | 0.2-2.0 | 0.64 | 28.85 |
| Nov. 3,1982 | " | 9 | 0.2-1.8 | 0.68 | 23.15 |
| Apr. 14,1983 | " | 12 | 0.04-5.7 | 2.07 | 18.14 |
| Aug. 31,1983 | " | 18 | 0.4-5.2 | 1.0 | - |
| Oct. 5,1983 | " | 27 | 0.1-1.0 | 0.42 | 26.14 |
| Apr. 17,1984 | " | 16 | 0.1-2.2 | 0.43 | 18.12 |
| Apr. 16,1983 | Mediterranean Sea | 18 | 0.1-3.8 | 1.17 | |
| June 18,1983 | " | 13 | N.D-0.4 | 1.62 | |
| Sept.22,1983 | " | 33 | 0.04-1.1 | 0.30 | |
| Apr. 17,1984 | " | 17 | N.D-1.2 | 0.30 | |
| June 25,1983 | Aegean Sea | 15 | N.D-0.7 | 1.83 | |
| Sept.20,1983 | " | 14 | 0.1-1.4 | 0.67 | |
| June 26,1983 | The Sea of Marmara | 16 | N.D-0.5 | 0.18 | |
| Sept.20,1983 | " | 56 | 0.2-8.1 | 0.88 | |
| Sept.19,1983 | Izmit Bay | 15 | 0.8-5.0 | 1.33 | |
| Sept.17,1983 | Black Sea | 5 | 0.4-0.8 | 0.54 | |

N : Number of Sample
R : Concentration Range (ug/l)
$\bar{X}$ : Arithmethical Mean
a : (81,85,7.1,6.5 ug/l) These values were not taken
N.D : Below the detection limit of the method

maximum (1.33 ug/l) in Izmit Bay and is observed to decrease in the following order : The Sea of Marmara (with an average 0.88 ug/l), the Aegean Sea (0.67 ug/l), the Black Sea (0.54 ug/l), Iskenderun Bay (0.42 ug/l) and the Mediterranean Sea (0.30 ug/l). Altough the concentrations are not very different from each other. Izmit Bay is the most polluted than the other regions whereas the Mediterranean is the least polluted. All the average DDPH concentration values obtained from around Turkish coasts are compared with those found in other parts of the Mediterranean, for example; the average DDPH concentration around the coast of Israel was 4.75 ug/l, around the coast of Crete was 6.25 ug/l, in the western Aegean Sea was 1.8 ug/l (1980) with a maximum at 6.4 g/l and a minimum at 0.7 ug/l. The concentrations were between 0.4-1. 3 ug/l around the coast of Malta and 0.5-50 ug/l around the coast of Adriatic Sea (UNEP,1980). Except for the Malta coasts,the Turkish surface waters were found to be much less polluted than most of the Mediterranean countries which were relatively polluted.

The high values found in Iskenderun Bay (FIGURE II-1) such as 260 ug/l in front of an oil pipeline terminal and 25.2 ug/l at station 11 were probably due to oil slicks formed very recently. It might be speculated that the concentrations such as 5.6 and 5.7 ug/l found at stations 20 and X-1 in April 1983 might have been caused by the two gyres around these stations (AKYUZ,1957) which can act as traps for the accumulation of hydrocarbons.

The gravimetric method was also used for the calculation of the concentration of total dissolved/dispersed petroleum hydrocarbons in sea water and the average values obtained are given in TABLE III-4.

In terms of gravimetric estimations the Black Sea, the Sea of Marmara and Izmit Bay showed more or less the same average values differing a little in the ranges. Whereas the Mediterranean, excluding Iskenderun Bay has shown the highest average and range, but the presence of samples whose concentrations were N.D (below the detection level of the method), prevents us from making a generalization about the Mediterranean being the most polluted area.

The relatively high average concentration for Iskenderun Bay could be explained with the presence of sources like pipeline terminals, harbours and heavy traffic of tankers but that of Mediterranean is difficult to explain. One reason for high concentrations might be the natural petroleum hydrocarbon formation at the northeastern Mediterranean as hypothesized previously (LE LOURD, 1977) but it is not well proved yet.

A relation was not observed between the chrysene equivalent (TABLE III- 3 & 4) and gravimetric findings for DDPH in sea water as was expected, because the gravimetric method gives information about the organic materials as a whole whereas chrysene findings were specific. The availability of chrysene as an international standard, because of its common presence in crude oils and highest solubility in sea water. However, the gravimetric values obtained in this study can also be compared with those from other regions. For instance, the Boston Harbour as a very polluted area yielded a maximum value of about 292 ug/l (HANNA, 1983) and some of the other areas have values shown in TABLE III-5. These values are much less than the average values found in September cruise.

TABLE III-4 The Range and Mean Values of DDPH Concentrations(ug/l) in September 1983, estimated by Gravimetric Technique

| Location | Number of Sample | Conc. Range (ug/l) | Arithmethical Mean |
|---|---|---|---|
| Mediterranean Sea | 14 | N.D-6860 | 2339 |
| Iskenderun Bay | 15 | 125-2707 | 1588 |
| Aegean Sea | 2[a] | 1182-1639 | 1410 |
| Black Sea | 5[a] | 71-1643 | 886 |
| Izmit Bay | 15 | 143-2714 | 843 |
| The Sea of Marmara | 48 | 71-2214 | 766 |

a: Insufficient data; N.D: Below the detection limit of the Method

TABLE III-5 The Comparison of the Concentration of Oil in Sea Water (ug/l) Found in Other Parts of the World (HANNA,1983)

| Site | Boston Harbour | HongKong Harbour | Halifax Bermuda | Pasific Ocean | Egyptian Red Sea Coastline 1981 & 1983 |
|---|---|---|---|---|---|
| Conc.of Oil in Sea Water (ug/l) | 292 | 3.67-11.98 | 0.56-3.7 | 0.016 | 80 & 10-105 |

TABLE III-6 The Comparison of the Concentration of DDPH in Sea Water in two Periods 1981-1982 and 1982-1984 in Iskenderun Bay

| Region | 1st Period (1981-1982) Conc.Range (ug/l) | 1st Period (1981-1982) Arith. Mean | 2nd Period (1982-1984) Conc.Range (ug/l) | 2nd Period (1982-1984) Arith. Mean |
|---|---|---|---|---|
| I | 1.3-11.5 | 4.12 | 0.1-25.2 | 3.32 |
| II | 1.1- 6.5 | 2.33 | 0.1- 3.4 | 1.05 |
| III | 0.7- 8.8 | 3.90 | 0.04- 1.8 | 1.04 |
| IV | 0.7- 2.2 | 1.20 | 0.1- 2.5 | 1.01 |
| V | 1.9-11.8 | 5.50 | 0.2- 5.6 | 1.56 |
| VI | Insufficient data for arithmetical mean | | 0.1- 5.7 | 1.45 |

b) Distribution of DDPH in Sea Water in Iskenderun Bay

The DDPH concentrations in the upper 1 meter column of the Bay of Iskenderun were monitored for the time period between 1982-84. During the monitoring period there has been a burst in the pipeline which carries Kirkuk crude oil to the bay. As a result considerable amounts of (approximately 8000 tons) crude oil introduced to the bay via Ceyhan River.

Since the monitoring has started before the incident occured it was hoped to see the immediate and after effects of such an unlucky event. In other words a chemical tracer, which can be measured relatively easily and accurately, has been introduced to a volume which has a dimensions of 60 km length x 30 km width and 1 meter depth. This volume of water has one major river input and open to general circulation of Mediterranean at one end.

The measured DDPH concentrations in the bay is given in TABLE III-3 and plotted in FIGURE III-2, for the 1982-1984 time period. The most striking feature of the FIGURE III-2 is that three minimum zones all in Aug-Nov period has been observed during 1981-1984 monitoring period such as 1.40 ug/l in Aug.1981, 1.44 ug/l in Nov. 1981, 0.64 ug/l in Aug. 1982, 0.68 ug/l in Nov. 1982 and 1.0 ug/l in Aug. 1983. During winter and spring the observed DDPH concentrations increased to higher levels which were 3.79 ug/l in Feb. 1982, 3.14 ug/l in Apr. 1982, 3.88 ug/l in May 1982, 2.07 ug/l in Apr. 1983.

This somewhat natural cycle has been disturbed by the introduction of some 8000 tons of crude oil to the surface waters of the bay. The immediate effect can be seen by the existence of a peak value of 25.2 ug/l DDPH concentration in surface waters of the gulf. But still the average values did not increased well above the expected annual cycle. Even after this event the minimum values has decreased to background levels again in Aug-Nov time period. These variations in concentration depends on the fate of oil which is influenced by different factors such as location, winds, waves, currents, water depth, temperature, salinity, organisms, nutrients and nature of oil.

During the monitoring of the bay DDPH, temperature, salinity and dissolved oxygen were also measured. If we plot the observed sea water temperature for the study period (TABLE III-3, FIGURE III-2), it can clearly be seen that temperature is the most critical factor in the self cleaning of the bay. It is known that evaporation is one of the most critical factor in petroleum spillages (BUTLER, 1976).

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. For instance a decrease in the temperature increases the solubility of the volatile components but decreases the solubility of the nonvolatile components (RICE et al., 1976). An increase in temperature of sea water leads to a decrease in concentration of DDPH in the measured upper 1 meter column of the sea water. Ofcourse, the exchange of water between the bay and the general Mediterranean currents also plays an important effect during the decrease in concentration of DDPH. As mentioned in Chapter 1 section b evaporation removes the most volatile components of crude oil from the emulsion the heavier parts then subject to some

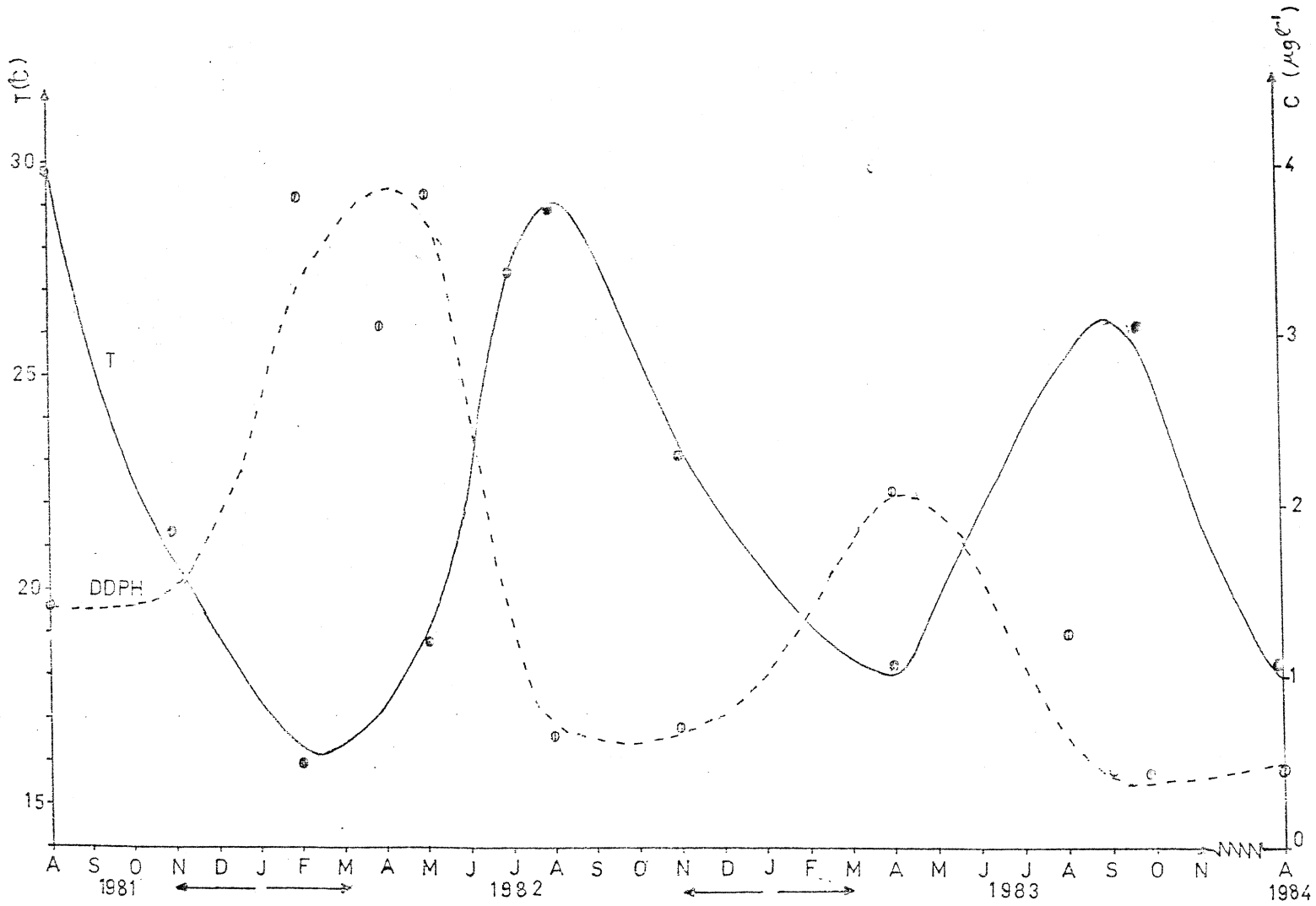



FIGURE III-2 The Seasonal Variation of DDPH and Temperature in Sea Water in Iskenderun Bay.

other events which removes than from the water column via different routes.

The observed maximas in Winter and Spring season can still be explained by temperature effect as well as by biological activity. During the monitoring two of such events has been measured, but in April 1982 the flow of crude oil has distributed the system which left us only one maximum range season in 1983. The combined effect of temperature and biological activity is the most likely explanation for the observed maximums in Winter and Spring seasons. Future monitoring programmes should include Winter and spring seasons in more detail as Aug-Nov period.

Distributions were also investigated by dividing the gulf into six regions (FIGURE II-1). Regions are namely Karatas (I), Botas+Dortyol (II), Iskenderun (III), south coast (IV) and two gyres (V & VI). Karatas region is expected to be influenced by Ceyhan River, while Botas+Dortyol region may be polluted by two oil-pipe terminals. Iskenderun region may be effected by the harbour and iron-steel plant. There is no significant source of pollution at the south coast. Two gyres at the centre may also act as a trap for the distribution of the pollutants.

The aim of tabulation of the results for two periods indicated above was to see if there is any increase in pollution via the discharge of crude oil through the Ceyhan River into the bay after the breakage of pipe-line in spring 1982 and compare the pollution results between different regions.

The average concentrations of DDPH were calculated before and just after the incident (TABLE III-6). At the first part of the table the concentrations in different regions I, II, III and V were changing from 2.3 to 5.5 ug/l. The south coast region IV has an average of about 1.2 ug/l concentration (S.U 1982, SUNAY 1982)

Immediately after the incident, the high concentration at Karatas region (4.12 ug/l) was an indication of the input by the river, and the higher concentration at the first gyre region (5.5 ug/l) may indicate a transportation of polluted surface waters from Karatas coast to the center of the bay. Altough the regions I and V were found to be more polluted from the other regions,the average concentrations were lower in the second period (1982-1984) which were between 1.56- 3.32 ug/l.

## 2- Petroleum Hydrocarbons (PHs) in Marine Biota

In the marine environment, fish may be exposed to a wide variety of petroleum hydrocarbons and polar compounds containing oxygen, nitrogen and sulphur in water, sediments and food supply which readily take up hydrocarbons. Fish living in petroleum contaminated environments accumulate and excrete hydrocarbons. But some lower molecular weight aromatic compounds of petroleum are most acutely toxic to fish (MALINS & HUDGINS,1981). In fact, crude petroleum contains only small amount of these highly toxic PHs, however fishing can be a problem in petroleum polluted areas.

There is a commercial fishing in Iskenderun Bay where crude oil was spilled in Spring 1982. Thus some fish species (their liver and flesh) were analyzed for the monitoring and comparison of PHs concentration.

a) Distribution of PHs in some Marine Organisms in Iskenderun Bay

During monitoring of DDPH in the bay of Iskenderun biological samples have also been analyzed. These includes Mullus barbatus, Solea solea, Epinephelus aeneus and Upeneus moluccensis species (TABLE III-7).

General frequency distribution of PHs concentration in fish flesh and liver is calculated from TABLE III-7 and plotted in FIGURE III-3 a,b. FIGURE III-3(a) shows about 82% of PHs concentration is less than 8 ug/l wet weight (wet wt.) and 17% is ranged between 10-24 ug/g, for fish liver samples. The PHs concentrations for fish flesh are shown in FIGURE III-3(b). It can be observed that nearly 76% is below the 0.9 ug/g and 24% is ranging between 1.0 and 2.5 ug/g (wet wt.).

No relationship has been found between the size and PHs concentration of the biological samples.

The monitoring period has strated couple of months before the oil spillage to the bay. There was an increasing trend in the concentration of PHs both in liver and flesh samples of biological species during 1982 Winter season.

This can be explained by the combined effects of temperature and biological activity within the sea water. The decrease in temperature of sea water increases the PHs concentration of liver and flesh. It is expected that the increasing of the PHs concentration in liver observed before the increasing of PHs concentration in flesh (LEE, 1976).

The seasonal variation of PHs concentrations in fish liver and flesh was investigated and found to have approximately similar distribution in each location. The average concentration of PHs (TABLE III-8) in M. barbatus liver reached maximum values (FIGURE III-4a) 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 PHs concentration of M. barbatus, S. solea flesh (FIGURE III-4b) had maximum value in April 1982 and March (E. aeneus) but concentrations decreased and then reached maximum value in October 1982 after the pipeline incident.

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 measured. After 5 months in fish flesh concentrations are affected. Rapid decrease in PHs concentration in both liver and flesh samples shows that there must be some enzymatic factors which becomes active to reduce the increased concentrations.

The range and average concentration in fish liver and flesh were also calculated to compare the results of Karatas-Yumurtalik with those of Botas region (TABLE III-9) before and after spillage.

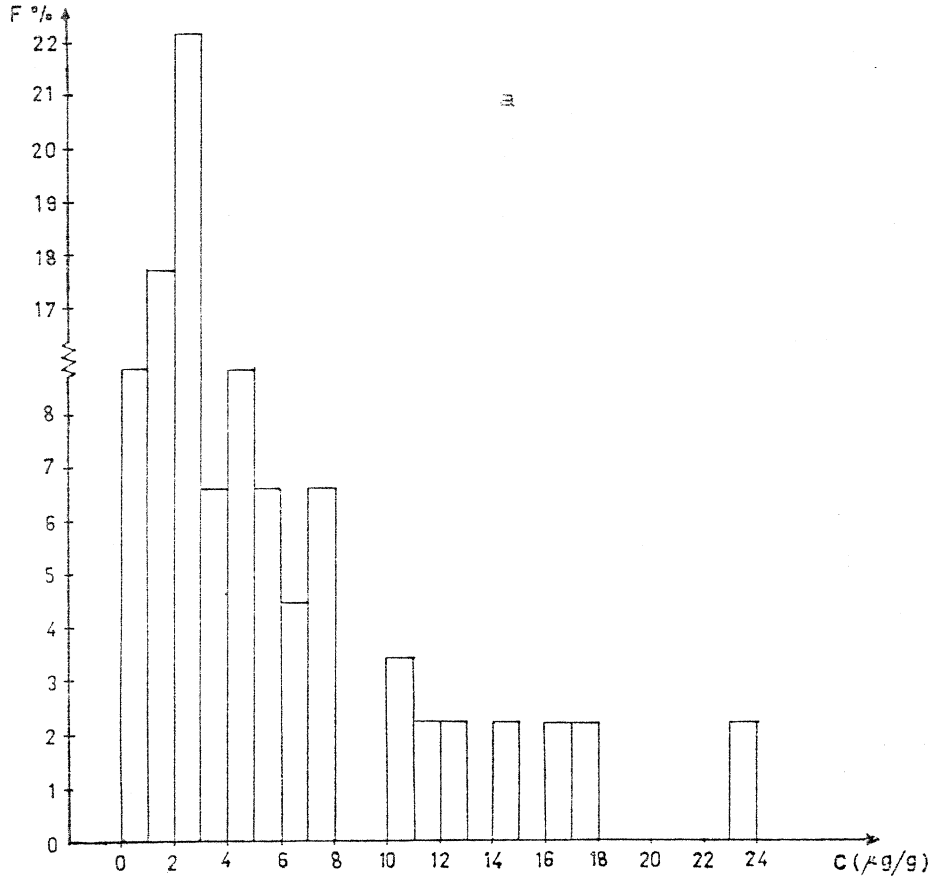
The ranges of PHs in fish liver extracts (wet wt.) collected between January and November 1982, was changing between 0.07-23 ug/g for M. barbatus, N.D-17.7 ug/g for S. solea, 0.50-7.69 ug/g for E. aeneus and between 2.8-5.2 ug/g for U. moluccensis. The change in fish flesh was between 0.05-2.32 ug/g for M. barbatus, 0.04-1.84 ug/g for S.solea, 0.02-2.42 ug/g for E. aeneus, and 0.30-2.50 ug/g for U. moluccensis.

TABLE III-7 Concentration of Petroleum Hydrocarbons (PHs) in Fish Samples in Iskenderun Bay

| Region | Species: / Date (1982) | M. Barbatus A | M. Barbatus $C_l$ | M. Barbatus $C_f$ | S. Solea A | S. Solea $C_l$ | S. Solea $C_f$ | E. Aeneus A | E. Aeneus $C_l$ | E. Aeneus $C_f$ |
|---|---|---|---|---|---|---|---|---|---|---|
| I Karatas | [b] Jan. | 11.5 | 0.76 | 0.08 | 17.17 | 2.15 | 0.04 | 13.5 | 0.69 | 0.02 |
| | | 14 | 0.38 | 0.05 | - | - | - | - | - | - |
| | [b] March | - | - | - | - | - | 0.17 | - | 7.69 | 0.94 |
| | Apr.28 | - | 1.02 | 1.03 | - | 1.90 | 0.16 | - | - | - |
| | May.13 | 17.25 | 1.93 | 0.36 | 20.75 | - | 0.24 | - | - | - |
| | June 7 | 14.67 | 17.15 | 0.49 | - | - | - | 14.5 | 1.12 | 0.21 |
| | July 8 | 13 | 3.3 | 1.03 | 10.73 | - | 0.82 | - | - | - |
| | Aug.31 | 11.17 | 14.92 | 0.51 | 12.36 | 12.35 | 0.54 | 28 | 0.49 | 0.55 |
| | Oct.21 | 15.67 | 2.61 | 1.61 | 16 | 3.04 | 0.69 | - | 5.60 | - |
| | Nov. 3 | - | 0.72 | 0.22 | - | 2.27 | 0.21 | - | - | - |
| II Yumur_ talik | [b] Jan. | 17.75 | 0.08 | 0.03 | 25.25 | 0.66 | 0.04 | - | - | - |
| | [b] March | - | 0.75 | - | - | - | - | - | 8.62 | 1.33 |
| | Apr.28 | 15.5 | 10.3 | 1.03 | 16 | 1.23 | 0.62 | - | - | - |
| | | 11.25 | - | 0.88 | - | - | - | - | - | - |
| | | - | 2.1 | 0.37 | - | - | - | - | - | - |
| | May 13 | 13.9 | 0.91 | 0.36 | 21.5 | - | 0.18 | - | - | - |
| | June 7 | - | 10.63 | 0.49 | - | 1.92 | 0.40 | - | - | - |
| | July 8 | 13.17 | 2.55 | 1.85 | 17.5 | 11.7 | 0.64 | 18.25 | 1.28 | 0.66 |
| | Aug.31 | 10.31 | 6.65 | 0.26 | 18.5 | 6.46 | 0.56 | - | - | - |
| | Oct.21 | 13.5 | 7.92 | 1.15 | 24.5 | - | 0.83 | 14 | - | 2.42 |
| | Nov. 3 | 15.88 | 1.06 | 0.13 | - | - | - | - | - | - |
| II Botas | [b] Jan. | 18 | 0.07 | 0.06 | - | - | - | 15 | 0.60 | 0.04 |
| | | 15.5 | 0.47 | 0.07 | - | - | - | 17.5 | 0.54 | 0.07 |
| | [b] March | - | 8.08 | 1.68 | - | - | - | - | - | - |
| | | - | 2.09 | 0.96 | - | - | - | - | - | - |
| | Apr.28 | 13 | 7.61 | 0.83 | 23 | 5.30 | 0.88 | 14 | - | 1.95 |
| | May 13 | 12.17 | 16.58 | 0.29 | 22.5 | 1.96 | 0.26 | 17.5 | 2.11 | 0.20 |
| | June 7 | 12 | 2.31 | 0.21 | 22 | 2.55 | 0.10 | 18.5 | 0.79 | 0.10 |
| | July 8 | 12.57 | - | 1.30 | 15.82 | - | 0.10 | 18 | 4.47 | 1.88 |
| | Aug.31 | 12.70 | 23.02 | 0.79 | 23.5 | N.D | 0.44 | 38 | 4.47 | 0.80 |
| | Oct.21 | 17.5 | - | 2.32 | 14 | - | 1.34 | 11.83 | 4.99 | 2.04 |
| | | - | - | - | 16 | - | 1.84 | 14.75 | - | 0.88 |
| | | - | - | - | 27 | - | 1.38 | - | - | - |
| | Nov. 3 | - | 3.82 | 0.25 | - | 0.62 | 0.06 | - | 2.40 | 0.59 |

| Region | Date (1982) | Upeneus Mollucsensis A | Upeneus Mollucsensis $C_l$ | Upeneus Mollucsensis $C_f$ |
|---|---|---|---|---|
| I | Oct.21 | - | 2.83 | 0.58 |
| | Nov. 3 | - | - | 0.59 |
| II | Nov. 3 | 11.67 | 5.22 | 0.71 |
| III | Oct.21 | 11 | 7.29 | 0.32 |
| | | 14.25 | - | 2.57 |
| | Nov. 3 | - | 4.04 | 0.43 |

A: Average Length(cm), $C_l$ : Concentra. of PHs in Fish Liver(Wet Wt.(ug/g)), $C_f$ : Concentra. of PHs in Fish Flesh (Wet Wt.(ug/g)), N.D : Below the De_ tection Limit, b: (SUNAY, 1982)



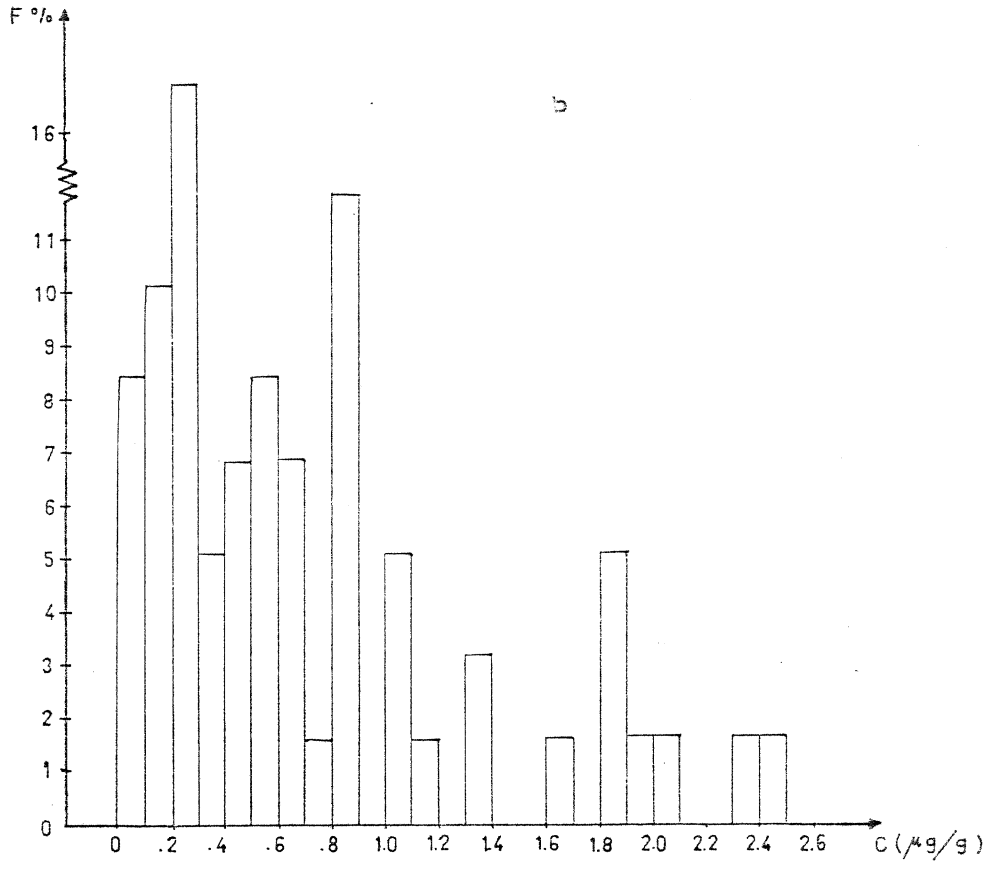




FIGURE III-3 The Average Frequency Distribution of PHs
a) Fish Liver Extract b) Fish Flesh Extract.

TABLE III-8 The Average Concentration of PHs in Fish Samples for all Regions in Iskenderun Bay

| Species: | M. Barbatus | | S. Solea | | E. Aeneus | |
|---|---|---|---|---|---|---|
| | $\bar{X}$ | | $\bar{X}$ | | $\bar{X}$ | |
| Date (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. 28 | 5.26 | 0.83 | 2.81 | 0.55 | - | 1.95 |
| May 13 | 6.47 | 0.34 | 1.96 | 0.23 | 2.11 | 0.20 |
| June 7 | 10.03 | 0.40 | 2.24 | 0.25 | 0.96 | 0.16 |
| July 8 | 2.93 | 1.39 | 11.70 | 0.52 | 2.88 | 1.27 |
| Aug. 31 | 14.86 | 0.52 | 9.41 | 0.51 | 2.48 | 1.22 |
| Oct. 21 | 5.27 | 1.69 | 3.04 | 1.22 | 5.30 | 1.78 |
| Nov. 3 | 1.87 | 0.20 | 1.44 | 0.14 | 2.40 | 0.59 |

c: Single sample value  L: Liver  F: Flesh

TABLE III-9 The Range and Average Concentrations of PHs in Fish Samples for Each Region in Iskenderun Bay

| Period & Region | M.B. Liver R | M.B. Liver $\bar{X}$ | M.B. Flesh R | M.B. Flesh $\bar{X}$ | S.S. Liver R | S.S. Liver $\bar{X}$ | S.S. Flesh R | S.S. Flesh $\bar{X}$ | E.A. Liver R | E.A. Liver $\bar{X}$ | E.A.Flesh R | E.A.Flesh $\bar{X}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1st P K | 0.38 | | 0.05 | | | | 0.04 | | 0.69 | | 0.02 | | |
| | 0.76 | (0.57) | 0.08 | (0.06) | | | 0.17 | (0.08) | 7.69 | (4.19) | 0.94 | (0.57) | |
| 1st P Y | 0.08 | | | | | | | | | | | | |
| | 0.75 | (0.42) | | | | | | | | | | | |
| 1st P B | 0.07 | | 0.06 | | | | | | 0.54 | | 0.04 | | |
| | 8.08 | (2.68) | 1.68 | (0.69) | | | | | 0.60 | (0.57) | 0.07 | (0.06) | |
| 2nd P K | 0.72 | | 0.22 | | 1.90 | | 0.16 | | 0.49 | | 0.21 | | |
| | 17.15 | (5.95) | 1.61 | (0.75) | 12.35 | (4.89) | 0.82 | (0.44) | 5.60 | (2.40) | 0.55 | | (*) |
| 2nd P Y | 0.91 | | 0.13 | | 1.23 | | 0.18 | | | | 0.62 | | |
| | 10.15 | (5.26) | 1.85 | (0.72) | 11.7 | (5.33) | 0.83 | (0.54) | | | 2.42 | | (*) |
| 2nd P B | 2.31 | | 0.21 | | N.D | | 0.06 | | 0.79 | | 0.10 | | |
| | 23.02 | (10.67) | 2.32 | (0.86) | 5.30 | (2.61) | 1.84 | (0.71) | 4.99 | (3.21) | 2.04 | | (*) |

1st P: First period(Jan.1982-March 1982)  2nd P: Second period(Apr.1982-Nov.1982)

R : Concentration Range (ug/g)  $\bar{X}$ : Arithmethical Mean (ug/g)

K : Karatas  Y : Yumurtalik  B : Botas  *: Insufficient data

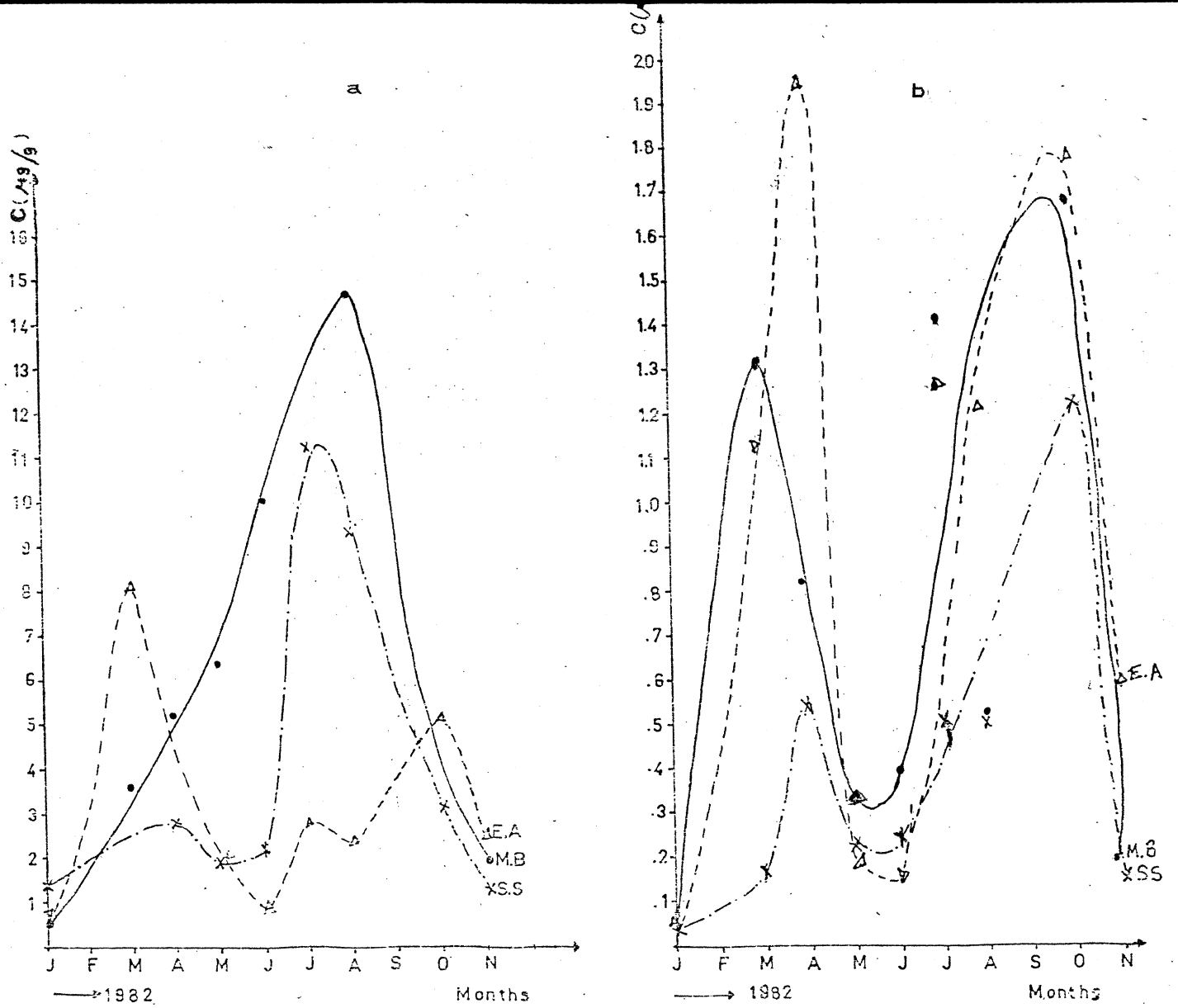



FIGURE III-4 The Seasonal Variation of PHs Concentration
a) Fish Liver Extract b) Fish Flesh Extract.

TABLE III-9 shows that the ranges and averages increased after the pipeline incident. For example, the liver concentration of M. barbatus in Karatas, Yumurtalik and Botas regions are 0.57-0.42 and 2.68 ug/g respectively in the first period (before incident) but they reached to 5.95-5.26 and 10.67 ug/g values after incident. So PHs concentration of fish liver were found to be about 10 times more for Karatas and Yumurtalik, 4 times more for Botas region after the pipeline incident. PHs concentrations of fish flesh were found about 12.5 times more for Karatas and 1.25 times more for Botas region after the pipeline incident. This shows that biological samples were also effected by such accidents and its remove some portion of the PHs from the sea water.

3- PHs in Sediment in Iskenderun Bay and the Mediterranean Sea

The distribution of PHs in sediments from the regions defined in FIGURE II-1 in Iskenderun Bay and concentrations are summarized in TABLE III-10. The frequency distribution for PHs values were plotted in FIGURE III-5.The 48% is below the 0.18 ug/g(wet wt.) and 31% is ranged between 0.18-0.46 ug/g(wet wt.) and 20% is ranged between 0.46-1.40 ug/g(wet wt.).

Limited number of sediment samples allow us to observe the change of PHs concentration after the incident except in the region I. The PHs in sediments of Karatas region (I) were studied in more detail due to collection of more samples in the same cruise of R/V Lamas and Erdemli research vessels. But the existence of data for the time period before and after the pipeline incidence showed the importance of sediments in the fate of crude oil as well. Some local increments were observed in Botas+Dortyol and in the gyre regions (TABLE III-10). During 1982 sampling period the concentration of PHs in sediments started to increase in April (FIGURE III-6) and reached its maximum in June. This abnormal increase in June while the DDPH concentration in sea water decreasing steadily clearly that the evaporated crude oil sinks to the bottom and fraction of it clearly reaches to the sediments. Some natural phonemenans then decreases the levels to background again (Nov.1981 value; SUNAY,1982).

The distribution of PHs in sediments of the Mediterranean Sea were analyzed in April 1983(TABLE III-10) and coastal locations are shown in FIGURE II-2. Concentration of PHs ranged between 0.01 and 0.60 ug/g for coastal sediments. Measurements were only made in April 1983 and locations were different. Thus, concentrations were also found to be lower than some other coastal regions of the Mediterranean,e.g.10-50 ug/g for Malta (SAMMUT, 1978) and 50 ug/g for France.

Another investigation was done for comparison both Kirkuk oil and Chrysene equivalent concentrations of PHs in the coastal sediment samples for Iskenderun Bay and the Mediterranean Sea in April 1983 . TABLE III-10 shows that the similar distribution of concentration and some high PHs values were found at station S-1 (in Iskenderun), 22 & 23 (in Mediterranean).At some stations which are close to harbours S-1 & S-2 and 22 & 23 Kirkuk oil equivalent concentrations were relatively more abundant than the Chrysene equivalent which is probably due to oil spills formed recently.

TABLE III-10 Concentrations and Average of PHs in Sediment Samples (ug/g)(wet wt.) and (Dry wt.)

(ISK): Iskenderun Bay
(ME) : Mediterranean Sea

| Regions & Stations | 1981 | | 1982 | | | | |
|---|---|---|---|---|---|---|---|
| | 21 Nov | 21 Dec | 24 Feb | 27 Apr | 14 June | 5 July | 2 Sept |
| I ISK C-I | - | 0.16 (0.28) | - | - | - | - | - |
| I ISK S-8 | - | 0.22 (0.38) | 0.21 (0.37) | - | - | - | - |
| I ISK 1 | - | - | 0.43 (0.75) | 0.17 (0.30) | - | - | - |
| I ISK C-2 | - | 0.27 (0.47) | 0.09 (0.16) | 0.14 (0.24) | - | - | - |
| I ISK 4 | 0.05 (0.09) | 0.13 (0.23) | 0.13 (0.23) | 0.21 (0.37) | - - | 0.27 (0.47) | 0.08 (0.14) |
| I ISK C-3 | - | 0.28 (0.49) | 0.12 (0.21) | 0.49 (0.86) | 1.43 (2.51) | - | 0.06 (0.11) |
| I ISK 11 | - | - | 0.09 (0.16) | - | - | 0.44 (0.77) | - |
| I ISK S-7 | - | - | 0.07 (0.12) | - | 0.81 (1.42) | - | - |
| $\bar{X}$ | - | 0.21 | 0.16 | 0.25 | 1.12 | 0.36 | 0.07 |
| II ISK S-6 | 0.33 (0.58) | 0.26 (0.46) | 0.08 (0.14) | - | 0.05 (0.09) | 0.14 (0.24) | 0.09 (0.16) |
| II ISK S-5 | - | - | 0.08 (0.14) | - | - | - | - |
| II ISK S-4 | 0.60 (1.05) | - | - | 0.57 (1.0 ) | - | - | - |
| II ISK 24 | - | - | 0.11 (0.19) | - | - | 0.03 (0.05) | - |
| II ISK 18 | - | - | - | - | - | 0.86 (1.51) | - |
| $\bar{X}$ | 0.46 | - | 0.09 | - | - | 0.34 | - |

TABLE III-10 (Continuation)

| Regions & Stations | -1981- 21 Nov | 1982 24 Feb | 27 Apr | 5 July | 2 Sept | ----1983---- 14 Apr | |
|---|---|---|---|---|---|---|---|
| III ISK 26 | - | 0.43 (0.75) | - | - | - | - | |
| III ISK 27 | - | - | - | - | - | 0.11 (0.19) | (0.16) k |
| III ISK S-3 | 0.51 (0.89) | - | - | - | - | 0.28 (0.49) | (0.25) k |
| III ISK S-2 | - | - | - | 0.03 (0.05) | - | N.D ( - ) | (0.62) k |
| III ISK S-1 | 0.11 (0.19) | - | - | - | - | 0.71 (1.24) | (2.26) k |
| III ISK 22 | - | 0.68 (1.19) | - | - | 0.08 (0.14) | - | |
| $\bar{X}$ | 0.31 | 0.56 | - | - | - | 0.37 | (0.82) k |
| IV ISK 2 | - | 0.68 (1.19) | - | - | - | 0.44 (0.77) | (0.67) k |
| IV ISK 3 | - | 0.11 (0.19 | - | - | - | - | |
| $\bar{X}$ | - | 0.40 | - | - | - | - | |
| V ISK 21 | - | - | - | - | - | 0.06 (0.11) | (0.15) k |
| V ISK 20 | - | 1.19 (2.09) | 0.08 (0.14) | - | - | 0.47 (0.82) | |
| V ISK 17 | 0.09 (0.16) | - | 0.34 (0.60) | - | - | - | |
| V ISK X-1 | - | - | - | - | - | 0.22 (0.38) | (0.43) k |
| V ISK 16 | - | - | - | - | - | 0.24 (0.42) | (0.47) k |
| V ISK 15 | - | - | - | 0.02 (0.04) | - | 0.10 (0.18) | (0.10) k |
| $\bar{X}$ | - | - | 0.21 | - | - | 0.22 | (0.29) k |
| VI ISK 5 | - | - | - | 1.01 (1.77) | - | - | |
| VI ISK 6 | - | 0.10 (0.18) | 0.70 (1.23) | - | - | - | |

TABLE III-10 (Continuation)

| Stations | | -1983- 17 Apr | |
|---|---|---|---|
| ME | B-3 | 0.38 (0.67) | |
| ME | B-9 | 0.25 (0.44) | (0.40)[k] |
| ME | 22 | 0.01 (0.02) | (1.41)[k] |
| ME | 23 | 0.34 (0.64) | (0.82)[k] |
| ME | 24 | 0.21 (0.37) | (0.51)[k] |
| ME | # | 0.06 (0.11) | (N.D )[k] |
| ME | 25 | 0.04 (0.07) | (0.17)[k] |
| ME | 26 | 0.55 (0.96) | |
| ME | 29 | 0.30 (0.53) | |
| ME | 31 | 0.39 (0.68) | |
| ME | 32 | 0.19 (0.33) | |
| | $\bar{X}$ | 0.25 | (0.66)[k] |

Chrysene equivalent concentration (wet wt.) (ug/g)
Chrysene equivalent concentration (Dry wt.) are given
in paranthesis ( ) (ug/g)
Concentrations with respect to Kirkuk oil (Wet wt.) are given
in paranthesis ( )[k] (ug-Oil/g)

$\bar{X}$ : Arithmethical Mean

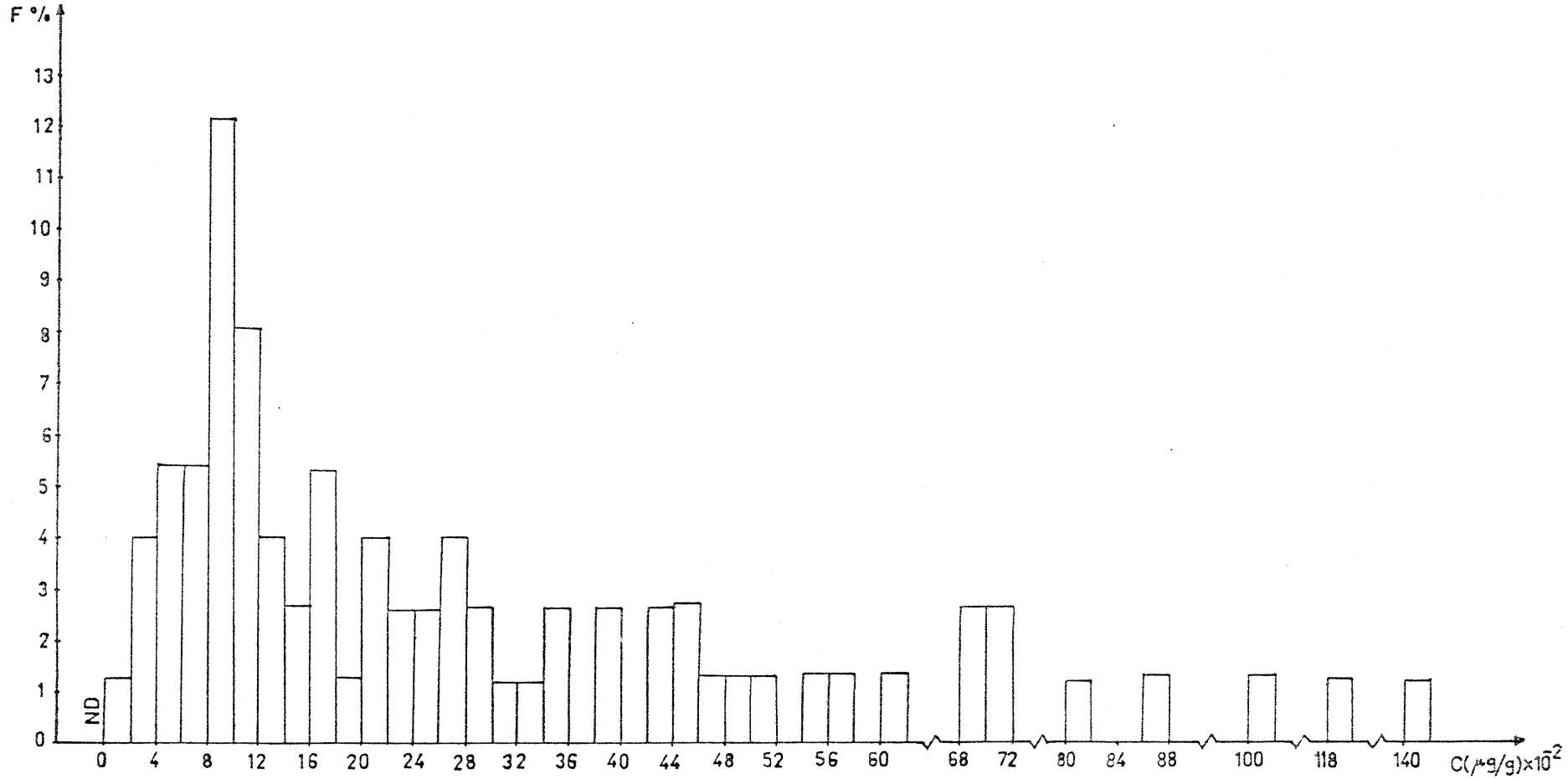



FIGURE III-5 The Frequency Distribution of PHs in Sediment Samples.

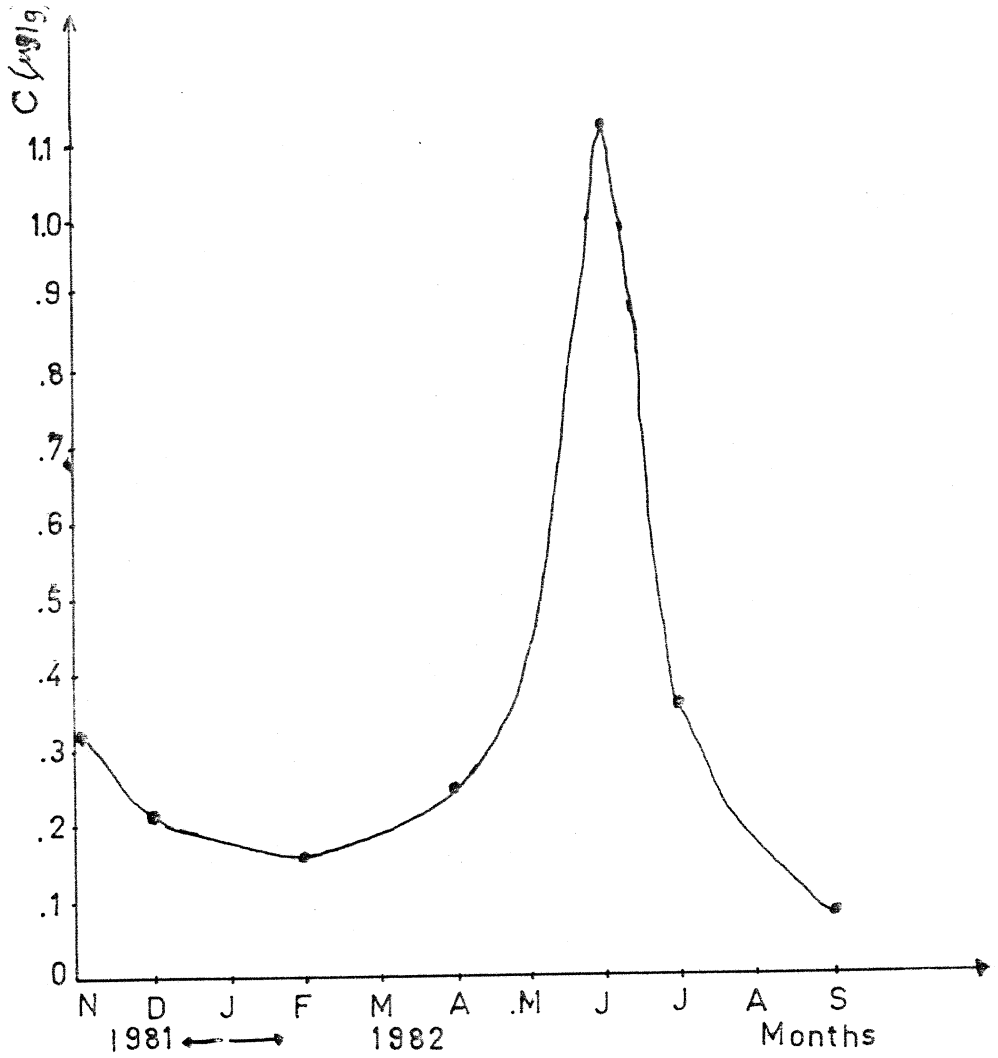



FIGURE III-6 The Seasonal Variation of PHs Concentration of Sediment in Iskenderun Bay.

## 4- Distribution of Petroleum Hydrocarbons in Agyatan (Hurma Bogazi) Lagoon

The Agyatan Lagoon (FIGURE II-3) has an area of about 11 square kilometers and the depth of this lagoon varies from 0.30 m to 1.25 m. It is separated from the sea by a narrow and long straigt. There is only a channel from Ceyhan River to the entrance of Agyatan Lagoon. The most important thing is that there is a fish farming in lagoon.

The spillage due to breakage of pipe-line which was carrying crude oil from Kirkuk in April 1982 has first flown into the Ceyhan River then into the bay as well as into the Agyatan Lagoon. Thus, the fate of petroleum hydrocarbons carried into the lagoon by river was also monitored in surface water, fish and in the sediments of the lagoon. The measurements are tabulated in TABLE III-11. DDPH concentration in surface water increased enormously (average value 1.38 ug/l in May 1982) just after the pollution but then decreased down to 0.5 ug/l (average) in Dec. 1982. Between December 1982 and October 1983 having no data, prevents us from monitoring the fate of oil in the lagoon.

Some physical parameters such as temperature and salinities were measured. For example, salinity values were from different part of the lagoon 34.7, 37.7 and 40.2 %o in September 1982 and 39%o in December 1982. Temperature value was 16°C in September 1982.

Agyatan Lagoon has shallow water so that it can be more effected than Iskenderun Bay by some physical factors such as temperature which causes evaporation, dissolution etc.

The PHs concentration increased in sediment in June 1982 TABLE III-11c shows that this increased values. But concentration decreased in the region far from the Kuzuluk. The Kirkuk oil concentration was found to be much more than chrysene equivalent concentration: Chrysene equivalent concentration was 13.5 ug/g in Kuzuluk and 0.02 ug/g 750 m away from the Kuzuluk but Kirkuk oil concentration was 117.5 ug-Oil/g in Kuzuluk and 16.4 ug-Oil/g in 750 m away from the Kuzuluk.

In the most cases, spectrofluorimetric analysis of sediments showed a broad peak with fluorescence excitation maxima between 362-370 nm and emission maxima between 400-402 nm which was due to Pyrenes (SUNAY, 1982) and it was similar to Kirkuk crude oil fluorescence excitation and emission maxima.

The effects of pollution on fish flesh and liver were not investigated exactly. Some dead fish flesh samples were analysed but it did not explain their death reason. Probably the flesh was the last organ affected among the other organs of the fishes and thus the death may be due to the preventation of oil from breathing by adsorption on their gills.

Consequently, the surface water was polluted with oil (Kirkuk crude oil) and caused to kill the fishes and then it settled till June 1982.

TABLE III-11 Concentration of Petroleum Hydrocarbons in Agyatan Lagoon

a) in Surface Waters (ug/l)

| Location | 1982 | | | | 1983 |
|---|---|---|---|---|---|
| | 1-11 May | 15-25 June | 9 Sept. | 7 Dec. | 11 Oct. |
| 1-Kuzuluk | 2330 | 2.7<br>5.7 | 5.6 | 0.1 | 2.3 |
| 2-Kuzuluk(2m away) | 300 | 0.5 | 1.8 | - | 2.3 |
| 4-Kuzuluk(50m away) | 496 | 4.2 | 1.4 | 0.9 | 2.4 |
| 5-Kuzuluk(300m away) | - | 3.9 | - | - | - |
| 6-Kuzuluk(750m away) | - | 2.0 | 2.3 | - | 1.4 |
| Average ($\bar{X}$) | 1038 | 3.2 | 2.8 | 0.5 | 2.1 |

b) in Fish (ug/g, wet wt.)

| Species | Organ | 1982 | |
|---|---|---|---|
| | | 1 May | 7 Dec. |
| Sparus aurata(Cupra) | Flesh | 0.9 | - |
| Diplodus annularis(Isparoz) | " | 0.9 | - |
| Mugil cephalus(Kefal) | " | 0.7 | 0.5 |
| " | Liver/Flesh | - | 1.5/0.5 |
| " | " | - | 1.3/0.7 |

c) in Sediment (ug/g, wet wt.)

| Location | 1982 | | 1983 |
|---|---|---|---|
| | 27 April | 15-25 June | 11 Oct. |
| 1-Kuzuluk | 0.6<br>(1.1) | 13.5 (117.5)[k]<br>(23.7) | 0.2 |
| 2-Kuzuluk(2m away) | - | 0.3<br>(0.5) | 0.3<br>(0.5) |
| 3-Kuzuluk(30m away) | - | 7.7<br>(13.5) | 0.1<br>(0.2) |
| 6-Kuzuluk(750m away) | - | 0.02 (16.42)[k]<br>(0.03) | - |

Note : Dry weight concentrations are given in paranthesis ( )

Kirkuk oil " " " " ( )[k]

## 5- Gas Chromatographic Measurements

As the final section of this work, the sea water, fish and sediment samples collected from Iskenderun Bay were analysed by gas chromatography for the determination of n-paraffinic range, $n\text{-}C_{17}$ + Pristane (Pr)/$n\text{-}C_{18}$ + Phytane (Ph) ratio and polycyclic aromatic hydrocarbon (PAH) individually. Altough the samples were analysed by fluorescence spectrometer for the quantification of PAH the results were obtained as chrysene equivalent.

Gas chromatographic analyses were performed mainly for the determination of PAHs other than chrysene. Paraffins were investigated to be able to predict that the hydrocarbons are originated from crude oils as well as to determine the fate of oil in the water column (e.g. in sea water, fish and sediments).

$n\text{-}C_{17}$ + Pr/$n\text{-}C_{18}$ + Ph ratio was calculated in order to identify the main source of pollutants.

### a) Gas Chromatography of Tar Balls

The gas chromatographic characteristics of tar balls collected from Iskenderun Bay are tabulated in TABLE III-12. Some chromatographic results of tar ball are shown in FIGURE III-7. The tar balls analysed were mostly collected from the surface of the sea water (FIGURE II-1) and a few from the beaches. As shown in TABLE III-12, the age of tar balls (determined by the method given by SUNAY (1982)) is not so large, they are mostly formed within a month, particularly within last 2 weeks.

The $n\text{-}C_{17}$+ Pr/$n\text{-}C_{18}$+ Ph ratios were in coincidence with that of Kirkuk crude oil ( ~ 1.2) which confirms that tar balls are also originated from the local sources, as observed in sea water, which will be discussed in the next section.

### b) Gas Chromatography of Sea Water Samples

Typical gas chromatograms of sea water samples are shown in FIGURE III-8 and the gas chromatography results are given in the TABLE III-13. The PAH concentration determined by fluorescence and gas chromatograph was mostly in the same order of magnitude, but without a general correlation between them. The general pattern of n-paraffins between $C_{10}$ - $C_{35}$ is observed in almost all sea water samples differing only in the C-range. The paraffinic profile on most of gas chromatograms provides typical features of oil slicks (EHRHARDT & BLUMER, 1972). Especially the samples from stations X-1 (VI), 21 (III) and S-8 (I) yielded varying characteristic patterns of crude oil with two distinct humps, first between $n\text{-}C_{12}$ , $n\text{-}C_{25}$ and the second between $n\text{-}C_{26}$ , $n\text{-}C_{35}$ (FIGURE III-8).

The crude oil chromatograms usually start with $n\text{-}C_9$ or $n\text{-}C_{10}$ (WONG *et al*,1976); therefore in these three stations as well as in stations 2 & 6 (IV) and Botas (II), samples were probably contaminated by oil slicks formed very recently (within a few days) because only a few percent of the n-paraffins were lost by evaporation and dissolution (SHEKEL & RAVID, 1977).

The age of pollutants in sea water determined by gas chromatography was changing without any correlation between the locations of samples and the concentrations of hydrocarbons.

TABLE III-12 Gas Chromatographic Analysis of Tar Ball

| Stations | n-Paraffin Range | $n\text{-}C_{17}$ + Ph / $n\text{-}C_{18}$ + Pr | UCM | Approx. Age |
|---|---|---|---|---|
| X-2 | C 13 - C 14 | 1.1 | Small | ~2 weeks |
| 2&6 | C 13 - C 35 | 1.1 | Medium | ~2 weeks |
| X-1 | C 14 - C 32 | 0.9 | Medium | 2-3 weeks |
| 21 | C 15 - C 35 | 0.8 | Medium | 1 month |
| Isdemir Beache | C 18 - C 37 | - | Large | 6-7 weeks |

TABLE III-13 Gas Chromatographic Analysis of Sea Water Extract

| Regions & Stations | Date (1982) | n-Paraffin Range | $n\text{-}C_{17}/n\text{-}C_{18}$ + Pr/ + Ph | Chry. equiv. Conc.PAH (ug/l) | PAH Identified & Conc.by GC(ug/l) | |
|---|---|---|---|---|---|---|
| I S-2 | Apr.27 | C 12 - C 35 | 1.1 | 4.5 | N.D | - |
| I C-2 | July 5 | C 17 - C 30 | 1.4 | 1.7 | N.D | - |
| II Bot. | Apr.27 | C 10 - C 28 | 1.3 | 260 | Fluorene | 4.2 |
| II S-6 | Apr.27 | C 14 - C 29 | 0.9 | 2.1 | - | - |
| II 24 | July 5 | C 15 - C 20 (T) | 1.4 | 1.2 | Fluorene | 14.6 |
| III 21 | Apr.27 | C 13 - C 35 | 0.9 | 1.3 | N.D | - |
| III S-3 | Apr.27 | C 15 - C 33 | 0.6 | 1.3 | - | - |
| III S-1 | July 5 | C 16 - C 30 | 1.3 | 1.6 | N.D | - |
| IV 2&6 | Apr.27 | C 10 - C 35 | 1.0 | 2.1 | N.D | - |
| V 17 | Apr.27 | C 15 - C 20 | 1.0 | 11.2 | Fluorene | 4.2 |
| VI X-1 | Apr.27 | C 13 - C 35 (T) | 1.2 | 1.2 | - | - |
| Kirkuk C.O | | C 10 - C 35 | 1.2 | - | - | - |

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

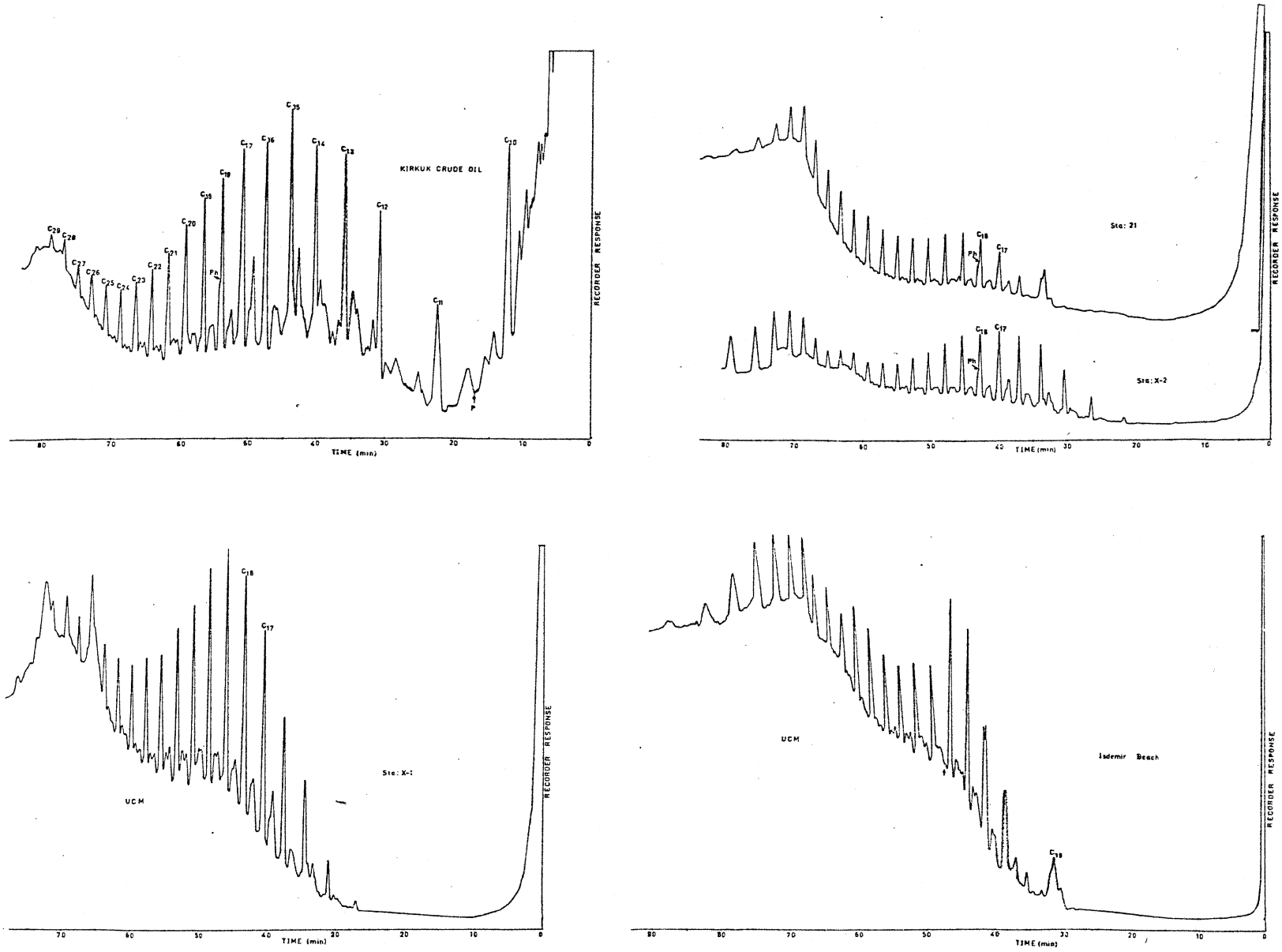



FIGURE III-7 Gas Chromatograms of Tar Ball Extracts.

In the regions (I) and (II) which are under the influence of sources like pipelines, river etc. The n-paraffin profile was variable from one sample to another, where on the first gyre (region V) only a small portion of the paraffins $n\text{-}C_{15}$- $n\text{-}C_{20}$ was left due to physical factors and at the south coast (IV) a very fresh oil slick was found which is the furthest station from the sources of pollution. But this slick in region (IV) was not observed again.

The $n\text{-}C_{17}$+ 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 crude oil. Both the n-Paraffinic pattern and $n\text{-}C_{17}$+ Pr/$n\text{-}C_{18}$+ Ph values indicated a probable pollution from the pipeline terminals or tankers approaching the terminal on else dealing with Kirkuk crude oil. However, in one of the previous studies it has been proved that Kirkuk and Turkish crude oils represent the same features (SUNAY, 1982), therefore it was difficult to differentiate the source of hydrocarbons as whether Kirkuk or Turkish crude oil, or in other words pollution originated from which pipeline. But we observed that the Kirkuk crude oil was flown into the bay via Ceyhan river after the pipeline breakage. In any case, the source was local.

The chrysene equivalent PAH concentrations of Iskenderun Bay and of all other coastal surface waters of Turkey discussed above, in Section III-1 a,b. The aim of gas chromatographic measurements carried out for the same region was to investigate if there is any other PAH concentrations than chrysene in the samples. A few of the sea water samples yielded mainly fluorene in the concentrations ranging between 4.2-14.6 ug/l (TABLE III-13) where chrysene equivalent concentrations range between 1.1 and 260 ug/l.

Actually, the retention times of fluorene and chrysene were very close on SE-30 column (SUNAY, 1982) therefore it was difficult to differentiate the identities of the PAHs in that region. But the chrysene and fluorene standarts were also used for gas chromatographic measurements. The retention times of fluorene and chrysene were not found to be very close on SE-30 column in this work. First, it was thought to be more reasonable to obtain a chrysene peak instead of fluorene, because chrysene is the most soluble PAH in sea water. Therefore, instead of chrysene, fluorene was observed in the results. Unfortunately, all PAH standarts were not used for gas chromatographic measurements thus it is not known whether retention time of any one of them is very close to the retention time on SE-30 column since such a procedure will involve very long time. It can be summarized that chromatographic analysis of sea water mainly represents the formation and probable source of oil slicks and provides more specific identification and quantification of PAHs than that of fluorescence spectroscopy.

c) Gas Chromatography of Fish Samples

The gas chromatographic measurements for fish liver extracts are tabulated in TABLE III-14, and some typical gas chromatograms for different species are given in FIGURE III-9. For the evaluation of gas chromatographic data of fish, the locations of samples are not given because the samples are mostly collected from the same location, e.g. the region between Karatas and Botas (regions I and II) as shown in FIGURE II-1.

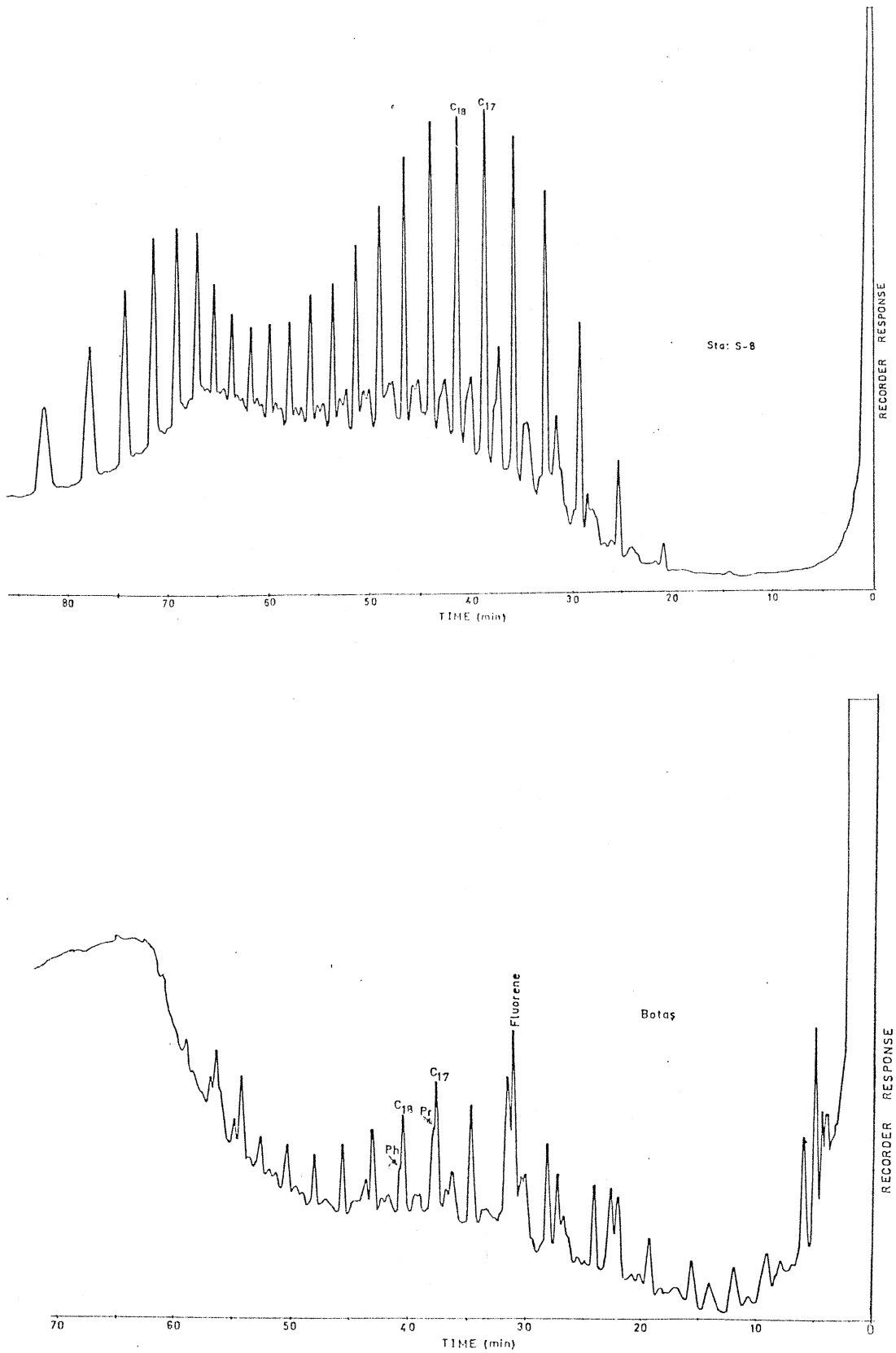



FIGURE III-8 Gas Chromatograms of Sea Water Extracts.

The gas chromatogram of fish flesh is not discussed here, because the concentration of PAHs in flesh was usually low and the PAH peaks were not precisely detectable.

The fish liver extracts analysed by gas chromatography contained mainly n-paraffin hydrocarbons in various proportions. The range between $n\text{-}C_{12}$ - $n\text{-}C_{30}$ was usually observed in all of them varying only in peak heights, e.g. concentrations. It was not possible to make a correlation between the time of catch (after the pipeline incident) and the concentration of PAH, because of the very limited number of samples analysed.

Altough the n-paraffinic profile obtained by gas chromatography in fish liver samples indicates a pollution from crude oil the $n\text{-}C_{17}$ +Pr/$n\text{-}C_{18}$ +Ph values did not agree with those of crude oils analysed previously (SUNAY,1982) except one, which is M. barbatus liver from Yumurtalik. The $n\text{-}C_{17}$ +Pr/$n\text{-}C_{18}$ +Ph values of its liver extract were found to be in good agreement with those of Kirkuk crude oil. The very small $n\text{-}C_{17}$ + Pr/$n\text{-}C_{18}$ +Ph values indicate either the effective metabolism of odd-carbon hydrocarbons or the natural hydrocarbons of the liver itself, where the former case is more probable.

As stated before, the PAH compounds, other than chrysene, were also identified and quantitied by gas chromatography and their concentrations are given in TABLE III-14 together with chrysene equivalent concentrations.

Actually, there was no correlation, between chrysene equivalent and GC determinations, because of the specific nature of the fluorescence technique, which gave emission only for chrysene, without any interference with or influence from the others,like benz(a)pyrene, fluorene etc. But the relatively high values of PAHs obtained by GC in the range of 1.47-11.37 ug/g for benz(a)pyrene and showed the requirement for the wider use of GC for qualification and especially quantification of PAHs in the marine environment of well proved research studies.

For the long term distribution of PAHs in sea water, chrysene may still be taken as the standard material and useful especially for the comparison with the other investigations carried out on the same basis.

It can simply be observed that fluorene concentration in M. barbatus increased from April to October 1982 approximately tenfold. The lack of sufficient data for the some species of fish prevented to make a similar comparision for E. aeneus and S. solea. But the high values compared with the previous works on the same species (SUNAY,1982) especially in the summer of 1982, may indicate an accumulation of petroleum hydrocarbons in fish livers. Acenapthene, phenantrene and especially benz(a)pyrene were measured in very high concentrations, greater than the tolerable limits (GESAMP, 1977) but it should be noted here that the number of analyses were not sufficient for a general conclusion about pollution. It should also be kept in mind that these are mostly carcinogenic substances.

A further detailed analysis of the samples given in TABLE III-7 for instance by GC/MS would be useful for the confirmation of such disastrous PAHs in fish livers.

TABLE III-14 Gas Chromatographic Analysis of Some Fish Liver Extracts

K: Karatas MB: M.Barbatus
Y: Yumurtalik SS: S.Solea
B: Botas EA: E.Aeneus
L: Liver

| Sample Code | Date (1982) | n-Paraffin Range | $C_{17}$ / $C_{18}$ + / + Pr / Ph | Chry. equiv. Conc.PAH (ug/g) | PAH Identified by GC | & Conc. (ug/g) |
|---|---|---|---|---|---|---|
| Y MB L | Apr.28 | C 15 - C 32 (large) | 1.2 | 10.3 | Fluorene | 0.04 |
| K MB L | May 13 | C 11 - C 30 (small) | 0.4 | 0.9 | Fluorene<br>Benz(a)_ pyrene | 0.02<br>1.47 |
| K MB L | June 7 | C 13 - C 26 (small) | 0.3 | 17.2 | Fluorene | 0.51 |
| K MB L | Oct.21 | C 12 - C 19 (large) | 0.4 | 2.6 | Acenapthene<br>Fluorene<br>Phenantrene | 14.96<br>0.14<br>11.58 |
| B SS L | May 13 | C 14 - C 28 (medium) | 0.3 | 2.0 | Fluorene<br>Benz(a)_ pyrene | 0.13<br>11.37 |
| K EA L | Aug 31 | Trace | - | 0.5 | Acenapthene<br>Fluorene<br>Benz(a)_ pyrene | 4.70<br>0.12<br>5.81 |

TABLE III-15 Gas Chromatographic Analysis of Sediment Extracts

| Regions & Stations | Date (1982) | n-Paraffin Range | $C_{17}$ / $C_{18}$ + / + Pr / Ph | Chry. equiv. Conc.PAH (ug/g) | PAH Identified by GC | & Conc. (ug/g) |
|---|---|---|---|---|---|---|
| II S-4 | Apr.28 | N.D | N.D | 0.57 | Fluorene | 0.07 |
| V 20 | Apr.28 | N.D | N.D | 0.08 | Fluorene | 0.02 |
| VI 6 | Apr.28 | N.D | N.D | 0.70 | Fluorene | 0.02 |
| Agyatan Lagoon | Apr.27 | N.D | N.D | 0.60 | Fluorene | 0.03 |
| III S-2 | July 7 | C 15 - C 30 | 0.7 | 0.03 | Fluorene | 0.003 |

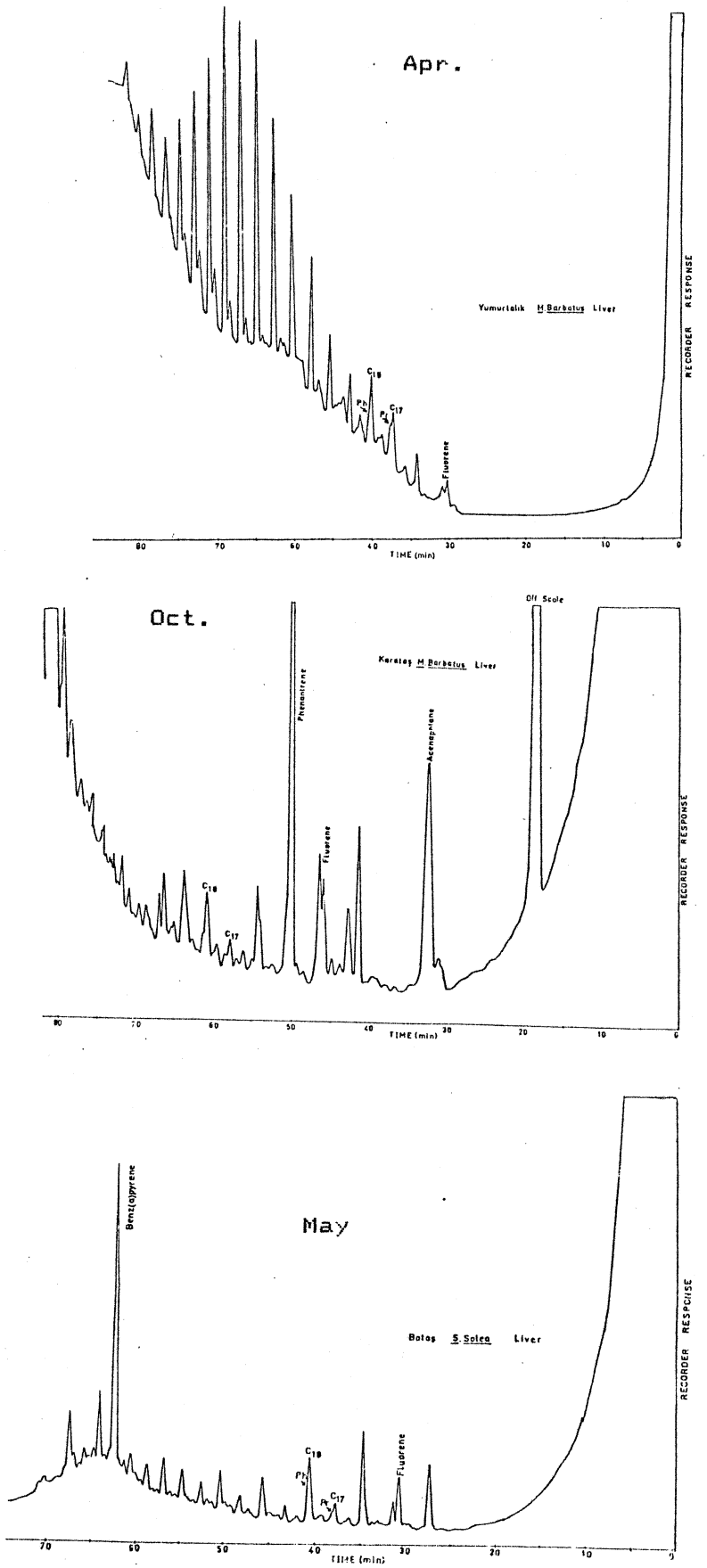



FIGURE III-9 Gas Chromatograms of Fish Liver Extracts.

d) Gas Chromatography of Sediment

The gas chromatographic measurements of sediments are summarized in TABLE III-15.

Except for one sample from the region III (FIGURE III-10) taken in July 1982, sediments analysed yielded no detectable n-paraffins on the gas chromatograms. The chrysene equivalent PAH concentrations ranged between 0.003-0.70 ug/g which were in agreement with the values measured previously (SUNAY, 1982a).

Gas chromatographic analysis also provided fluorene, but in very minute concentrations compared to chrysene. The absence of n-paraffinic patterns prevented the estimation of $n\text{-}C_{17}$+ Pr/$n\text{-}C_{18}$+ Ph ratio for source determinations. Petroleum hydrocarbons were probably subjected to very heavy weathering while they sunk to the sediments on the bottom.

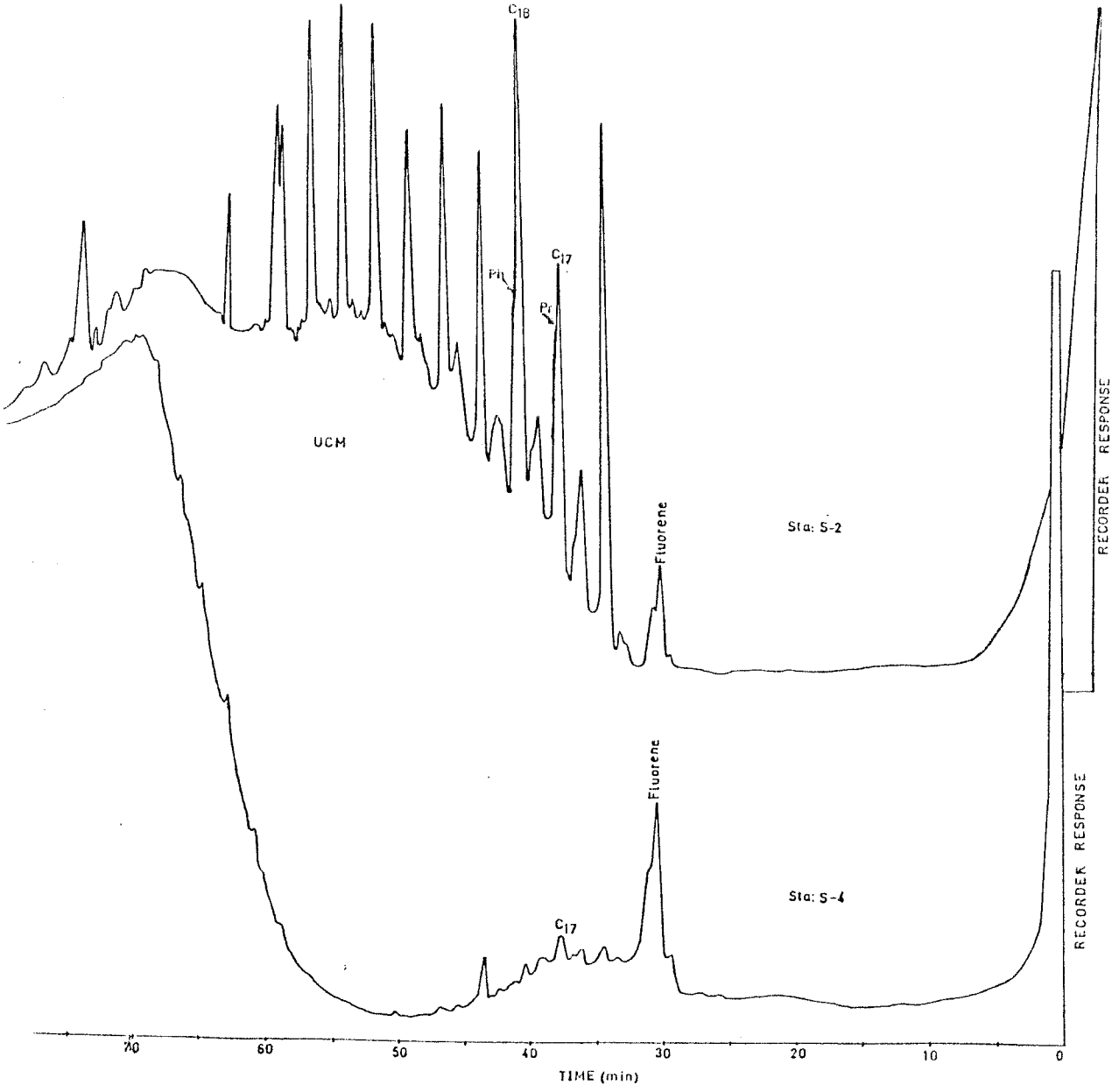



FIGURE III-10 Gas Chromatograms of Sediment Extracts.

# CONCLUSIONS

This work was based on the monitoring of PHs in the marine environment, especially around the southern coasts of Turkey, particularly Iskenderun Bay. The major aim of the work was the evaluation of the fate of petroleum hydrocarbons, carried into the bay via Ceyhan River specially after the pipeline incident and then effects on living of the sea. The results obtained in this work were compared with those obtained before the incident. As a secondary aim, the distribution of DDPH in Turkish coastal waters from Iskenderun Bay to the Black Sea was investigated in particular cruise in Sept.17-Oct.5 1983.

The conclusions obtained from this work can be summarized as followed.

i- In terms of DDPH concentrations, the surface waters around Turkey may be considered as unpolluted by petroleum hydrocarbons, because the average concentrations remain much below the tolerable level and comparatively smaller than those in the other parts of the Mediterranean. Four major coastlines Turkey, e.g. Mediterranean, Aegean, Marmara, partly Black Sea and Izmit Bay were compared in terms of petroleum based DDPH in surface waters.

Izmit Bay surface waters were found to be the most polluted as expected because of the heavy pollution by refineries and industrial activities around the bay as well as the dense tanker and ship traffic. The lack of sufficient circulation in the bay probably yielded the highest concentration of DDPH and of many other pollutants. Decreasing orders of petroleum pollutant concentrations were found in the Sea of Marmara, Aegean Sea, Black Sea, Iskenderun Bay and Mediterranean Sea respectively.

However, almost 63% of the results were found to be below 1 ug/l for averaging all samples, indicated insignificant pollution by petroleum hydrocarbons relative to NAS Report (1975) and other regions such as Malta, Crete or Israel coastal waters.

ii- The major aim of this work was to investigate the progress of petroleum pollution in Iskenderun Bay in the whole water column, including fish and sediments by comparing the analytical results obtained before and after the breakage of crude oil pipeline in April 1982.

This comparison can yield the residence time of petroleum pollutants, particularly PAH in Iskenderun Bay. Two years monitoring of DDPH in sea water generally provided first a sharp increase in concentration in April 1982, then a decay back to the background values in July-Aug.and Sept.1982. i.e. When the seasonal variations of DDPH in seawater were investigated, the concentrations were found to be at minimum values in Summer periods and reached to maximum values in Spring periods. Besides the other factors winds, waves, currents etc especially the increase of temperature caused to decrease the DDPH concentration.

Petroleum hydrocarbon concentrations were found to be increased about after 3 months in fish liver and after 5 months in fish flesh. These increased values were 10 times more in Karatas+Yumurtalik and 4 times more in Botas region for fish liver extracts, 12.5 times more in Karatas and 1.25 times more in Botas region for fish flesh extracts after the pipeline incident. Thus, the petroleum hydrocarbons were accumulated first in liver then flesh of fish in the bay and depuration occured.

Petroleum hydrocarbon concentration of sediment from Iskenderun Bay, first increased from April till June 1982 and then dropped down to the November 1981 value. Evaporation effected to decrease DDPH concentration of sea water and sinking the PHs into the sediment, also uptake of PHs from fish for example by M. barbatus which usually inhabits shallow, sandy and muddy bottoms and its feed predominantly on small bottom- living invertebrates (crabs,worms,etc.).

iii- Monitoring of PHs in the Agyatan Lagoon was of special interest, because this region was under the direct influence of the crude oil carried by the Ceyhan River after the pipeline breakage. The DDPH concentration in sea water samples increased sharply between April and September 1982, then decreased to safe levels in December 1982. Simultaneously, oil settled till June 1982 to the bottom. But DDPH concentration increased in October 1983 in surface water. Temperature effected the dissolution of petroleum hydrocarbons which was in sunken oil in sea water.

The fate of oil in the lagoon could not be observed in fish because of the insufficient sampling. However, the high concentration of surface water caused to death the fishes during pollution.

iv- The gas chromatographic analysis of tar balls, sea water, fish and sediments were carried out mainly to investigate the source of petroleum hydrocarbon, particularly PAHs and to identify different PAH compounds if present. The PAHs other than chrysene, e.g. benz(a)pyrene, fluorene, acenapthene etc. were also observed in the samples, which were probably not taken into account by fluorescence measurement (via chrysene). The difference in concentration measurements between the two techniques,e.g. fluorescence and gas chromatography, confirms this prediction. As expected the tar balls analysed were found to be originated from Kirkuk crude oil, when they were compared in terms of $n\text{-}C_{17}$ + Pr /$n\text{-}C_{18}$+ Ph values.

The DDPH concentrations in sea water determined by fluorescence and gas chromatography were mostly in the same order of magnitude, but without a general correlation between them, which is also caused by the different PAH compounds observed by two techniques. The paraffinic profile on most of gas chromatograms provided typical features of oil slicks and approximately $n\text{-}C_{17}$ + Pr/$n\text{-}C_{18}$+ Ph values of some sea water samples were the same as Kirkuk crude oil value. Thus it can be said that the pollution occured recently and originated by Kirkuk crude oil.

v- The typical n-paraffin profiles observed in gas chromatograms of fish liver extracts indicated the uptake of crude oil, but the $n\text{-}C_{17}$ + Pr/$n\text{-}C_{18}$ + Ph values disagreed with those determined previously for various types of crude oil, probably because of the metabolism of the liver. Only one sample (e.g. M. barbatus from Yumurtalik in April 1982) yielded the same value as Kirkuk crude oil and large n-paraffin peaks which may be due to recent pollution.

When the PAH concentrations before and after April 1982 were compared,the relatively high concentrations of PAH like benz(a)pyrene in fish liver extracts 1.5-11.4 ug/g were observed should require therefore further studies showed be carried out using on more samples because of high carcinogenic properties of these compounds.

Significantly higher concentrations in the latter measurements especially with GC have indicated an accumulation of hydrocarbons in fish organs.

vi- Finally, the gas chromatography of sediments yielded unexpectedly lower values for the quantities of PAHs in terms of fluorene. The n-paraffins were not detectable on gas chromatogram, except for one sample (July 1982), which probably signifies a long term weathering for petroleum hydrocarbons while sinking to the sediments.

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