MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION

BASELINE STUDIES AND MONITORING OF OIL AND PETROLEUM HYDROCARBONS IN MARINE WATERS (MED POL I)

ETUDES DE BASE ET SURVEILLANCE CONTINUE DU PETROLE ET DES HYDROCARBURES CONTENUS DANS LES EAUX DE LA MER (MED POL I)

FINAL REPORTS OF PRINCIPAL INVESTIGATORS
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This volume is the first issue of the Mediterranean Action Plan Technical Reports Series.

This Series will collect and disseminate selected scientific reports obtained through the implementation of the various MAP components: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas and Regional Oil Combating Centre.

Ce volume constitue le premier numéro de la série des Rapports techniques du Plan d'action pour la Méditerranée.

Cette série permettra de rassembler et de diffuser certains des rapports scientifiques établis dans le cadre de la mise en oeuvre des diverses composantes du PAM: Programme de surveillance continue et de recherche en matière de pollution (MED POL), Plan Bleu, Programme d'actions prioritaires, Aires spécialement protégées et Centre régional de lutte contre la pollution par les hydrocarbures.

INTRODUCTION

The United Nations Environment Programme (UNEP), in co-operation with the relevant specialized United Nations Agencies (FAO, WHO, IOC, WMO) , presented to the Intergovernmental Meeting of Mediterranean countries (Barcelona, 1975) a proposal for a Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL).

MED POL was approved and UNEP was requested to implement the Programme, consisting of seven pilot projects, in close collaboration with the relevant specialized United Nations Agencies.

Its pilot phase (MED POL-Phase I) was designed as the precursor of a long-term programme for pollution monitoring and research in the Mediterranean (MED POL-Phase II) to be carried out according to the provisions of the legal component of the Mediterranean Action Plan.

The pilot projects approved at the 1975 Barcelona Meeting as parts of MED POL-Phase I were:

MED POL I: Baseline Studies and Monitoring of Oil and Petroleum Hydrocarbons in Marine Waters

MED POL II: Baseline Studies and Monitoring of Metals, particularly Mercury and Cadmium, in Marine Organisms

MED POL III: Baseline Studies and Monitoring of DDT, PCBs and Other Chlorinated Hydrocarbons in Marine Organisms

MED POL IV: Research on the Effects of Pollutants on Marine Organisms and their Populations

MED POL V: Research on the Effects of Pollutants on Marine Communities and Ecosystems

MED POL VI: Problems of Coastal Transport of Pollutants

MED POL VII: Coastal Water Quality Control

Subsequent to the 1975 Barcelona Meeting, several other projects were added or considered as collaterals to MED POL to broaden the scope of the programme and to provide the necessary support to it. They were:

MED POL VIII: Biogeochemical Studies of Selected Pollutants in the Open Waters of the Mediterranean

MED POL IX: Role of sedimentation in the Pollution of the Mediterranean Sea

MED POL X: Pollutants from Land-Based Sources in the Mediterranean

MED POL XI: Intercalibration of Analytical Techniques and Common Maintenance Services

MED POL XII: Input of Pollutants into the Mediterranean Sea through the Atmosphere

MED POL XIII: Modelling of Marine Systems

Participants in the pilot projects were national research centres designated by the States participating in the Mediterranean Action Plan.

The co-ordination of the MED POL-Phase I (1975-1981) was carried out by UNEP as a part of the Mediterranean Action Plan (MAP).

The following United Nations Co-operating Agenicies were responsible for the technical implementation of various pilot projects :

- The Food and Agriculture Organization of the United Nations (FAO) through the General Fisheries Council for the Mediterranean (GFCM) (MED POL II, III, IV and V),
- The United Nations Educational, Scientific and Cultural Organization (UNESCO) (MED POL IX and XIII),
- The World Health Organization (WHO) (MED POL VII and X),
- The World Meteorological Organization (WMO) (MED POL XII),
- The International Atomic Energy Agency (IAEA) (MED POL VIII and XI) and
- The Intergovernmental Oceanographic Commission (IOC) of UNESCO (MED POL I and VI)

This volume of the MAP Technical Reports Series is the collection of final reports of the Principal investigators who participated in the pilot project : "Baseline Studies and Monitoring of oil and Petroleum Hydrocarbons in Marine Waters (MED POL I)".

INTRODUCTION

Le Programme des Nations Unies pour l'environnement (PNUE), en coopération avec les organismes spécialisés compétents des Nations Unies (FAO, OMS, COI, OMM), a présenté à la Réunion intergouvernementale des pays méditerranéens (Barcelone, 1975), une proposition de Programme coordonné de surveillance continue et de recherche en matière de pollution dans la Méditerranée (MED POL).

Le MED POL a été approuvé, et il a été demandé au PNUE de mettre en oeuvre le programme qui se compose de sept projets pilotes, en étroite collaboration avec les organismes spécialisés compétents des Nations Unies.

Sa phase pilote (MED POL - Phase I) a été conçue comme le prélude d'un programme à long terme de surveillance continue et de recherche en matière de pollution dans la Méditerranée (MED POL - Phase II) à mettre en oeuvre conformément aux dispositions de l'élément juridique du Plan d'action pour la Méditerranée.

Les projets pilotes approuvés à la Réunion intergouvernementale de Barcelone, en 1975, dans le cadre de la Phase I du MED POL, comprenaient:

MED POL I: Etudes de base et surveillance continue du pétrole et des hydrocarbures contenus dans les eaux de la mer

MED POL II: Etudes de base et surveillance continue des métaux, notamment du mercure et du cadmium, dans les organismes marins

MED POL III: Etudes de base et surveillance continue du DDT, des PCB et des autres hydrocarbures chlorés contenus dans les organismes marins

MED POL IV: Recherche sur les effets des polluants sur les organismes marins et leurs peuplements

MED POL V: Recherche sur les effets des polluants sur les communautés et écosystèmes marins

MED POL VI: Problèmes du transfert des polluants le long des côtes

MED POL VII: Contrôle de la qualité des eaux côtières

A la suite de la Réunion de Barcelone de 1975, plusieurs autres projets ont été adjoints ou considérés comme subsidiaires au MED POL en vue d'étendre la portée du programme et de lui assurer l'appui indispensable. Ce sont:

MED POL VIII: Etudes biogéochimiques de certains polluants au large de la Méditerranée

MED POL IX: Rôle de la sédimentation dans la pollution de la mer Méditerranée

MED POL X: Polluants d'origine tellurique dans la Méditerranée

MED POL XI: Inter-étalonnage des techniques d'analyse et services communs d'entretien

MED POL XII: Polluants d'origine tellurique dans la Méditerranée

MED POL XIII: Modélisation des systèmes marins

Les participants aux projets pilotes étaient des centres nationaux de recherche désignés par les Etats prenant part au Plan d'action pour la Méditerranée.

La coordination de MED POL - Phase I (1975-1981) a été assumée par le PNUE dans le cadre du Plan d'action pour la Méditerranée.

Les organismes coopérants des Nations Unies qui étaient chargés de l'exécution technique des divers projets pilotes sont les suivants:

- Organisation des Nations Unies pour l'alimentation et l'agriculture (FAO) par l'entremise du Conseil général des pêches pour la Méditerranée (CGPM) (MED POL II, III, IV et V).

- Organisation des Nations Unies pour l'éducation, la science et la culture (UNESCO) (MED POL IX et XIII).

- Organisation mondiale de la santé (OMS) (MED POL VII et X).

- Organisation météorologique mondiale (OMM) (MED POL XII).

- Organisation internationale de l'énergie atomique (AIEA) (MED POL VIII et XI) et

- Commission océanographique intergouvernementale (COI) de l'UNESCO (MED POL I et VI).

Ce volume de la série des *Rapports techniques du PAM* rassemble les rapports finaux des chercheurs responsables qui ont participé au projet pilote intitulé: "Etudes de base et surveillance continue du pétrole et des hydrocarbures contenus dans les eaux de la mer (MED POL I)".

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Research Centre: Fisheries Department
Ministry of Agriculture and
Natural Resources
NICOSIA
Cyprus

Principal Investigators: A. DEMETROPOULOS - L. LOIZIDES

INTRODUCTION

The report has been updated to include results up to December 1979.

The Fisheries Department has been carrying out pollution research and monitoring of oil in the Mediterranean since October 1976.

AREA(S) STUDIED

The main areas of study are Limassol, Larnaca Bay and Lara (Paphos).

(a) Limassol Bay: Faces south with cape Akrotiri sheltering the bay from westerly winds. Limassol is situated on the bay; it is a town of about 65,000 people and two commercial ports.

The coast is mainly sand or shingle beach where town or port development has not affected it.

Freshwater inflow is limited to run-off from winter rains entering the sea at various places.

On this coast there are mainly wine, spirit and soft-drinks factories. These and a slaughter house pollute the sea. The total amount of waste water entering Limassol Bay from industries is about 210,000 tons containing about 100 tons of suspended solids, mainly of organic origin. The resulting BOD_5 is about 270 tons per year.

There is also some small-scale pollution from ships.

(b) Larnaca Bay: Faces south being reasonably protected from westerly winds.

The coast is sandy and shingle beach on the whole except for the town where the beach has been encroached upon by the construction of a commercial port and marina. Part of the old Larnaca town is also built on the sea and affects the coast.

Freshwater inflow is limited to winter rains.

There is some very limited industrial pollution and some oil pollution. The total amount of waste water from industries was about the same (62,000 tons) for 1976 and 1977. Pollution load, expressed as BOD_5, was the same (about 60 tons) for 1976 and 1977, and for 1979 reported to be 20 tons.

Some oil pollution exists and is due to discharge of ship bilges in this area.

(c) Lara (Paphos)

This area is situated on the west coast of the island. It is a rocky coast with occasionally continuous beaches; it receives the full effect of the westerly winds and waves generated over a considerable stretch. There is no habitation in the vicinity.

Freshwater inflow is very limited to winter rains, a small stream in the vicinity of the bay flows in winter only over limited periods.

There is no pollution apart from tar from the open sea, and floating debris.

The three sampling stations for tar on beaches and sampling stations for pelagic tar and dissolved hydrocarbons are shown in Figure 1.

MATERIAL AND METHODS

(a) Oil slicks and other floating pollutants

Observation of oil slicks and other floating pollutants was carried out by air (the Sovereign Base Area's Royal Air Force and Cyprus Airways were contacted and requested to report oil slicks), at sea (fisherman have been contacted and requested to report oil slicks), and on the coast (daily observations were carried out by the three district offices, at Limassol, Larnaca and Paphos).

(b) Floating particulate petroleum residues (tar balls)

Sampling of particulate petroleum residues was carried out using a neuston net. This net was made by this Department, according to the description by Sameoto and Jaroszynski (1969). In each station the net was towed over a distance of one nautical mile using standard procedures: 4 knots for 15 minutes; therefore, about 740 m^2 of sea surface is filtered to a depth of approximately 20 cm. The contents of the cod-end of the net were emptied into a fine sieve from which the tar balls were then recovered and placed in a glass jar. The tar balls were then weighed.

(c) Dissolved petroleum hydrocarbons in the surface water

Sampling procedure and analytical methods used were as described in IOC Manuals and Methods No. 7.

The Department of Fisheries has not participated in any intercalibration exercise relevant to MED POL I.

(d) Tar on beaches

At the beginning, a sampling strip 6 m wide was used. The strip was perpendicular to the sea and covered the distance from the water to the upper-most point on the beach that the waves could reach.

After January 1978 the sampling method was changed. Four strips, each one metre wide and five metres from one another, were set up. The reason for this was to obtain greater statistical accuracy in the results.

Sampling was carried out every 9th and 10th days. Collected tar was measured as dry weight (g/m^2).

RESULTS

(a) Oil slicks

The reported oil slicks for the years 1976 (since September), 1977, 1978 and 1979 are given in Table I.

The number of reported oil slicks for each year with the percentage of the total are also given in Table I.

Just over half (56%) of the reported oil slicks were observed from the coast, whereas the rest were seen from the air or at sea.

Of the reported oil slicks, 42.2% were of small size ($<500 m^2$), 31.5% of medium size (500 - 1500 m^2) and 26.3% large ($>1500 m^2$). Most of the oil slicks occurred in the Larnaca area.

Eleven (11) out of the fifty-seven (57) oil slicks were combatted.

As is shown in Table I, the number of oil slicks apparently increases from year to year. The slicks appear at all seasons and there is no particular month in which they are more frequent.

(b) Floating particulate petroleum residues (tar-balls)

A cruise starting from Limassol port to Paphos covered a distance of about 34 miles. Nine near-shore stations were sampled. It was found that the amount of tar was higher at the stations off the western part of Cyprus.

Concentrations of pelagic tar varied widely at the different stations (0.0 to 5,557 $\mu g/m^2$ at the sea surface). The highest concentrations were found at the stations along the western part of Cyprus (Phaphos area). The results are given in Table II.

Four stations in Limassol bay were sampled four times for petroleum residues. The results are shown in Table III.

(c) Dissolved and dispersed petroleum hydrocarbons in the surface waters

Preliminary results of this part of the project are given in Table IV. The observed concentrations of these hydrocarbons varied between 0.0 and 6.9 $\mu g/l$.

(d) Tar on beaches

The collected tar (g/m^2) per month for the years 1976 (since October), 1977, 1978, and 1979 for the Lara and Ladies Mile stations, are given in Tables V and VI, respectively.

The amount of collected tar was higher for the year 1978 than for the year 1977 at both stations.

Collected tar was higher in 1979 than in 1978 at Lara station.

The amount of collected tar was higher at Lara than at the Ladies Mile station for the years 1977 and 1978 (see also Table V).

The highest amounts of tar were collected during winter and spring at both stations.

Collected tar samples were mostly non-sandy at Lara station, whereas they were always sandy at Ladies Mile station, indicating that the samples taken at Lara were of fresh tar.

The weight of tar (g/m^2) for one- and nine-day accumulations for each month for the year 1978 at the Lara and Ladies Mile stations were calculated.

The nine-day concentrations are always higher than the one-day concentrations.

Relevant meteorological and oceanographic data (e.g. wind velocity, sea-surface water temperature, etc.) were obtained during the period of observation.

DISCUSSION OF RESULTS

(a) Oil slicks and other floating pollutants

Most of the reported oil slicks were small or medium-sized and occurred very close to the shore, mainly in the Larnaca area, where there is an oil refinery near a commercial port.

Many oil slicks were reported south-west of Cyprus during a geological cruise of the R.R.S. Discovery in the eastern Mediterranean (Morris, 1974).

(b) Floating particulate petroleum residues (tar balls)

The higher quantities of petroleum residues at sea collected at the stations situated to the west of Cyprus are in agreement with the high amounts of collected tar at this side on the beaches.

The prevailing westerly winds blowing in this area play an important role in these higher concentrations. The tar is transferred from the open sea to this area. The area south-west of Cyprus is open for the dumping of oil which may reach the shore assisted by the prevailing onshore winds in this area.

Values obtained for petroleum residues (tar balls) at sea are comparable with those obtained by others (Morris, 1974) in the same region.

(c) Dissolved petroleum hydrocarbons in the surface water

Preliminary results on concentrations of dissolved/dispersed petroleum hydrocarbons are within the range of the values obtained by other workers in other Mediterranean regions.

(d) Tar on beaches

The amount of beach tar has increased from year to year at both stations. This increase might be due pollution. The increase in the number of oil slicks supports this hypothesis.

Another reason for this difference might be the differences between the

sampling procedure followed in 1976 and that used in 1979 which is considered to be less biased. Nevertheless, the sampling method does not take into consideration the long-shore drift of tar on the beach due to wave action.

Similar values were reported in a study of tar quantity on beaches of the Mediterranean coast from El Arish to Rosh Hamikkan, Israel. Sampling was carried out every two weeks during spring 1975 and winter 1976. (O.H. Oren, 1977).

The results obtained indicate that oil pollution significantly affects the coastal waters and beaches of Cyprus.

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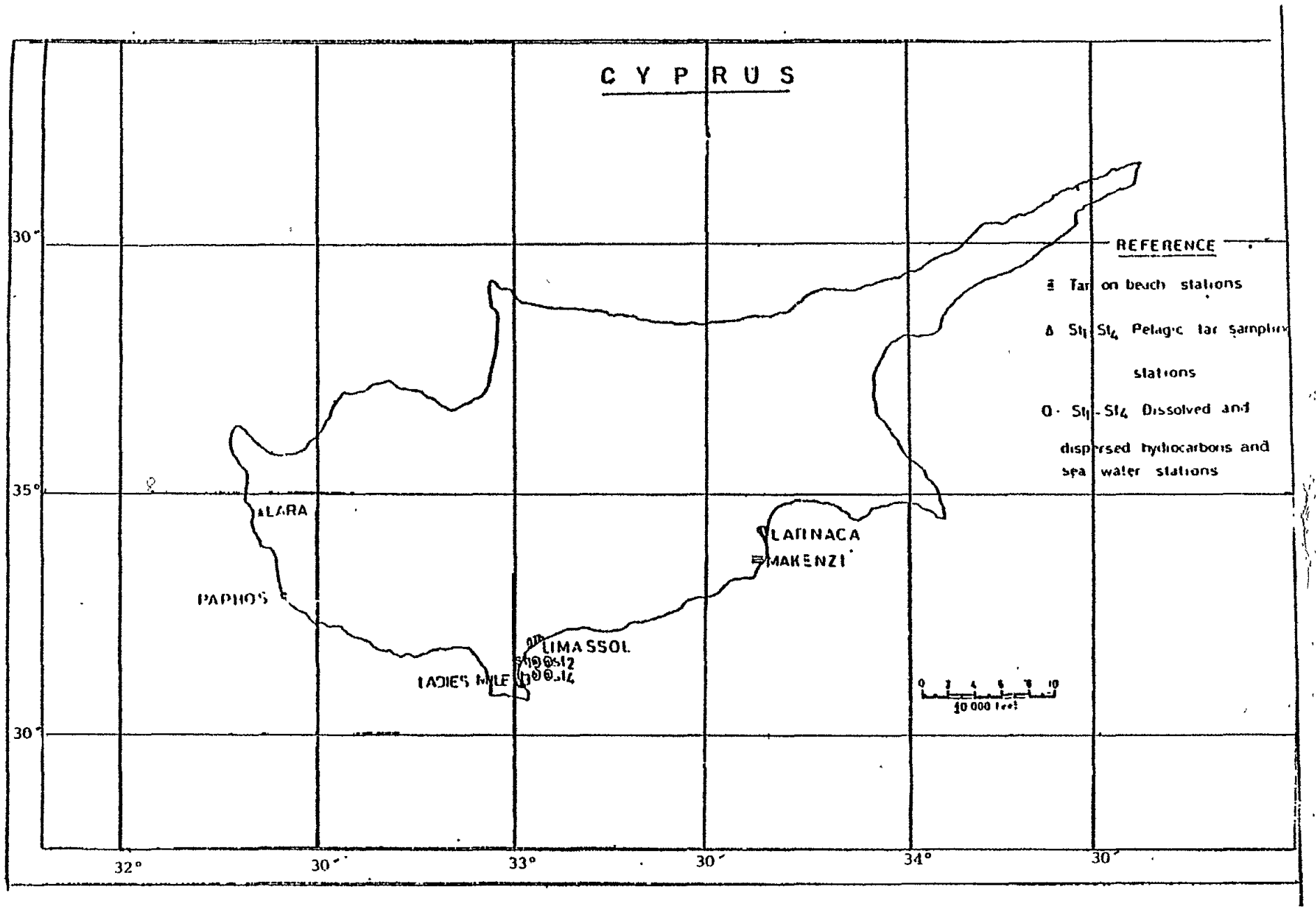
TABLE I : Summary of oil slick observations

Year	Number of oil slicks	% of the total	Estimated size			No. of observations by area		
			small $<500\ m^2$	medium $500\text{-}1500\ m^2$	large $>1500\ m^2$	Larnaca	Limassol	Paphos
1976	10	17.5	3	4	3	10	--	--
1977	11	19.2	4	4	3	11	--	--
1978	17	29.8	6	5	6	12	5	--
1979	19	33.3	11	5	3	8	11	--
Totals	57		24	18	15	41	16	0

Table II : Pelagic tar concentration ($\mu g/m^2$ sea surface) at corresponding stations

Date	Station No.	Location	Position		Tar Concentration ($\mu g/m^2$)	Remarks
			Lat.	Long.		
	1	Limassol Bay	33°38'	33°02'	13.0	
	2	Cape Gata	33°35'	33°02'	0.0	
	3	Cape Gata	33°34'	33°33'	10.5	
18.5.1978	4	Episkopi Bay	32°52'	33°01'	5.8	
	5	Episkopi Bay	33°38'	32°47'	2.5	
Cruise No. 1	6	Cape Aspro	33°37'	32°43'	267.5	
	7	Petra tou Romiou	34°39'	32°37'	88.9	
	8	Point Zephyros	34°30'	32°32'	10.4	
	9	Moulia Rocks	34°43'	32°00'	5,557.0	



SAMPLING STATIONS FOR MED I

Table III. Pelagic tar concentration ($\mu g/m^2$ sea surface) at fixed stations in Limassol (Akrotiri) Bay.

Date	Station 1 (N 34°39',E 33°03')	Station 2 (N 34°39',E 33°04')	Station 3 (N 34°38',E 33°03')	Station 4 (N 34°38',E 33°04')
27. 6.1978	0.0	51.0	1,099.0	1,999.0
4.12.1978	1217.0	186.0	0.0	0.0
31. 1.1979	165.0	129.6	86.5	54.7
9. 3.1979	4.1	6.8	50.5	9.3

Table IV. Concentration ($\mu g/l$) of dissolved and dispersed petroleum hydrocarbons in sea water at fixed Stations in Limassol Bay.

Station / Date	St1 (N31° 39',E33° 03')	St2 (N34° 39',E33° 04')	St3 (N34° 38',E33° 03')	St4 (N34° 38',E33° 04')	REMARKS
31.1.1979	6.9	3.5	0.0	2.1	
9.3.1979	1.4	1.1	4.4	4.5	

Table V. Beach tar (g/m^2) at Lara (Paphos) station

Month / Year	January	February	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
1976										13.9	257.5	301.6	
1977	158.9	111.5	132.0	49.2	33.4	11.1	14.1	0.0	8.9	9.27	23.7	230.6	782.8
1978	321.9	62.5	471.5	967.1	421.8	536.7	357.2	520.1	221.8	93.7	481.2	1,701	6,156.5
1979	912.2	2,493.9	1,277.9	780.9	0.0	53.7	0.0	0.0	437.9	232.2	516	279.6	6,984.3

Table VI. Beach tar (g/m^2) at Ladies Mile (Limassol Bay) station

Month / Year	January	February	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
1976										6.0	4.5	5.5	
1977	24.0	25.4	31.3	5.1	1.1	1.6	5.8	3.6	27.4	30.0	16.2	35.5	207
1978	31.8	83.4	102.0	34.0	35.5	23.0	10.7	5.2	20.7	20.6	8.4	11.5	386.8
1979	8.1	21.7	8.6	8.5	12.2	4.7	7.9	10.5					

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INTRODUCTION

In view of the threat to coastal regions from pollution by petroleum hydrocarbons, and in view of the fact that Alexandria, which has a total population of 3 million increasing to about four million in summer, is the main summer resort of Egypt, the study of oil pollution along its beaches and coastal water became a necessity. The problem made itself clear some years ago as tarring of beaches became obvious, a matter that affected the recreational value of the coast near Alexandria. Complaints by fishermen who had their nets smeared with oil were not uncommon.

The hydrography of the Mediterranean water off the Nile Delta was studied by Hassan (1969). Coastal waters are cooler in autumn and winter and warmer in summer and spring than the offshore waters. This may be attributed to the continental influence due to the presence of the shallow and broad continental shelf and embayments characterizing the Egyptian Delta.

The following table gives the average salinity and temperature values of Alexandria coastal waters for the years 1976-1977 (Wahby and Hanafy, unpublished).

	Jan.	March	May	July	Sept.	Nov.
			Salinity °/oo:			
Nearshore	38.067	38.56	38.60	37.71	39.17	37.63
Offshore	38.511	38.57	38.57	37.74	39.47	37.63
			Temperature (°C):			
Nearshore	17.8	16.0	20.6	26.3	27.5	19.0
Offshore	17.2	16.0	20.2	26.0	27.5	19.2

In January and February the prevailing wind is mainly south-westerly. In April, May, June, July, August and September the wind is north-west. In October and November it is north-easterly and it becomes south-westerly in December. In January, February and March, the wind speed may exceed 22 knots.

AREA(S) STUDIED

The coast in the vicinity of Alexandria was chosen as the site for the pilot project. The area is about 33 km long, extending from E 29° 47' to E 30° 4' (Fig. 1).

The shoreline of Alexandria exhibits typical features of a young shoreline. Between Mex and Mamaura it extends more or less straight with slight undulations forming small embayments. It is characterized by being rocky in most places with narrow sandy beaches which are used as recreational sites, especially in summer.

MATERIAL AND METHODS

Tar on beaches: Sampling started on 27 February 1977 and continued, in two forms, till October 1979. From 27 February to 19 March 1977 samples were collected along a longitudinal strip 6 metres in length running from the shore line inwards. The area of collection was thoroughly cleaned and staked out. Samples were collected every one and nine days. The total amount of tar in each sample was weighed. If the tar balls were coated, totally or partially, with sand and shell fragments, they were cleaned prior to weighing or dissolved in $CCl_4$and evaporated.

From April 1977 till January 1978 samples were collected every fifteen days, from each of four stations and from a one-metre square of each station, and presented as g/m^2 for each fifteen-day period, from which a monthly average was calculated for each station, as well as an overall monthly average. From February 1978 to October 1979 only the overall monthly average has been given.

Floating tar balls: These were collected by phytoplankton net from the surface from two zones (El-Max and West) in the vicinity of Alexandria. Collection of floating tar balls started in May 1977, and is being done as frequently as possible. An ordinary phytoplankton net (200 mesh) is used for collection. Tar balls are collected by hand, if sticky they are dissolved in CCl_4, evaporated and weighed. The results are expressed as mg/m^3.

Dissolved/dispersed hydrocarbons: Sampling and fluorescence analysis followed the procedures given in the "Manual for monitoring of oil and petroleum hydrocarbons in marine waters and on beaches" IOC/WMO/UNEP/Med-MRM/3, Suppl. 2, 1977. Samples were taken from 1 m depth. The results were calculated as ug of oil or chrysene equivalents per litre of sea-water.

The laboratory has not participated in the intercomparison exercise.

RESULTS AND THEIR INTERPRETATION

Tar on beaches: The weight of tar per square metre, from 27 February to 20 March 1977, for one-day and nine-day accumulations are given in Table I. Weight of tar collected from an area of 1 m^2 from four stations every 15 days from April 1977 to October 1979 was measured. Results are given in Table II; more than one sample was taken from every station. Average monthly values (g/m^2/15 days) for four stations for the period are given in Table III.

Tar balls on beaches were generally hard in texture, coated with sand and containing fragments of shells. We noted that the weight of tar was less in summer than in winter. This is probably an under-estimation, due to the inevitable cleaning of the beaches which is carried out by the local authorities.

Floating tar balls: The results from May 1977 to April 1979 are given in Table IV.

Samples collected from the Mex area, being to the east of the "Somid" pipelines, have higher tar content than those collected from areas west of the pipeline. This is due to the direction of currents and prevailing winds.

Dissolved/dispersed hydrocarbons: Sea-water samples for the detection of dissolved/dispersed hydrocarbons were collected in November and December 1979 from areas about 2 km offshore. In February 1980, samples were collected about 5 km offshore.

Table V gives the hydrocarbon content of the water samples in µg/l, chrysene equivalents. The inshore samples are richer in diesel-hydrocarbons than offshore ones, although the inshore levels are the more important from the fishery and recreational point of view.

CONCLUSION

This study on the levels of petroleum hydrocarbons on Alexandria beaches and in adjacent waters is an important one from the point of view of the Institute of Oceanography and Fisheries because it is modern in scope and affords chances for training in modern techniques.

It is the intention of the Institute to broaden the scope of this study to cover better the monitoring of dissolved and dispersed hydrocarbons and to participate in any eventual follow-up to MED POL.

Table I. The weight of tar per M^2

Station	Nine days' accumulation (weight in grammes)		One day's accumulation (weight in grammes)	
1	27.2.77	6	28.2.77	3.0
2		10		6.0
3		16		1.0
4		20		9.0
5		10		2.0
6		11		1.3
1	7.3.77	10.1	10.3.77	4.0
2		16.1		6.2
3		13.0		1.4
4		33.7		14.3
5		11.3		2.5
6		18.5		4.0
1	19.3.77	9.0	20.3.77	2.0
2		14.0		3.5
3		11.0		2.0
4		18.0		6.0
5		11.0		5.0
6		8.0		1.5

Table II. Average weight of tar (g/m^2) for each of four stations for each month from April 1977 to January 1978, calculated from 15-day accumulations

Month	Station	g/m^2/15 days	Month	Station	g/m^2/15 days
April 1977	1	105	September	1	21.7
	2	48		2	41.5
	5	225		5	3.5
	6	118		6	1.0
	Mean	120		Mean	16.9
May	1	90	October	1	80
	2	60		2	90
	5	100		5	140
	6	100		6	110
	Mean	87.5		Mean	105
June	1	60	November	1	90
	2	33		2	90
	5	37		5	160
	6	33		6	128
	Mean	41		Mean	117
July	1	66	December	1	320
	2	40		2	380
	5	40		5	115
	6	20		6	200
	Mean	41		Mean	254
August	1	40	January 1978	1	290
	2	22		2	300
	5	26		5	100
	6	21		6	160
	Mean	27		Mean	2122

Table III. Average monthly weight of tar (g/m^2) taken from a one-metre square at each of four stations each month, calculated from 15-day accumulations

Year	Month	Average	Year	Month	Average
1977	April	127	1978	January	212
	May	87.5		February	347
	June	41		March	202
	July	41		April	160
	August	27		May	110
	September	17		July	80
	October	105		September	112
	November	117		November	160
	December	254			
			1979	January	220
				April	150
				July	90
				October	185

Table IV. Weight of floating tar balls in mg/m^3

Month	Area	Weight of floating tar balls mg/m3
May 1977	Mex	0.3 - 0.2
July	Mex	1.06
August	West	0.15 - 0.07
November	West	0.05 - 0.08
October 1978	Mex	1.33
December	Mex	0.8 - 1.0
April 1979	West	0.22 - 0.18

Table V. Dissolved/dispersed hydrocarbons off the Alexandria coast, expressed in µg/l as chrysene equivalents

Sample no.	Distance from shore	Hydrocarbon µg/l as chrysene equivalents
	(1	9.8
Nov. 1979	(2	7.0
	(3	6.7
	(4	41.4
	(5	13.1
	(6	10.2
Dec. 1979	(7	10.4
	(8	11.8
	(9	6.6
	(10	0.7
	(11	2.3
Feb. 1980	(12	2.1
	(13	2.5
	(14	2.7

	2 km	
	2 km	
	5 km	

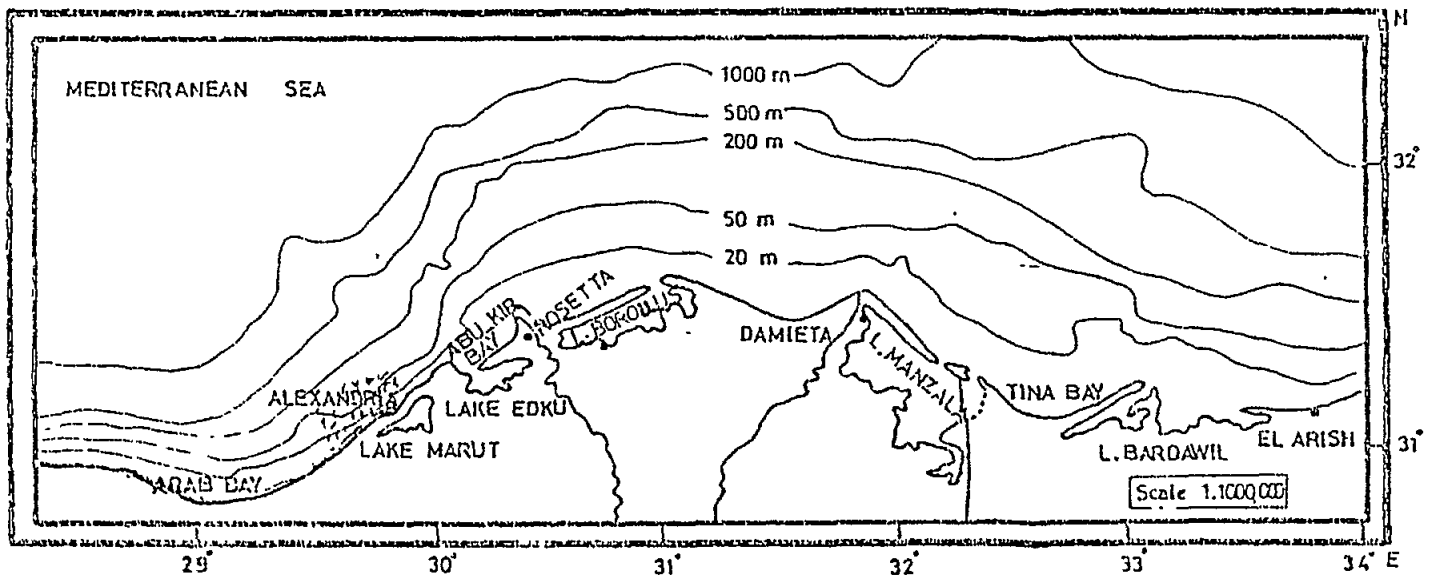

Figure 1. Map showing area of study

Centre de Recherche : Laboratoire de Chimie appliquée à l'expertise
Faculté de Pharmacie
MONTPELLIER
France

Chercheur Principal : C. CAUSSE

INTRODUCTION

Le Laboratoire de Chimie appliquée à l'expertise étudie principalement l'analyse des micropolluants dans l'environnement pour en favoriser l'inventaire. Parmi les travaux antérieurs intéressant le projet MED POL I, nous pouvons indiquer l'étude des résidus d'hydrocarbures dans les eaux des canaux et étangs de Camargue qui avait été réalisée en 1971, et celle des sédiments du plateau continental languedocien. Ce rapport a été mis à jour jusqu'à fin mars 1980.

ZONE(S) ETUDIEE(S) :

- Zone de Port Vendres et Banyuls-sur-Mer
- Port Vendres, petit port voyageurs et frêt maritime
- Banyuls, petit port pêche et tourisme
- Côte rocheuse des Pyrénées Orientales

La Figure 1 montre la région étudiée et les stations.

MATERIEL ET METHODES :

Echantillonnage : Les échantillons sont prélevés par les soins du laboratoire ARAGO au sein du milieu ambiant à un mètre de profondeur, dans des flacons en verre teinté d'une capacité de deux litres à bouchon vissé et disque d'étanchéité en téflon.

Ils sont conservés au réfrigérateur à + 4° sans ajout d'aucun réactif et acheminés le plus rapidement possible en emballage isotherme jusqu'au laboratoire d'analyse.

Analyse : Les mesures sont effectuées par spectrophotométrie infra-rouge par une procédure adaptée d'après Beynon, Kasnitz et Rijnders (The Strichting Concave, 1968), en utilisant le standard API 733-58. Cette methode mesure fondamentalement des alcanes, des alcènes et des aromates qui sont solubles dans tetrachlorure de carbone et qui absorbent des longueurs d'ondes de 3.38 - 3.42 et 3.50 µm. La limite de détection est de 0.05 mg/l.

L'institution n'a pas participé au programme d'interétalonnage dans le cadre du projet pilote MED POL I.

RESULTATS ET LEUR INTERPRETATION

Des valeurs en µg/l ont été données dans le Tableau I pour deux stations pour la période de novembre 1975 à janvier 1980.

La surveillance bi-mensuelle de la pollution par les hydrocarbures dispersés ou dissous dans l'eau de mer dans la zone de Banyuls montre que les teneurs observées se répartissent ainsi :

80% des cas se situent entre la limite de détection 50 µg/l et 500 µg/l
12% des cas se situent entre 500 µg/l et 1 000 µg/l
8% des cas excèdent 1 000 µg/l traduisant probablement une pollution accidentelle

L'étude de la répartition saisonnière des données permet de constater que la moyenne mensuelle ne dépasse pas 250 µg/l pour les mois de mars - avril - mai - juin et juillet. Des concentrations plus élevées sont observées pendant les mois d'hiver.

Les résultats obtenus pendant la période de surveillance indiquent un niveau croissant de pollution qui s'établit entre 50 et 500 µg/litre d'eau de mer assez comparable à celui que traduisent les études d'autres institutions participant à ce projet pilote.

Il est à noter cependant que la méthode d'analyse des hydrocarbures par spectrophotométrie infra-rouge, que nous utilisons, manque de finesse par comparaison avec l'analyse par spectrofluorimétrie, que nous n'avons pu mettre en oeuvre faute d'équipement.

Tableau I. Teneurs en hydrocarbures - résultats en microgrammes par litre

Rapport n°	Date prélèvement	Station n° 2	Station n° 4
1	04 - 11 - 75	500	1150
2	25 - 11	200	200
3	10 - 12	400	200
4	22 - 12	200	250
5	13 - 01 - 76	50	150
6	02 - 02	50	100
7	23 - 02	4000	4000
8	01 - 03	600	1400
9	18 - 03	100	100
10	01 - 04	250	150
11	20 - 04	120	100
12	04 - 05	130	160
13	20 - 05	160	200
14	01 - 06	50	200
15	14 - 06	140	300
16	09 - 09	200	500
17	22 - 09	550	2500
18	06 - 10	700	400
19	22 - 10	100	100
20	04 - 11	150	150
21	26 - 11	100	200
22	10 - 12	100	50
23	10 - 01 - 77	150	150
24	24 - 01	200	350
25	21 - 02	150	150
26	18 - 03	50	50
27	07 - 04	50	50
28	06 - 05	100	300
29	17 - 05	100	100
30	21 - 06	50	50
31	05 - 07	100	50
32	13 - 07	50	50

Tableau I. Teneurs en hydrocarbures - résultats en microgrammes par litre (suite)

Rapport n°	Date prélèvement	Station n° 2	Station n° 4
33	08 - 09 - 77	50	50
34	20 - 09	100	50
35	04 - 10	50	50
36	26 - 10	100	50
37	08 - 11	250	350
38	24 - 11	120	<50
39	06 - 12	5000	750
40	19 - 12	130	<50
41	01 - 02 - 78	800	1050
42	15 - 02	300	950
43	28 - 02	750	2500
44	14 - 03	200	250
45	04 - 04	200	200
46	27 - 04	200	300
47	13 - 05	<50	200
48	23 - 05	<50	<50
49	24 - 07	200	200
50	10 - 08	100	200
51	23 - 08	100	150
52	19 - 09	500	200
53	24 - 10	200	1000
54	15 - 11	250	600
55	12 - 12	200	100
56	Janvier 79	50	150
57	Février 79		50
58	07 - 03		50
59	02 - 05	100	100
60	22 - 05	250	100
61	21 - 06		400
62	02 - 08	2200	1800
63	22 - 08	600	
64	18 - 10	500	500
65	29 - 11		<50
66	16 - 01 - 80	250	200

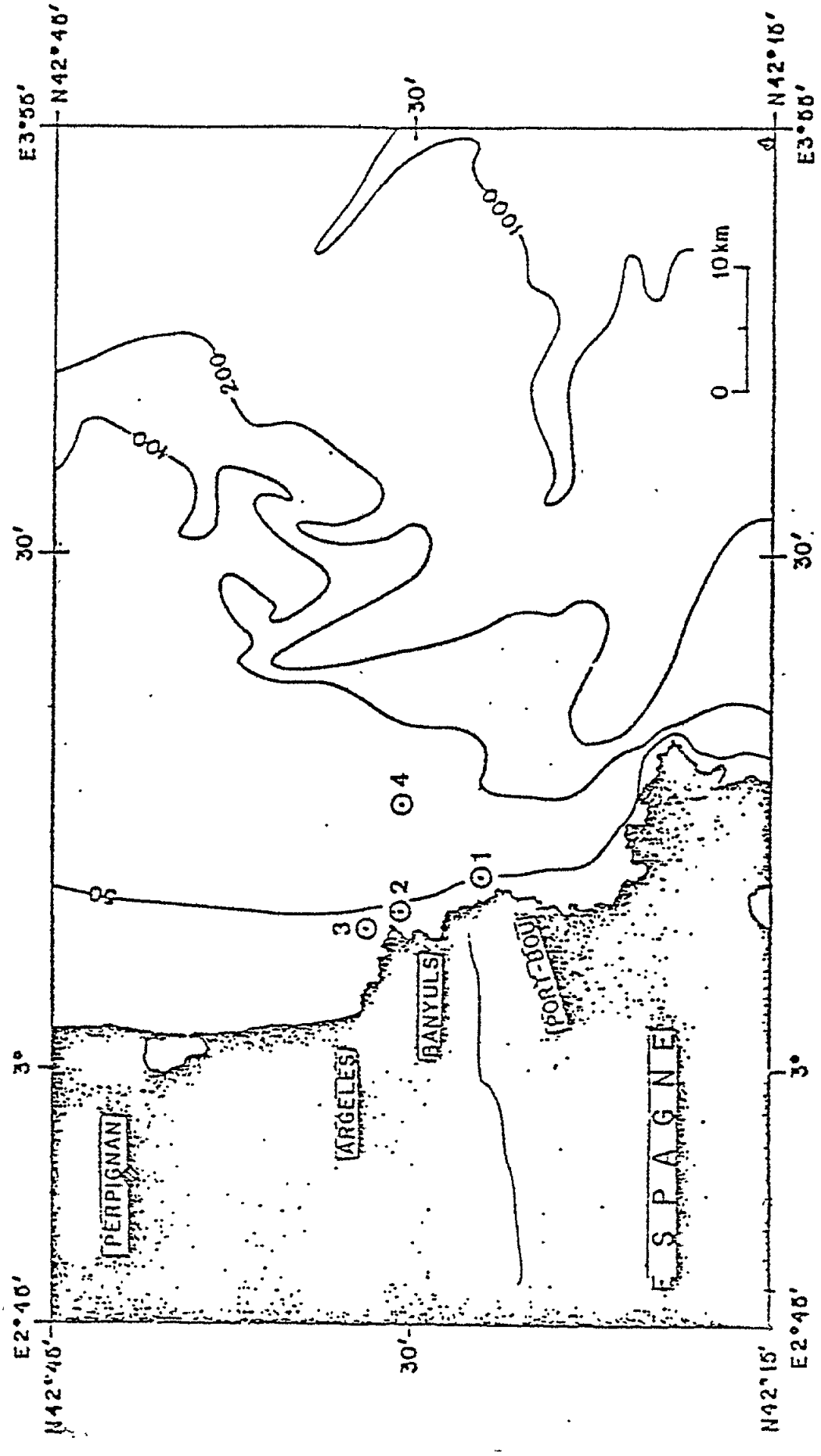

Figure I. Zone etudiée le long la côte de Banyuls-sur-mer, et localisation des quatre stations

Research Centre: Laboratory of Organic Chemistry
University of Thessaloniki
Thessaloniki
GREECE

Principal Investigator: N. E. ALEXANDROU (December 1975 - September 1979)
A. J. MAROULIS (October 1979 - March 1980)

INTRODUCTION

Between October 1976 and April 1977 the laboratory started measurements on the extent of petroleum hydrocarbon contamination in Thessaloniki and Kavala harbours and Strymonikos Bay. In these places are located the most important industries in northern Greece. These measurements covered the period May 1977 to March 1980.

AREA(S) STUDIED

The sampling sites in Thessaloniki and Kavala harbours and in Strymonikos Bay are shown in Figure 1.

MATERIALS AND METHODS

Samples (one each) were taken from the above-mentioned areas from various stations and at three depths (0-5 cm, 1-10 m, 10-15 m). As the sampling is conducted by another laboratory no further details are known about the procedures. The determinations were made using the carbon tetrachloride extraction method and the oil content was measured using the infra-red method. Only the last batch of samples (February 1979) was analysed by the fluorescence method.

Infra-red spectra of carbon-tetrachloride-water extracts (500 ml sea-water were extracted twice with 20 ml carbon tetrachloride) were measured in a 5 cm cell with quartz windows using a Perkin-Elmer Model 257 infra-red spectrophotometer. Spectra were scanned from 3,400-2,500 cm^{-1}. The C-H stretching band at 2,930 cm^{-1} was used for analysis. The absorptivity at this wavelength was calibrated with petroleum (kerosene fraction b.p. 150-200°). The straight line of the correlation diagram was obtained by measuring samples containing a known weight of petroleum in distilled water. The accuracy in petroleum concentration is in the range of $\pm$ 0.2 mg/l.

For a preliminary examination, the carbon tetrachloride extracts of Thessaloniki harbour sea-water were evaporated and the whole residue was submitted to mass spectrometric examination. The mass spectra taken with a Hitachi-Perkin-Elmer-RMU-6L spectrometer at 70 eV were very similar to the spectrum of the petroleum fraction (b.p. 150-200) used for calibration for oil determination. They mainly showed ion fragments differing by 14 mass units up to 278 m/e. This study is, however, under further consideration.

The last batch of samples was analysed using the infra-red method (diesel oil b.p. 232 - 360° as standard) and the fluorescence method. The latter was performed generally according to the IOC Manuals and Guides No. 7, but the excitation wavelength was 295 nm and the emission was measured at 330 nm. The diesel oil was used for calibration. Blank samples were analysed and their results were subtracted.

The laboratory has not taken part in the intercomparison exercise, because the chrysene samples have not yet been provided.

RESULTS AND THEIR INTERPRETATION

The annual mean concentrations of dissolved/dispersed hydrocarbon concentrations are given in the table, and are plotted in Figure 2 for the months in which measurements were taken. Values are apparently higher in winter than in summer, possibly owing to more rapid breakdown in the higher ambient temperatures of summer.

Table: Mean hydrocarbon concentration for the Thessaloniki, Thermaikos, Kavala and Strymonikos Bays.

Bay	Concentration (mg/l)				
	1976	1977	1978	1979	1980
Thessaloniki	0.3(3)*	0.1(8)	0.1(4)	0.2(3)	0.4(1)
Thermaikos	0.2(2)	0.2(7)	0.2(5)	0.1(3)	0.2(1)
Kavala	0.3(2)	0.2(7)	0.2(4)	0.1(3)	0.4(1)
Strymonikos	0.2(1)	0.1(7)	0.3(3)	0.1(3)	0.4(1)

* The numbers in parentheses represent the number of batches analysed during the corresponding year.

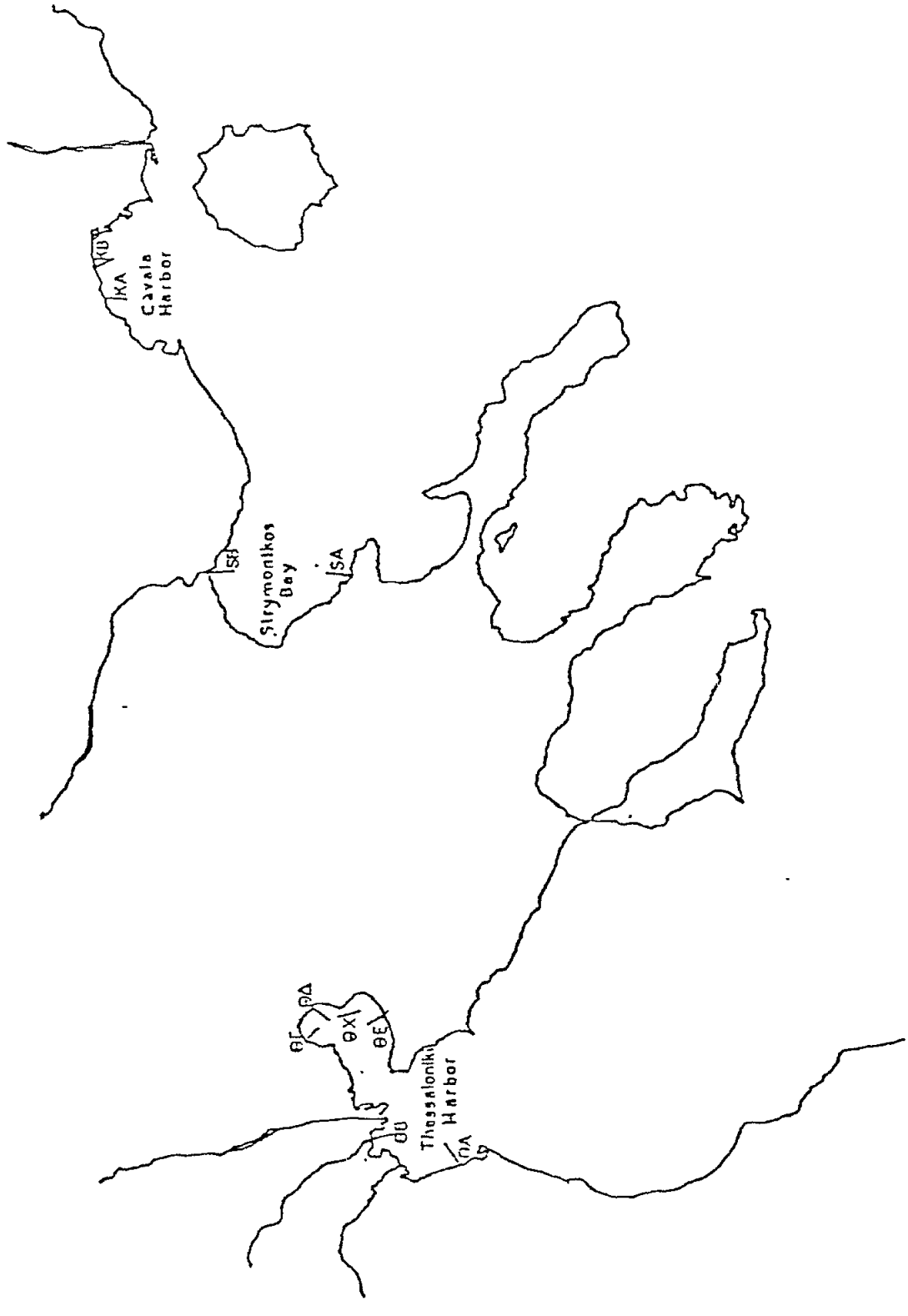

Figure 1. Sampling Stations

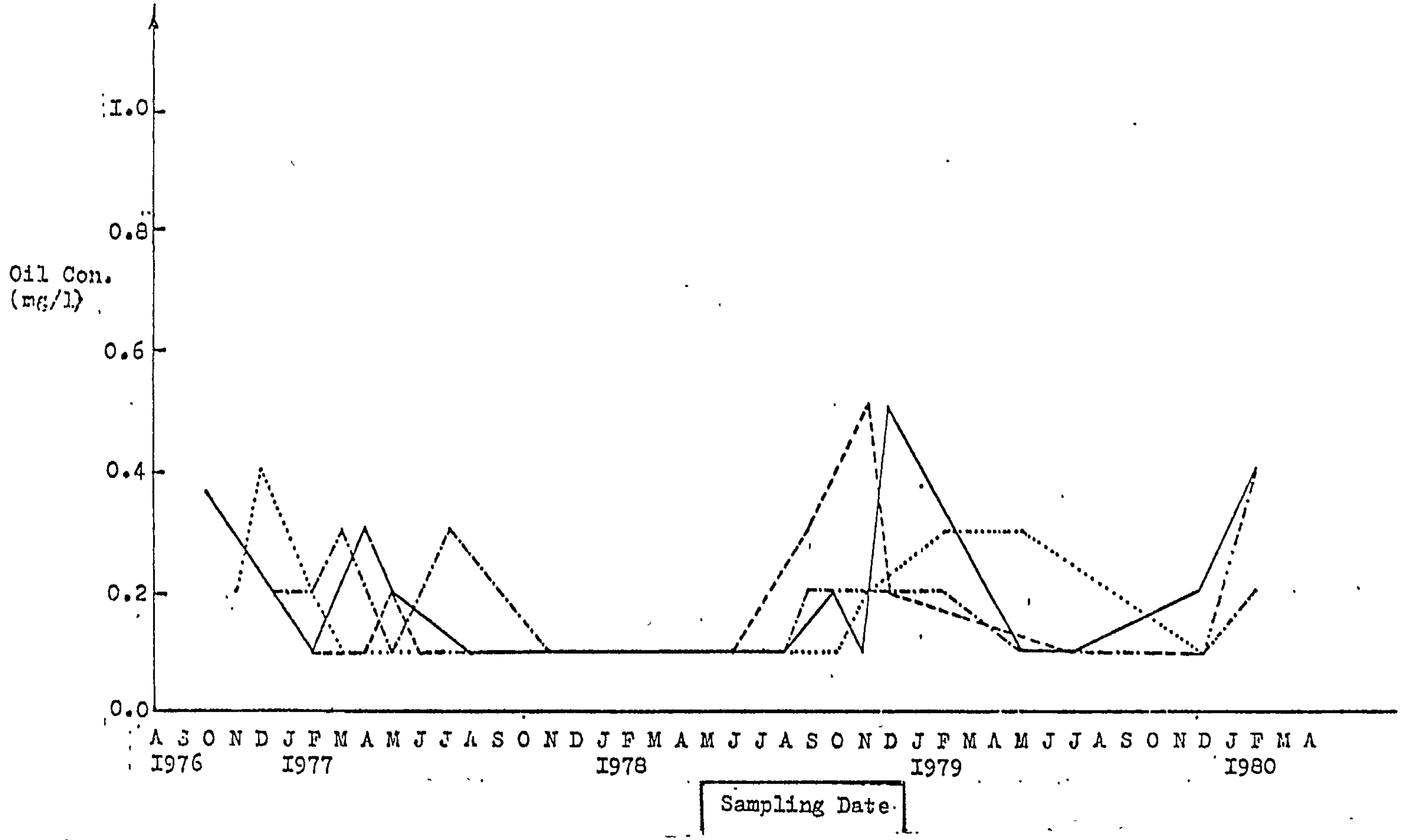

Figure 2. Mean Hydrocarbon Concentration in Sea-water

Thessaloniki Bay: ....
Thermaikos Bay: -.-.-.-.-.-.-
Strymonikos Bay: - - - - - - - -
Kavala Bay: ―――――――

Research Centre: Analytical Laboratory
Nuclear Research Centre "Demokritos"
ATHENS
Greece

Principal Investigator: N. MIMICOS

INTRODUCTION

Owing to the geographical position of Greece, with a very extended coastline (about 15,000 km), it is of utmost importance to study marine pollution and its effects on fisheries and other economic activities, such as tourism.

During 1975-1976 the Analytical Laboratory of the Nuclear Research Centre "Demokritos" participated in a programme entitled "Study of the Ecological response of phytoplankton to chronic oil pollution". This work was carried out in collaboration with the Hydrobiology Group of the Centre, and the main work of the laboratory was the determination of the concentration of petroleum hydrocarbons in sea-water. The results are reported in the two publications listed at the end of this report.

The present report has been updated to March 1980.

AREA(S) STUDIED

Sampling sites were chosen on the basis of the expected relatively high incidence of oil pollution. Therefore, the water column was sampled near oil terminal sites and near urban and industrial sites. Also, sites with a special touristic interest were included. So the following sites were chosen:

- Patraikos Gulf (important industrial zone, ship traffic); 7 stations
- Messiniakos Gulf (important harbour); 7 stations
- Rhodos (Rhodes) Island (important harbour, tourist centre); 7 stations
- Kriti (Crete) Island (important harbour, tourist centre); 7 stations
- Lesbos Island (important harbour, tourist centre); 6 stations

Recently, sampling was initiated on the islands of Cephalonia and Corfu and at Katakolon (Arcadia Bay).

Seven sampling stations (only six for the islands of Lesbos and Corfu) about three to four miles offshore, with four to five miles between each station were chosen for sampling the water column. As far as tar balls on beaches are concerned one sampling point was chosen (two for Lesbos Island) on a convenient beach at each of the above sites. Later, with the expansion of the studied sites from five to eight, we increased to twenty the number of beaches monitored.

MATERIALS AND METHODS

The sampling was carried out in co-operation with the port authorities following the sampling procedure described in IOC Manuals and Guides, No. 7 suppl.

Dissolved/dispersed hydrocarbons: Sampling was carried out every three months at each sampling station. On each occasion three samples were taken at 1 m depth at each station. Dark glass bottles of 2.8 l capacity and containing 50 ml carbon tetrachloride were used, and the samples were analysed as soon after as possible.

Initially the determination of the concentration of petroleum hydrocarbons was performed by infra-red spectrophotometry (Perkin-Elmer, Model 521).

A composite standard mixture (benzene 25%, iso-octane 37.5% and n-hexadecane 37.5%) was used for calibration of the photometer.

Later, we continued the determination of petroleum hydrocarbons using ultra-violet spectrofluorimetry (Perkin-Elmer Model 203), as described in he IOC Manuals and Guides No. 7 and its supplement, and in IOC Workshop Report No. 10, using South Louisiana crude oil for calibration of the fluorimeter.

Our laboratory participated in the intercalibration exercise organised within the framework of the IGOSS Pilot Project on Marine Pollution (Petroleum) Monitoring by Duke University Marine Laboratory. The results of the Chrysene I exercise have shown a proper operation of our instrument with a decreased linearity with the higher concentrations of chrysene, e.g., above the 4.0 µg/ml of chrysene, which is equivalent, assuming a comparison of ratio of 4.0, to the fluorescence of 4 litres of sea-water containing 20 µg/l of crude oil. Unfortunately the Chrysene II bottles had presented a partial leakage with a consequent low recovery.

Tar on beaches: At each sampling site we generally staked out one or two strips but in some cases more. The size of each sampling strip was not less than 40 m^2 but later, for practical reasons, we reduced it to about 10 m^2. The sampling was done monthly, on the 9th and 10th days of each month.

The amount of tar was estimated by weight or volume, depending on the nature of the tar lumps (clean, or covered with sand, etc.).

RESULTS AND THEIR INTERPRETATION

Dissolved/dispersed petroleum hydrocarbons: The concentrations are given in Table I; they are reported as mean of three separate samples taken at three-month intevals. The results, unless otherwise noted, are expressed in chrysene units (comparison ratio: 5,35) in µg/kg of seawater.

The amounts present range from 0,6 µg/kg to 28,2 µg/kg; however, only a very small percentage ($\backsim$ 4.5%) of them has concentrations in excess of 10 µg/kg. On the contrary, the values of about the half of the results (48.2%) are between 0 and 3 µg/kg.

There is a tendency for the concentrations to be higher at the sites in Patraïkos and Messiniakos Gulfs and in the Katakolon area, which are important harbours and urban sites. Generally, the arithmetic mean concentration increases in the following order: Rhodes, Crete, Lesbos, Corfu, Cephalonia, Messiniakos, Arcadia bay (Katakolon) and Patraïkos Gulf.

Tar on beaches: the results are expressed in terms of g/m^2 and are included in Table II.

The following publications were based on the work done under MED POL I:

IGNATIADES, L. and MIMICOS, N. (1977) Ecological response of phytoplankton to chronic oil pollution. Environ. Pollut. 13, 109-118.

IGNATIADES, L. and MIMICOS, N. A survey of petroleum hydrocarbons in Elefsis Bay, Aegean Sea and their effect on phytoplankton growth. Paper presented at XXVth Congress and Plenary Assembly in Split, 22-30 October 1976, Committee for Marine Pollution Fighting.

Table I: Concentrations of dissolved and dispersed Oil Hydrocarbons in Sea Water at 1m depth in µg/kg expressed in terms of chrysene units. (Mean of three separate samples)

	Sampling station	1	2	3	4	5	6	7	8	9	10	Cruise Number / Dates of Sampling	N° of samples	Range of amounts	Mean µg/kg	S.D. µg/Kg
Lesvos Island		7.4.77	1.8.77	24.11.77	31.1.78	27.5.78	30.8.78	24.11.78	16.3.79	10.5.79	18 8.79					
	L_1	0,50	1,7	2,7	1,5	2,7	3,1	8,0	3,1	4,9	4,5					
	L_2	0,30	0,8	3,2	1,3	1,7	3,5	3,0	1,8	9,3	6,3					
	L_3	0,20	2,5	1,4	1,2	2,1	4,7	8,5	2,0	5,5	2,5					
	L_4	0,11	2,5	2,4	1,9	2,7	1,2	9,8	1,0	5,0	1,7		54	0,8-11,5	3,4	2,4
	L_5	0,22	1,0	1,5	2,7	3,2	4,7	4,9	1,2	5,4	1,9					
	L_6	0,23	1,2	3,0	3,1	11,5	1,7	4,9	1,3	4,3	2,9					
		3.5.77	4 7.77	8.11.77	25.2.78	6.7.78	11.9.78	4.12.78	9.3.79	20.5.79	0.8.79					
Kriti Island	K_1	0,20	3,6	2,8	6,7	3,0	4,5	0,6	2,5	1,0	5,3					
	K_2	0,20	2,8	3,7	3,0	2,5	4,0	5,3	2,8	1,3	7,2					
	K_3	0,31	2,2	2,3	4,4	2,0	2,0	3,8	3,3	2,0	5,9		63	0,6-11,2	3,2	1,8
	K_4	0,18	4,4	2,2	2,5	2,2	4,9	2,6	1,9	3,5	3,8					
	K_5	0,84	0,9	2,6	11,2	2,7	3,4	3,6	1,7	5,0	1,6					
	K_6	0,52	2,8	3,2	6,6	2,1	3,9	6,5	2,9	5,8	1,5					
	K_7	0,34	1,8	1,2	3,5	1,0	2,7	4,5	2,5	4,0	4,0					
		5.5.77	6.10 77	15.1.78	21 4.28	19.6.78	21.8.78	11.11.78	24.3.79	1.6 79	23.8.79					
Rhodos Island	R_1	0,9	2,8	2,1	3,2	12,1	3,4	4,8	2,0	2,6	1,6					
	R_2	3,3	2,1	1,3	2,2	5,9	3,2	1,8	1,0	2,3	3,2					
	R_3	3,6	2,8	2,3	3,9	8,1	2,9	2,2	6,8	2,5	1,8		66	0,9-12,1	3,3	2,0
	R_4	1,8	4,6	1,1	2,2	6,3	3,4	2,4	2,7	5,1	2,1					
	R_5	1,7	1,5	4,0	4,5	2,3	4,0	1,5	1,4	2,9	2,0					
	R_6	3,3	4,9	2,9	3,1	3,5	6,6	1,0	4,0	5,0	+ + +					
	R_7	0,8	1,7	3,6	4,7	4,7	+ + +	2,0	8,9	3,6	2,0					
		0.4 77	0.8 77	7.12.77	27.3 78	26 6 78	7 8 78	17.11.78	7.2.79	7.4.79	3.7.79					
Messiniakos Gulf (Kalamata)	M_1	3,1	1,7	1,7	4,9	6,6	2,6	6,5	4,7	1,7	2,9					
	M_2	1,9	1,7	3,6	3,2	12,3	2,3	5,3	5,9	1,5	2,8		70	1,0-16,7	4,6	3,2
	M_3	1,8	1,3	3,4	6,2	5,5	3,8	3,2	6,0	1,0	7,6					
	M_4	2,9	2,9	3,6	9,0	8,4	3,3	3,5	9,0	4,0	6,9					
	M_5	1,6	1,7	4,0	11,5	7,0	3,2	3,5	5,2	4,8	3,5					
	M_6	1,7	1,4	2,2	4,7	13,7	7,9	4,3	11,3	2,0	4,7					
	M_7	1,9	1,6	2,7	5,3	16,7	4,7	3,5	5,5	9,1	4,4					
		13.3.77	5 5.77		20.2.78	6.6.78	31.7.78	27.10.78	17 3.79	5.5.79	31.8.79					
Petraïkos Gulf	P_1	0,43	10,3		1,3	2,3	0,8	4,9	7,9	7,2	3,6					
	P_2	0,30	9,8	+ +	1,3	3,1	1,4	1,3	15,9	12,5	3,9					
	P_3	0,21	9,5		1,4	9,7	1,8	1,8	14,9	9,8	4,6		55	0,8-28,2	6,1	3,5
	P_4	0,28	15,3		2,1	3,4	3,1	4,0	11,7	6,7	3,5					
	P_5	0,14	14,0		1,1	7,8	3,3	3,6	20,8	3,8	3,8					
	P_6	0,12	8,6		2,3	1,7	+ + +	3,4	28,2	3,5	2,6					
	P_7	0,11	14,5		3,8	3,6	1,2	2,1	6,6	7,4	3,7					
											2.8.79					
Cephalonia Island	A_1										2,4					
	A_2										4,6					
	A_3										4,7		7	2,4-6,7	4,4	1,6
	A_4										3,5					
	A_5										2,9					
	A_6										6,7					
	A_7										6,0					
											28.8.79					
Corfu Island	C_1										9,2					
	C_2										4,7					
	C_3										2,8		6	2,6-4,8	3,7	1,0
	C_4										3,1					
	C_5										4,8					
	C_6										2,6					
											30.8.79					
Katakolon (Arcadia Bay)	B_1										4,6					
	B_2										3,8					
	B_3										7,9		7	2,1-7,3	5,3	2,4
	B_4										8,8					
	B_5										2,1					
	B_6										6,7					
	B_7										3,8					

+ Values expressed in mg/Kg and measured by the I.R. technique and were not taken into account in statistical treatment.

+ + No sampling owing to very bad weather conditions.

+ + + Samples lost.

T A B L E II : Tar balls on beaches in g/m2. In each group the first figure is the result from the 9th day and the second figure represents the 10 day.

Site / S. Point / Date	Lesvos		Crete		Rhodes		Messiniakos Gulf				Patraikos G.		Corfu			Cephalonia		Katakolon	
	LT_1	LT_2	KT_1	KT_2	RT_1	RT_2	MT_1	MT_2	MT_3	MT_4	PT_1	PT_2	CT_1	CT_2	CT_3	AT_1	AT_2	BT_1	BT_2
9/10. 9.77											221/17								
9/10.10.77					102/0						255/51								
9/10.11.77					102/0						170/51								
9/10.12.77																			
9/10. 1.78					337														
9/10. 2.78											85/0								
9/10. 3.78			136/0																
9/10. 4.78											221/0								
9/10. 5.78					139/49						365/85								
9/10. 6.78					32/0						302/85								
9/10. 7.78											109/0								
9/10. 8.78											17/0								
9/10.10.78																			
9/10.10.78					48/0						36/0								
9/10.11.78			15/0								12/0								
9/10. 1.79	17/0										2/0								
9/10. 2.79											4/0								
9/10. 3.79					37/0						15/0								
9/10. 4.79					73/2						16/0								
9/10. 5.79					124/27						20/0								
9/10. 6.79					24/0														
9/10. 7.79																			
9/10. 8.79		31/0									15/0					21/0	17/0		
9/10. 9.79					18/0				41/0									12/0	6/0
9/10.10.79				41/0														20/0	10/0
9/10.11.79	13/2					31/0		6/0		32/0	7/0	13/0							15/0
9/10.12.79			31/0																10/0

Research Centre: Israel Oceanographic and Limnological Research Ltd.
Haifa
ISRAEL

Principal Investigator: O. H. OREN

INTRODUCTION

The Mediterranean coast of Israel is a densely inhabitated area where there are many coastal industries and activities, including a continuous and relatively heavy traffic of ships.

Centres of maritime activities connected with the disposal of oil residues are:

Haifa Bay - port, oil terminal (mainly fuel oil), petroleum industrial petrochemical plants, power stations;

Tel Aviv (including Ashdod area) - port, power stations, refineries;

Ashkelon - power station, oil port, loading terminal of the pipeline Eilat-Ashkelon.

All these centres can become sources of oil pollution, not only as a result of incidents and accidents, but also from regular activities.

In addition, there are several sewage outfalls: one of the biggest is the Tel Aviv domestic and industrial sewage pipeline, north of Tel Aviv; and there are smaller outfalls from other large cities. Several industrial outfalls are planned. The outfall discharges mineral oils from garages, fuel pumping stations, etc.

AREA(S) STUDIED

The work comprises a study of tar-ball pollution on Israeli beaches, the oil pollution (as measured by the concentration of dissolved/dispersed hydrocarbons) along the Israeli coast and in the open sea of the levantine basin.

METHOD AND MATERIALS

Tar on beaches: The collection of tar was carried out between spring 1975 and winter 1976 along the shore of six stations from El Arish in the south to Rosh Hanikra in the north. The collection was carried out every fortnight in duplicates.

The table shows the mean quantities of tar along the beach and the relevant standard deviation.

Dissolved/dispersed hydrocarbons along the coast: This report reflects the state of oil pollution along the Israeli coast between August 1977 and March 1978; four cruises were carried out, and water samples from a depth of one metre were collected and analysed for dissolved oils. The sampling stations, with average concentrations, are shown in Figures 2 - 5.

The sampling was generally carried out with the aid of the R/V Shikmona. This is a 120 ton, 25-metre-long trawler converted into a research vessel. The vessel has a crew of eight with accommodation for eight additional scientists. The ship has a cruising speed of 9 knots and an endurance of 21 days.

Samples for analysis were collected by the aid of a one gallon brown chemical reagent glass bottle suspended on a nylon rope in a stainless steel wire cage weighted by a lead bottom. A buoy was attached to the cage on a one-metre-long rope to ensure that the sampling bottle collected was from exactly one metre below the surface of the sea.

Between 24 May and 16 June 1978, 29 water samples were collected off the National Oceanographic Institute at Tel-Shikmona, Haifa. About half the samples were surface samples, the other half being samples taken from one metre depth with the above-described sampler.

Dissolved/dispersed hydrocarbons in the levantine basin: We are reporting here on four cruises in the open levantine basin:

1) 9 July - 16 July 1977

2) 10 October - 15 October 1977

3) 26 March - 3 April 1978

4) 27 June - 2 July 1978

The geographical locations of the sampling stations are shown, together with average concentrations, in Figures 6 - 9. The samples were collected in the same way as described above and with the same R/V Shikmona.

RESULTS AND THEIR INTERPRETATION

Tar on beaches: The mean quantity of tar found was 3,625 g/m offshore with a standard deviation of 2,834 g. (see also table). Figure 1 shows that the quantity of tar decreased from spring 1974 to winter 1976, from 6,107 g/m to 1,344 g/m. From 1976 the quantity of tar increased to 4,361 g, decreasing thereafter.

One of the reasons for the appearance of larger quantities of tar on the centrally located beaches of Israel is probably the transport of oil, the existence of oil loading and unloading ports, as well as in the area about 150 - 200 km offshore (determined from the age of tar balls formed). The other reasons are the local meteorological conditions and ocean current regime.

Besides the two factors increasing beach tar, one has to take into account the factors causing its disappearance: one of the most important is the weathering of tar, its disintegration by wind and water action and sand abrasion.

Dissolved/dispersed hydrocarbons along the coast: The sampling stations are shown on the four maps attached (Figures 2 - 5). During Cruise No. 1 most of the samples were collected from the southern part of the coast, between Gaza and Tel-Aviv.

The southern oil port of Israel is situated in Ashkelon (station 3 on Cruises No. 1 and No. 3). During both cruises, the concentration of dissolved oils in this region was the highest (9.38 µg/l and 19.38 µg/l, respectively) except for Haifa Bay, where the second oil port of Israel is situated. Haifa Bay shows the highest values of dissolved oil (15.00 µg/l, Cruise No. 1, and 15.63 µg/l, Cruise No. 3) because of the great activity in this bay. Here, large quantities of bilges are released by ships awaiting unloading of various cargoes, including oil: two extremely active harbours, Haifa and Kishon, are situated here. In addition, the extremely polluted Kishon river discharges into the bay, bringing wastes from the oil refinery and industrial sewage from the Haifa industrial area, the fishing harbour, the shipyard, etc.

Off Palmachim, a station south of Tel-Aviv, larger quantities of dissolved oils (12.50 µg/l, Cruise No. 1, and 10.71 µg/l, Cruise No. 3) were found. These may come from the urban and industrial sewage entering the sea nearby.

The largest quantities of dissolved oils were found during the present survey off a drilling raft in the Bardawil Lagoon (20.63 µg/l, Cruise No. 2). Although the quantities of dissolved oils found are not large and critical, they give a true indication of the state of pollution in locations where activities connected with oil and shipping take place.

Off Tel Shikmona, on three occasions during the short sampling period (2 May - 16 June 1978), relatively large quantities of dissolved petroleum hydrocarbons were found. This may indicate that some slight spillage or bilge spot reached the shore near the institute.

The quantities of oils found in samples taken from one metre depth varied very little from sampling day to sampling day. The largest quantity found was 7.5 µg/l.

The largest quantity of oil from surface samples was found on May 29th (more than 45.3 µg/l). The lowest quantity was 1.1 µg/l found on three occasions. During the rest of the sampling days, quantities of oil varied between 5.7 µg/l and 0.9 µg/l.

Dissolved/dispersed hydrocarbons in the levantine basin: Relatively large quantities of dissolved oils were found in the area between Cyprus and Crete, the area in which dumping of ballast and wash waters from tankers was permitted in the past and is probably still practised by many tankers. This was confirmed by a conversation with a First Officer serving on an oil tanker. One may conclude from this that illegal dumping of oily wastes is still taking place in that area.

One should note that during Cruises No. 3 and No. 4, large quantities of dissolved petroleum hydrocarbons (40 µg/l) were found in the south of Cyprus at stations 15 and 20 (Cruise No. 3), and above 25 µg/l (Cruise No. 4), practically in the same area.

Another area of relatively large quantities of dissolved oils was found in the south-east of Crete: above 40 µg/l, at station 40 on Cruise No. 3.

The waters on the edges of the surveyed areas contain low quantities of dissolved oils (generally less than 10 µg/l).

In general, one could say that only small areas of the levantine basin can be considered as slightly polluted by petroleum hydrocarbons, but if the rules and regulations adopted by the Mediterranean States are observed, one can obviously expect that in a few years the quantity of dissolved oils will diminish in the open sea, if no catastrophies occur.

TABLE 1

MEAN QUANTITIES OF TAR ON THE BEACHES OF ISRAEL IN GRAMMES PER 1 METRE OF COAST

COASTAL AREA	ROSH HANIKKA	ATLITH	BEITH YANAI	GA'ASH	ASKALON	EL ARISH
Mean quantity of tar (g)/m	3902	4388	4114	4186	3014	884
Standard deviation	2612	3185	3562	2493	2407	666

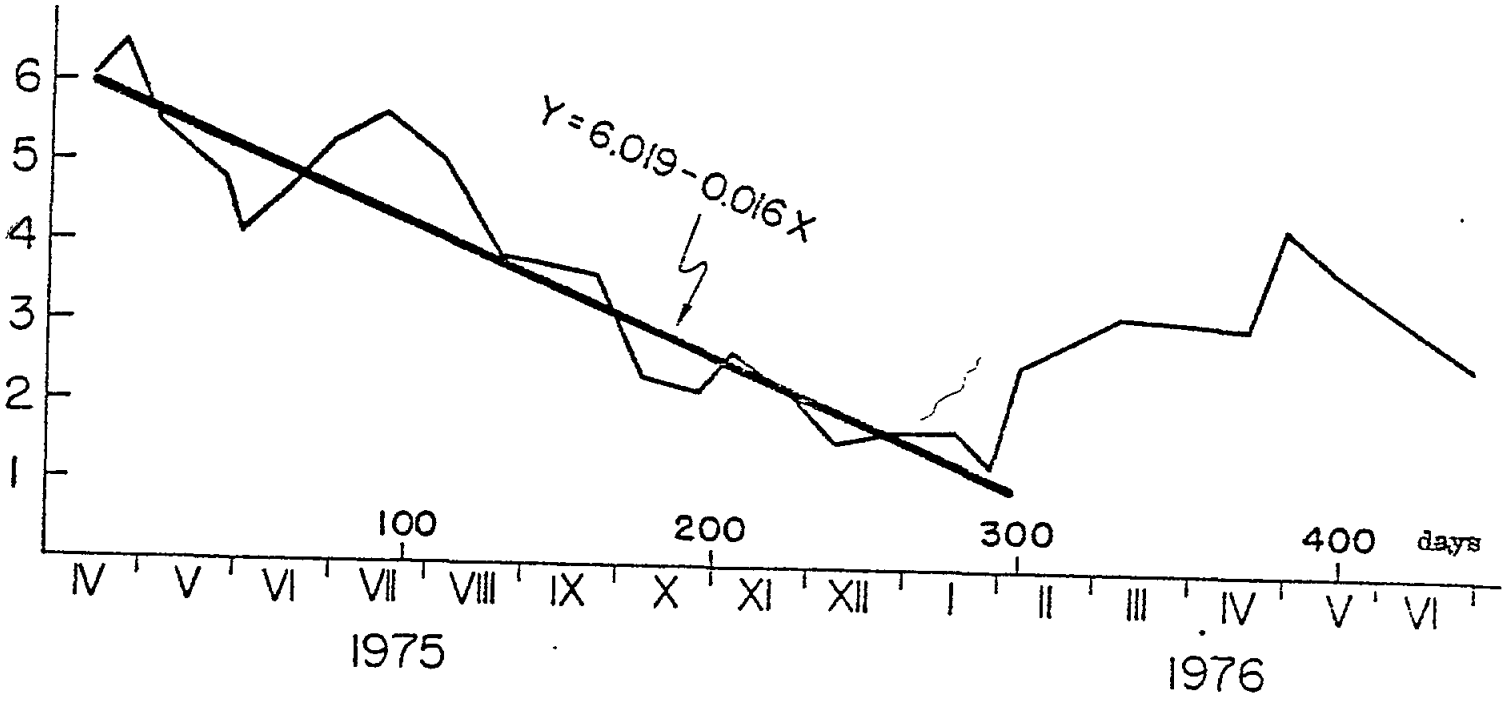

Fig. 1. Mean quantity of tar on Israeli coast of the Mediterranean as a function of time.

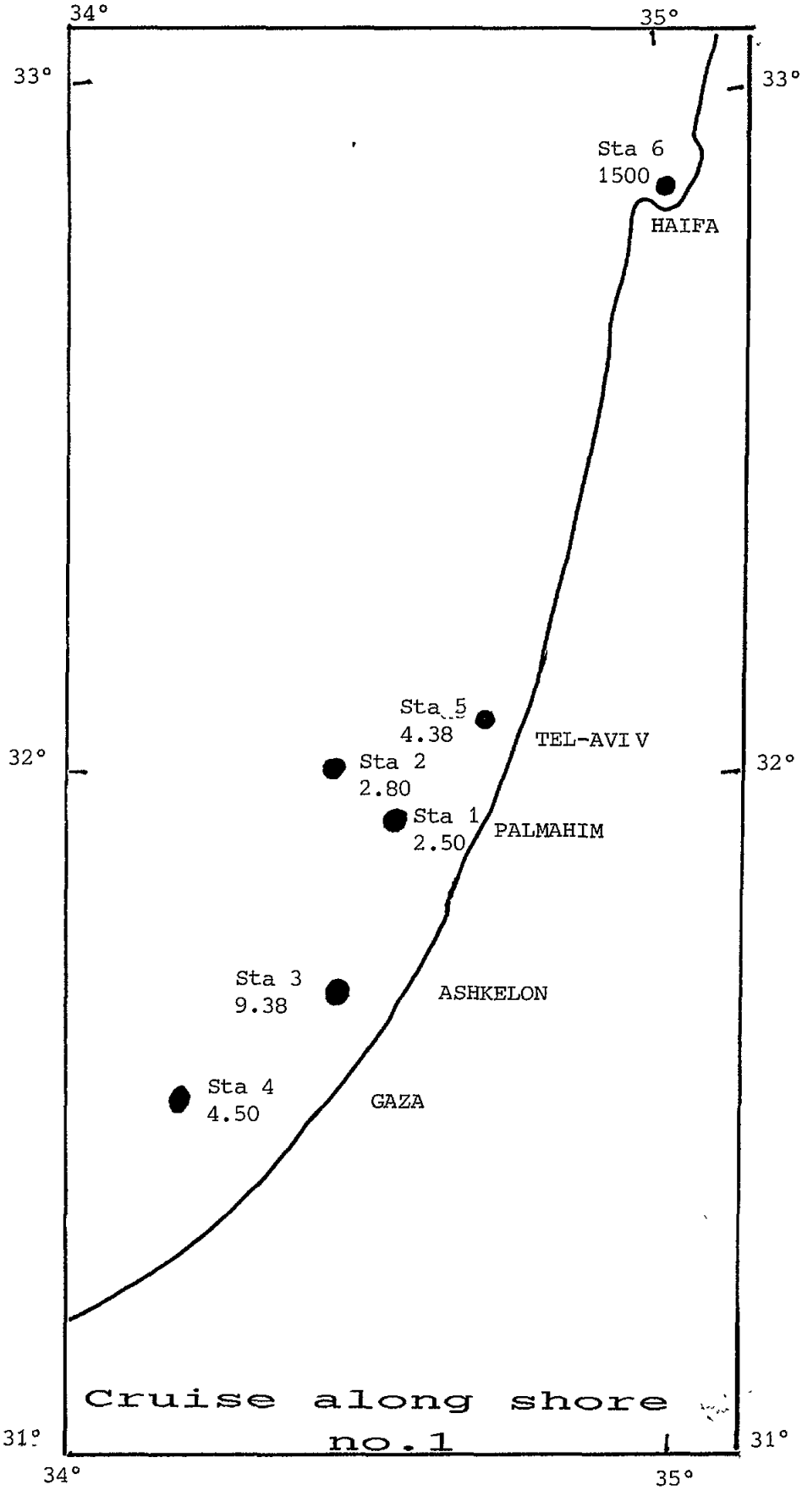

Figure 2. Dissolved/dispersed hydrocarbons along the coast (concentration in µg/l)

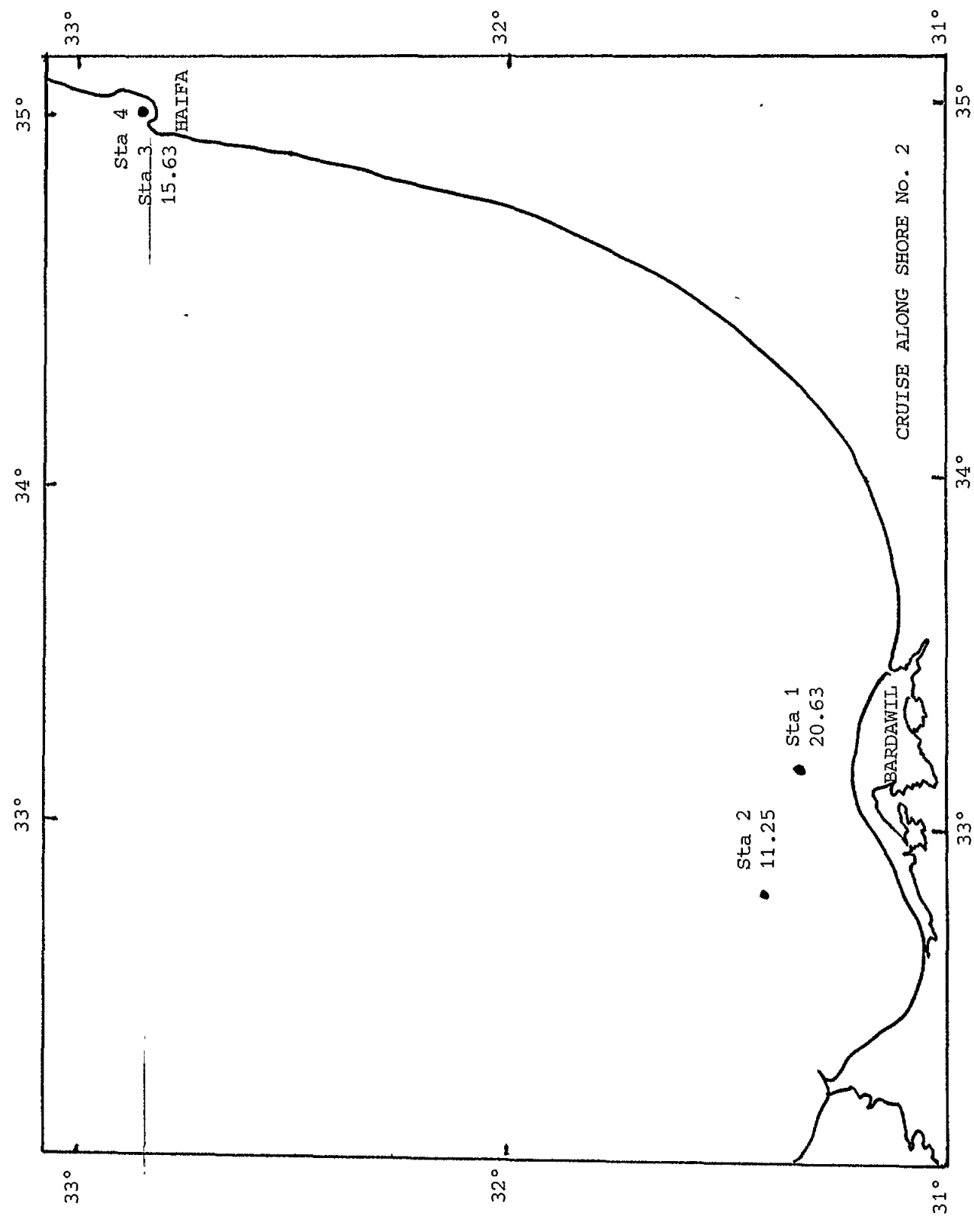

Figure 3. Dissolved/dispersed hydrocarbons along the coast (concentration in µg/l)

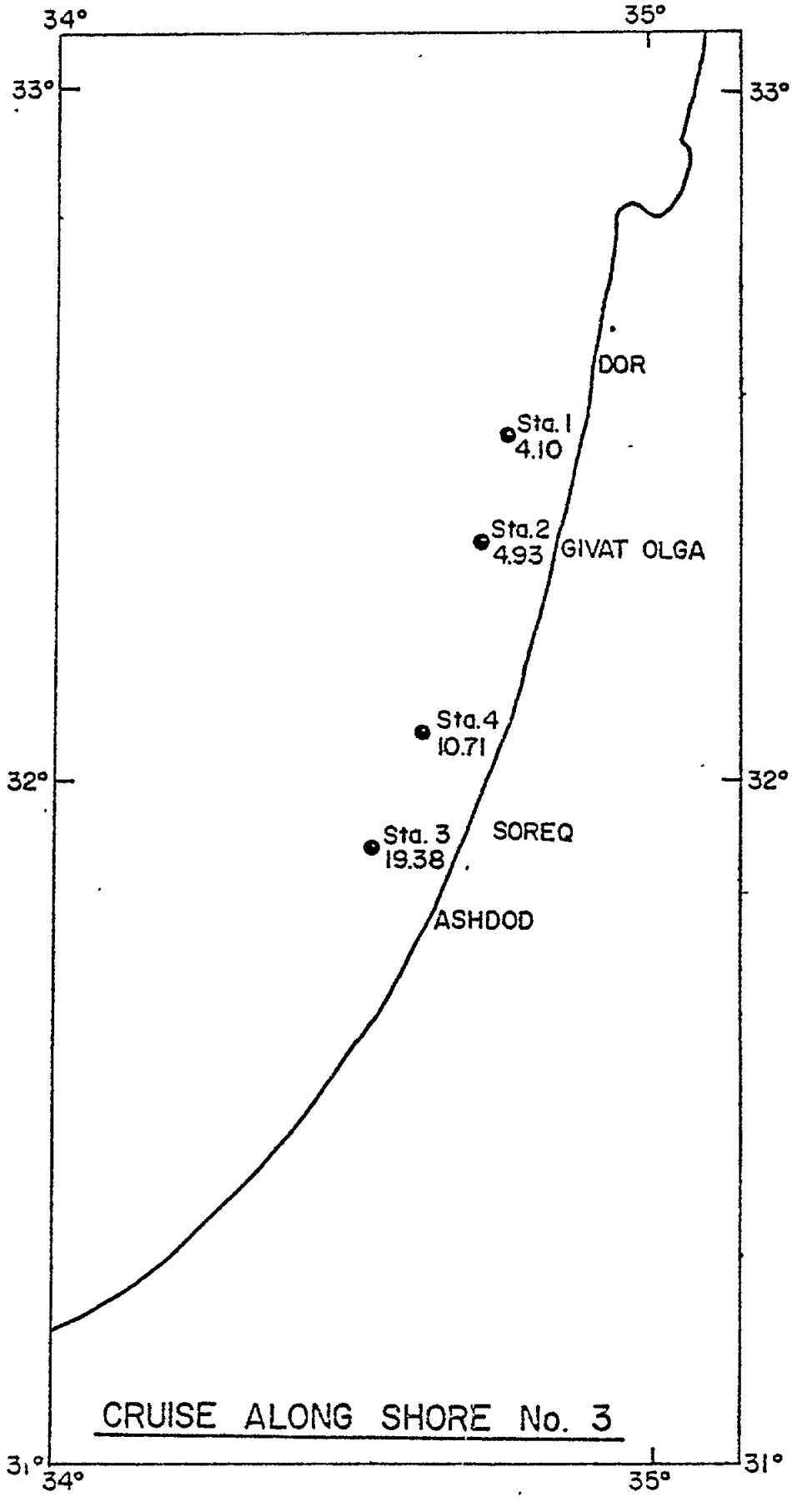

Figure 4. Dissolved/dispersed hydrocarbons along the coast (concentration in µg/l)

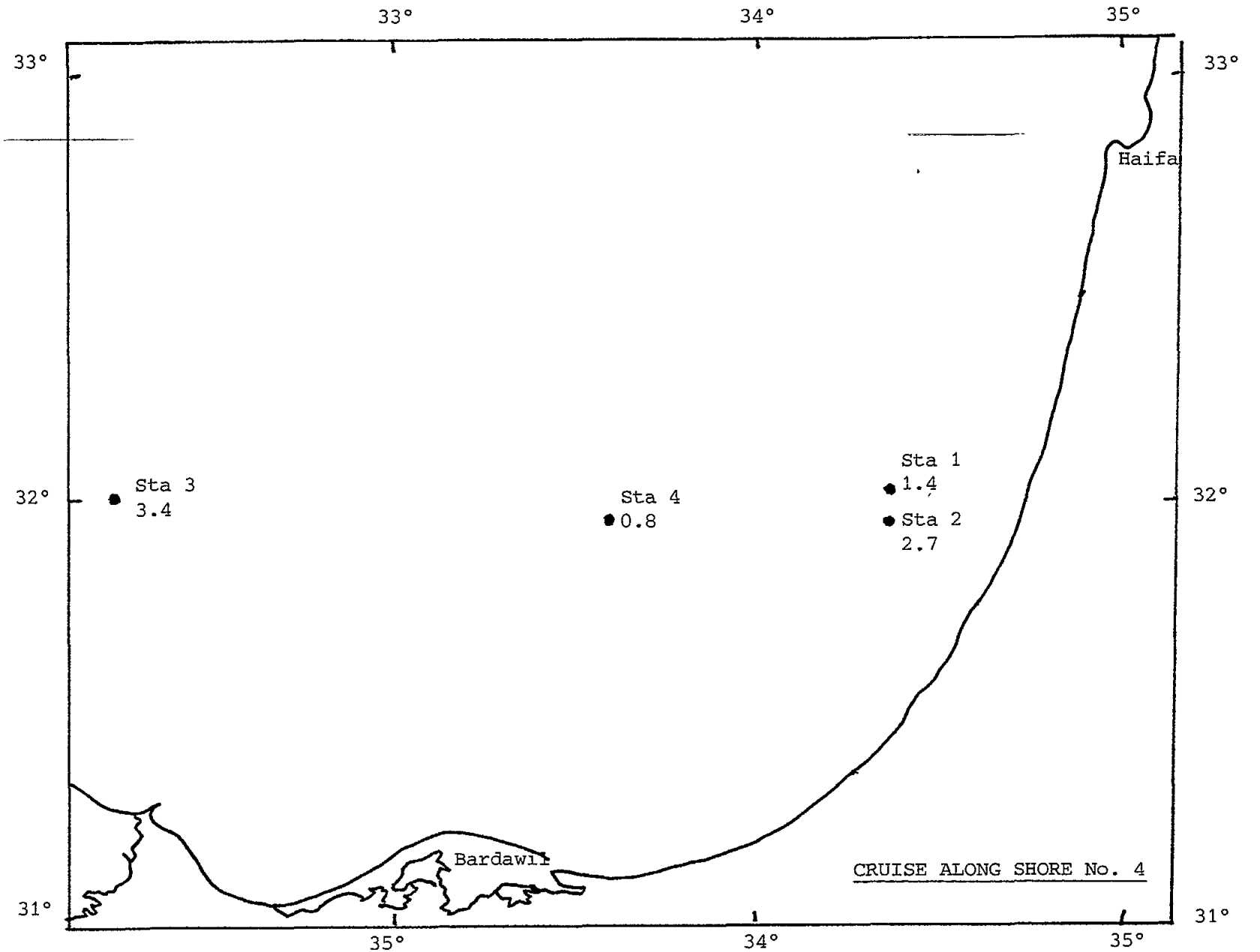

Figure 5. Dissolved/dispersed hydrocarbons along the coast (concentration in µg/l)

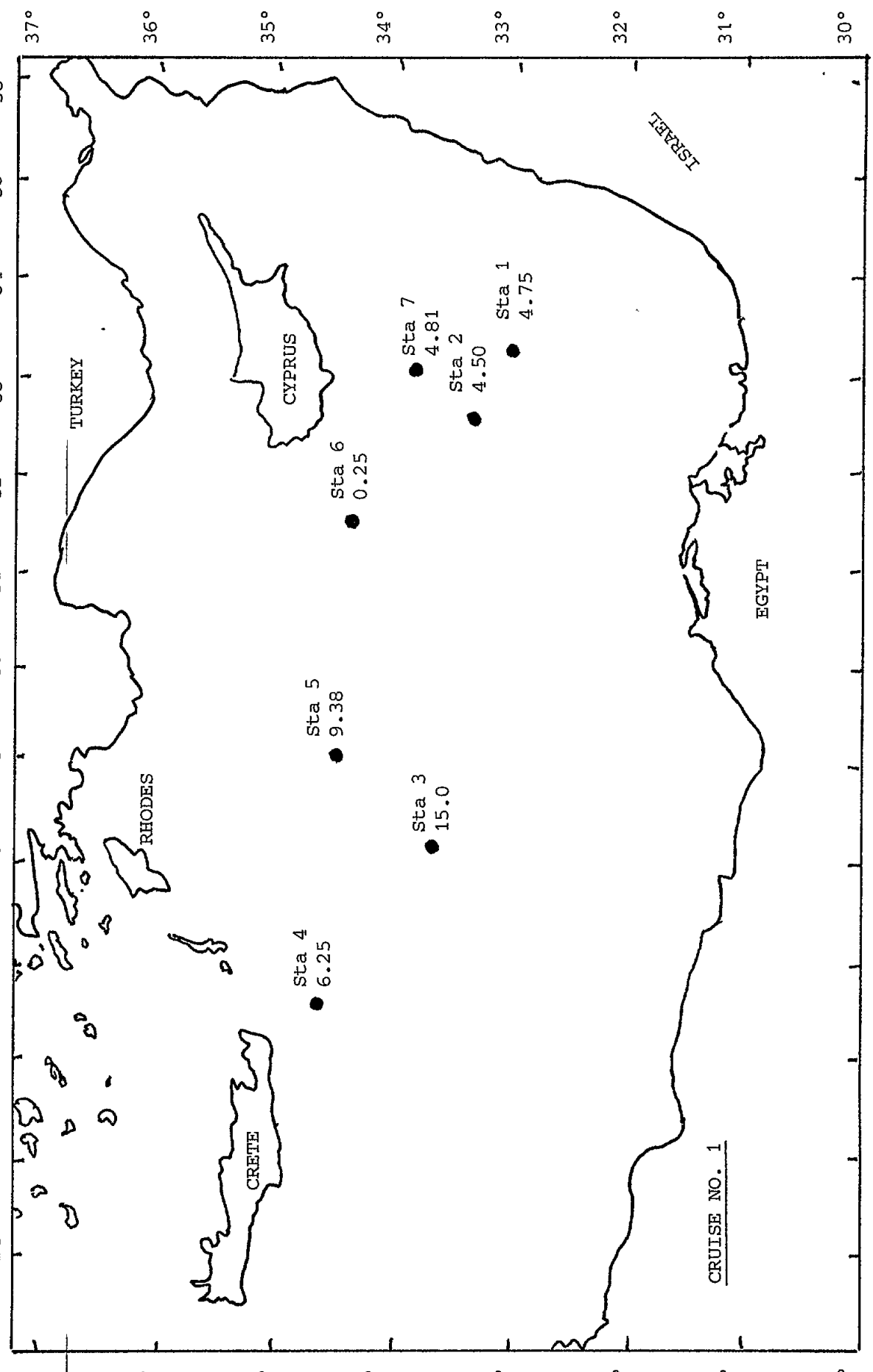

Figure 6. Dissolved/dispersed hydrocarbons along the coast (concentration in µg/l)

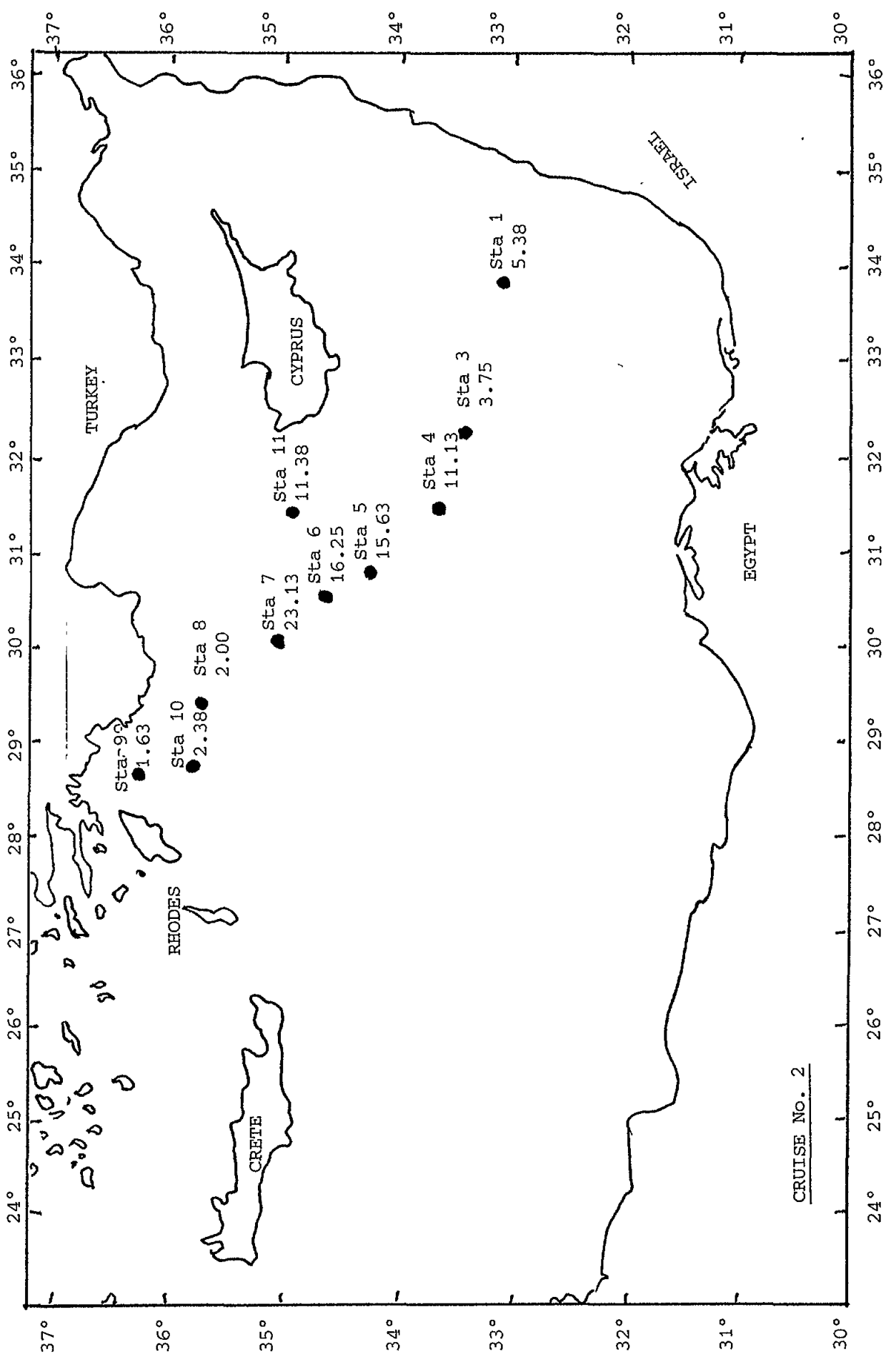

Figure 7. Dissolved/dispersed hydrocarbons along the coast (concentration in µg/l)

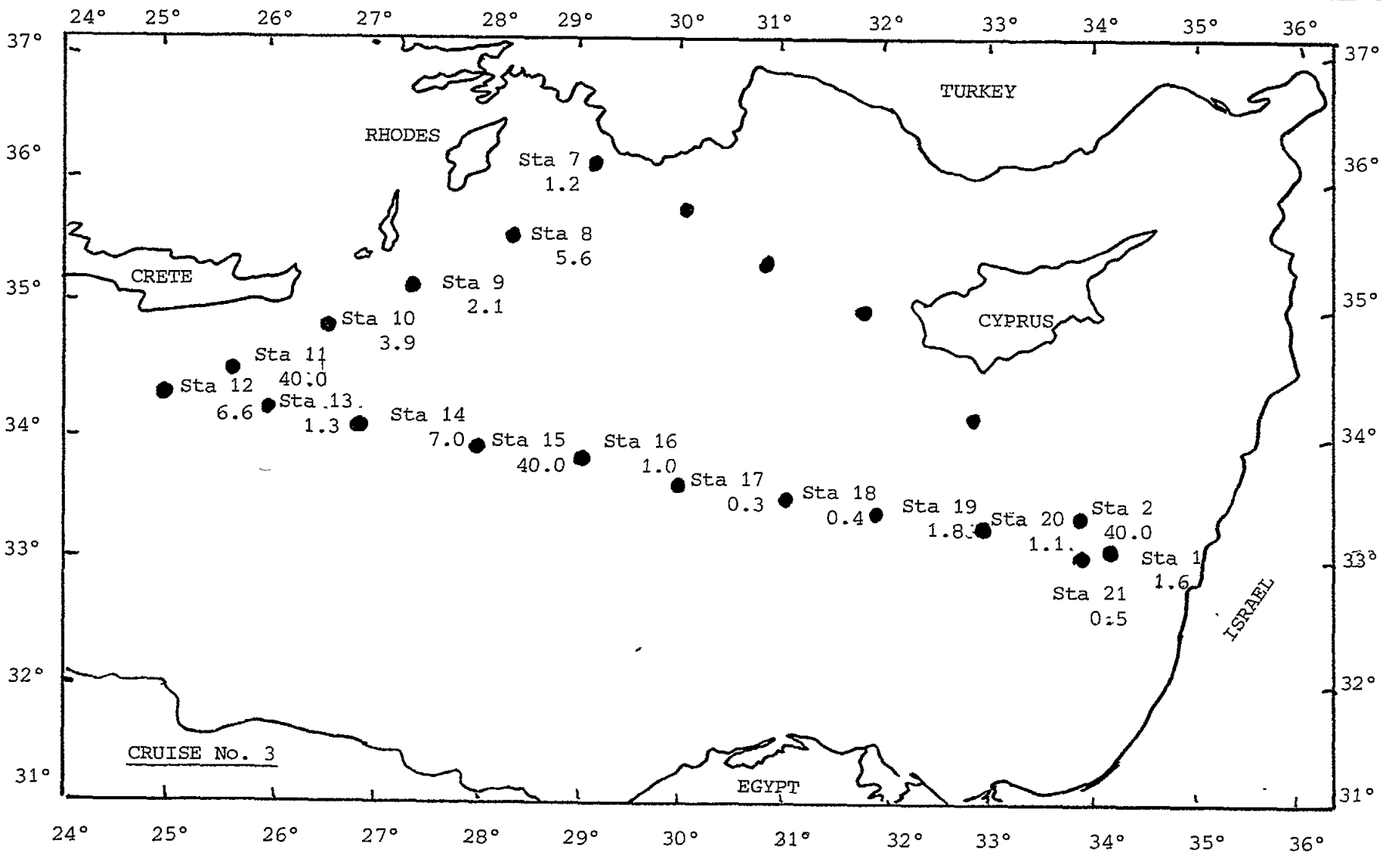

Figure 8. Dissolved/dispersed hydrocarbons long the coast (concentration in µg/l)

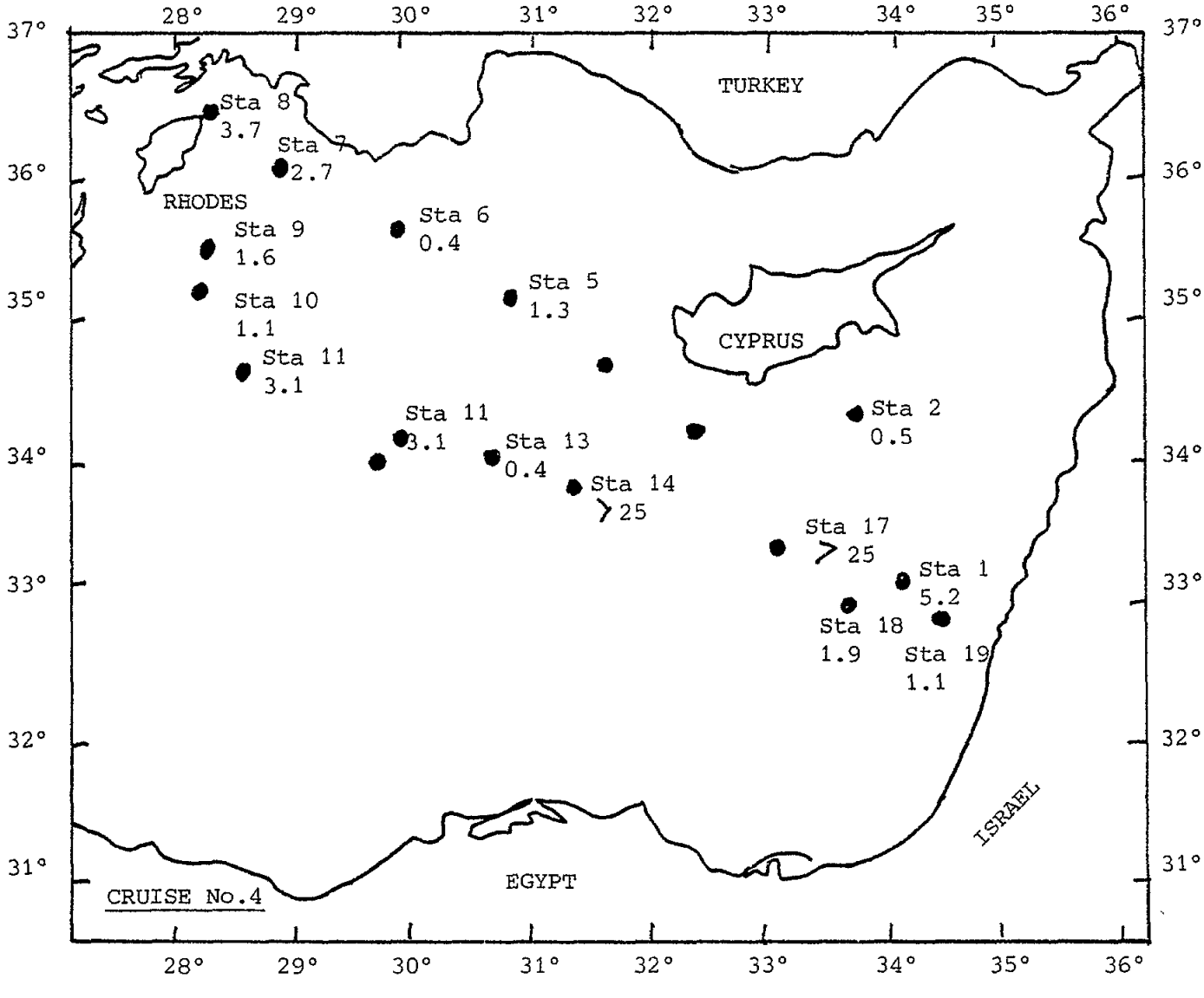

Figure 9. Dissolved/dispersed hydrocarbons along the coast (concentration in µg/l)

Research Centre: Instituto di Chimica Generale
ed Inorganica
Universita degli Studi di Venezia
VENEZIA
Italy

Principal Investigator: A. A. ORIO

INTRODUCTION

The work started in October 1978; its purpose was to monitor petroleum hydrocarbons dispersed or dissolved in sea-water. The previous and present activities of the Institute relevant to this MED POL project are concerned with the presence and the dynamics of organic (PCBs, DDTs and other chlorinated hydrocarbons) and inorganic (heavy metals) pollutants in the marine surface sediments. Although this research field is not specifically mentioned in any of the seven MED POL projects there is a clear relationship with projects II and III.

AREA(S) STUDIED

The area is given in the figure in which are also indicated the six stations initially proposed for monitoring the dispersed or dissolved hydrocarbons. The area is characterized by low water depths (15-20 m) and by counterclockwise currents from the north-east. Quite heavy commercial traffic reaching the industrial zone inside the Venice Lagoon is generally observed. Large ships and oil tankers coming from the southern Adriatic Sea enter the Lagoon through the port entrances of Lido and of Malamocco.

MATERIALS AND METHODS

The sampling, sample treatment, analysis of the samples and the procedures used for evaluating the results were previously discussed with Dr. M. Sammut of the University of Malta acting as Regional Activity Centre for this pilot project. All the steps have been performed following the procedures described in the IOC Manual and Guides No. 7.

We have been able to analyse only water samples from station D where a survey platform is located. The personnel of the R/V Umberto D'Ancona were supposed to collect the water samples from the remaining stations, but technical reasons prevented them from carrying out this important work for our Institute.

No intercalibration exercises have been carried out as the entire experimental part, from sampling to the analysis, was accomplished following the exact instructions of the Malta Regional Activity Centre The analysis of the first two samples collected in the Adriatic Sea was completed.

RESULTS AND THEIR INTERPRETATIONS

The results of the analyses are reported in the table. The concentration of dissolved/dispersed hydrocarbons is in the range 0.22-1.0 µg/l (with an average of 0.66 µg/l). No seasonal trend can be observed since the results cover too short a period of time.

The values of concentration reported here fall within a short range compared to the results obtained in other areas (see FARACO et al., IV Journées Etud. Pollutions, 117-121, CIESM, Antalya, (1978) and references therein). Similarly, the average of 0.66 µg/l is quite a bit lower than the averages obtained in other areas of the Mediterranean Sea (averages in the range 3.3-580 µg/l). These values compare well with the concentrations of 0.1-1.2 µg/l found in Rijeka Bay, Yugoslavia, just opposite Venice, (M. Ahel et al., IV Journées Etud. Pollutions, 99-101, CIESM Antalya (1978)), indicating that the station examined is not polluted by hydrocarbons. However, the low concentrations observed in Rijeka Bay and in our area do not necessarily mean that the northern Adriatic Sea is not polluted by hydrocarbons. A larger number of data on more stations are needed to draw valid conclusions.

Concentrations of dissolved/dispersed hydrocarbons at Station D

STATION NUMBER	SAMPLE NUMBER	DATE	CONCENTRATION µg/l
D	P 1	2.3.79	0.87
D	P 2	30.3.79	0.77
D	P 3	9.4.79	1.11
D	P 4	10.5.79	0.68
D	P 5	25.5.79	0.60
D	P 6	12.6.79	0.56
D	P 7	28.6.79	0.54
D	P 8	11.7.79	0.22
D	P 9	7.8.79	0.56
D	P 10	14.9.79	0.67

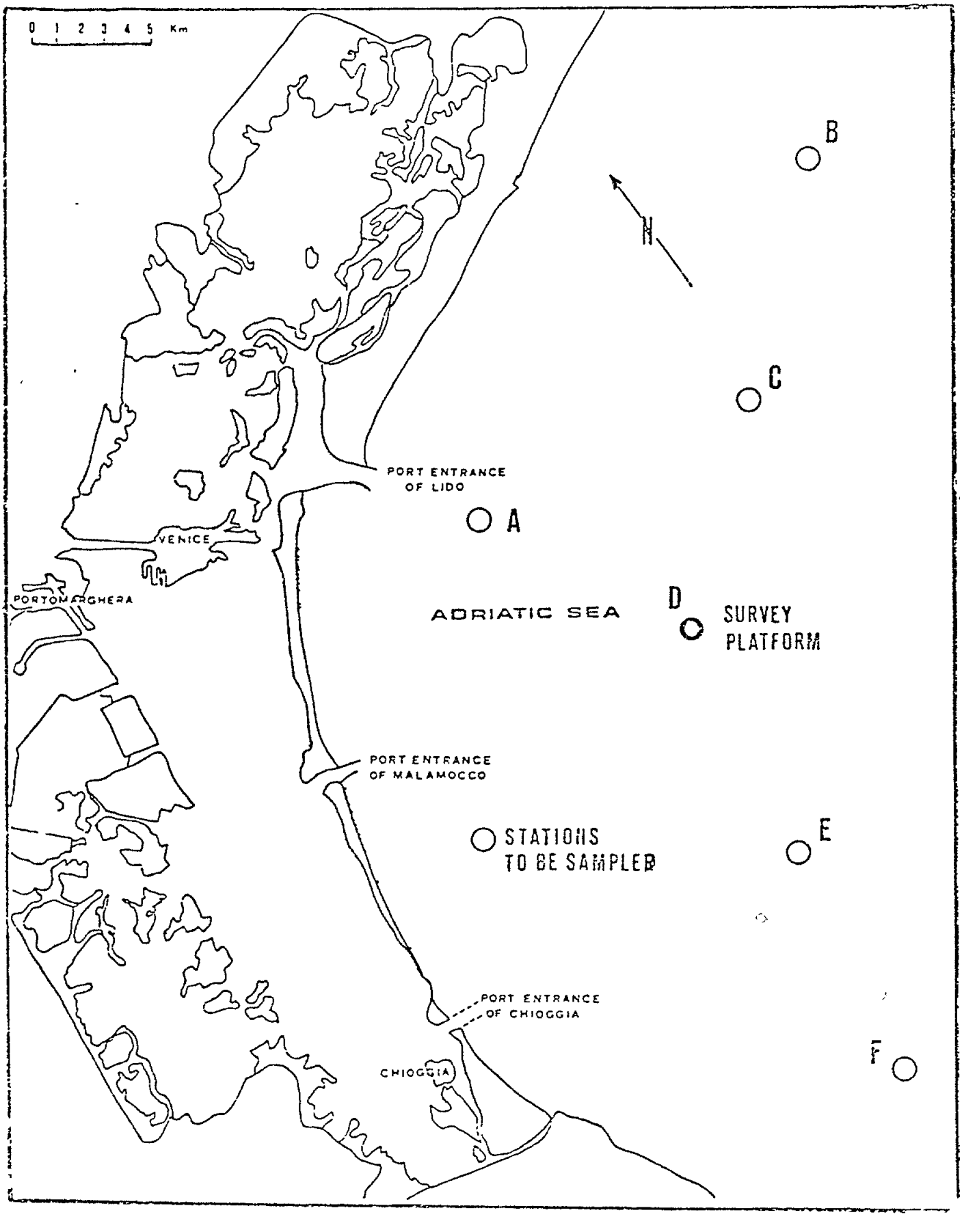

Figure 1. Area studied and sampling sites

Research Centre: Centre de Recherche marine
Conseil national de la Recherche scientifique
BEYROUTH
Liban

Principal Investigator: H. H. KOUYOUMJIAN

INTRODUCTION

The Centre sampled tar on beaches from April 1977 till August 1978.

AREA(S) STUDIED

Two principal zones were sampled: Ramlet al Baida to the south of Beirut, and Fidar, to the north. A third zone, Tripoli, was sampled three times. There are three sampling sites in each zone. Additional parameters were measured whenever possible (waves, winds, temperatures - air and sea - pH, salinity).

MATERIAL AND METHODS

The standard method was used. The data are shown in Table I.

RESULTS AND THEIR INTERPRETATIONS

The data generally suggest higher values in mid-summer, but are not adequate for firm conclusions.

Table I

Average weights (from three samples) of tar beaches (in g/m^2) for three stations, monthly, for the period April 1977 till August 1978

Year/month	STATIONS Ramlet	Sidar	Tripoli
1977 April	1.4	0.6	0
May	-	-	-
June	-	-	-
July	14.8	33.6	-
August	11.0	0.5	-
September	0	6.7	-
October	0	0	-
November	8.4	0	-
December	2.9	0	-
1978 January	3.3	0.2	-
Febraury	-	-	-
March	1.4	0.5	-
April	-	-	-
May	0.8	0	0.4
June	0.8	0	0.3
July	-	-	-
August	-	0	-

Research Centre: The University of Malta
MSIDA
Malta

Principal Investigator: V. FERRITO (up to the end of September 1978)
M. SAMMUT (from October 1978)

INTRODUCTION

Work on MED POL I started in April 1977. At first, owing to lack of equipment, only tar on beaches was measured.

Arrangements were made with the Malta Armed Forces and the Regional Oil Combating Centre at Manoel Island to forward information regarding sightings of oil spills and other floating pollutants when these occur in the vicinity of Malta. Appropriate log forms were distributed to facilitate exchange of information. Initial attempts to measure floating tar particulates were unsuccessful since the neuston net then available could not withstand the lowest speed of the boat available for sampling. A high speed neuston net sampler (Derenbach and Ehrhardt, 1975) was constructed, but because of logistic difficulties and lack of manpower, sampling for floating tar could not be carried out.

Meteorological data is provided by the Meteorological Office, Luqa.

This report covers the period up to February 1980.

AREA(S) STUDIED

Oil spills and other floating pollutants: The whole of the Maltese coast was observed.

Dissolved/dispersed hydrocarbons: Sampling sites were around the coast of Malta, usually about 1 km from shore. The sites were:

		Latitude	Longitude
1.	Off Grand Harbour	35 54'N	14 33'E
2.	Off Marsaxlokk Bay	35 49'N,	14 33'E
3.	Off Ghar Lapsi	35 48'N,	14 26'E
4.	Malta Channel	36 00'N,	14 21'E
5.	Off Qawra	35 58'N,	14 26'E

Tar on beaches: Three sites, Qawra, Anchor Bay and Marsaxlokk, were sampled approximately monthly (weather permitting). Three strips were sampled at each site. The sites are shown in Figure 1.

Qawra, on the north-east coast of Malta, is directly affected by easterly and north-easterly winds; Anchor Bay, on the north-west coast of Malta, is directly affected by westerly and north-westerly winds; and Marsaxlokk Bay, on the southern coast of Malta, is directly affected by southerly and south-westerly winds.

The shoreline is quite uniform in all three areas, straight at Qawra and Marsaxlokk Bay and slightly concave at Anchor Bay. The slope is gentle in all three areas. Substrate and shoreline are sand and gravel at Anchor Bay, sand at Qawra and muddy sand at Marsaxlokk Bay. A considerable quantity of Posidonia is deposited on all three areas especially during the winter months. There is a minimum of human activity at all three sites although there is some bathing in peak summer months. No land-based sources of heavy-oil residues exist at these sites; however, slight spillage of diesel oil occurs at Marsaxlokk Bay, but this is not considered to have any significant influence on tar-ball deposits on the beach.

As from September 1979 Anchor Bay was leased to a commercial filming company and, therefore, sampling on this site had to be discontinued. No other site with the same characteristics could be found.

There are no rivers on the Maltese Islands and the only water entering the sea from the land is rainwater run-off. The sea around Malta is practically tideless. The predominant water currents in the area are generally NW to SW (mean speed about 0.2 m/sec). In summer, the surface currents reflect the flow of water from the western to the eastern Mediterranean. In winter, the surface currents are highly influenced by the prevailing wind conditions. The surface water currents in the vicinity of Malta are very complex.

One major sewage outfall exists at Wied Ghammieq in the vicinity of Station 1. Another sewage outfall is in the vicinity of Anchor Bay. The northern side of Malta, which has a gently sloping shoreline, is the most urbanized coastal area (population of Malta approximately 320,000, and the number of visitors in 1979 was about 620,000) while the southern side consists mainly of cliffs. There are no oil refineries on the Island and any 'oil' from land probably originates from sewage effluents. At times, very small oil spills occur in harbours such as Grand Harbour, Marsamzett Harbour, Marsaxlokk Bay. Most of the oil on beaches is a result of tanker operations in the vicinity of Malta.

The sample sites are shown in Figure 1.

METHODS AND MATERIALS

The methods used were according to the Manual for Monitoring of Oil and Petroleum Hydrocarbons in Marine Waters and Beaches (Suppl. to IOC Manuals and Guides No. 7).

Oil slicks and other floating pollutants: the position and estimated area of each slick observed was recorded.

Dissolved/dispersed petroleum hydrocarbons: Sea-water samples were collected in triplicate at a depth of 1 metre. Measurement was by a Turner Model 430 ultra-violet spectrofluorimeter, after extraction of the sample by carbon

tetrachloride, without clean-up. Chrysene was used as a standard for the calibration of the instrument. Besides the three main sites (off Grand Harbour, off Marsaxlokk, and the Malta Channel), two other sites (off Ghar Lapsi and off Qawra) were later included so as to assess the levels of dissolved/dispersed hydrocarbons all around the coast of Malta. A patrol boat of the Malta Armed Forces was used for sampling; our intention was always to sample on a monthly basis, but this actually depended on weather conditions and availability of a boat.

The inter-comparison exercise for dissolved/dispersed hydrocarbons organized by Dr. A. Zsolnay of Duke University, N.C., USA, was carried out four times (October 1977, November 1977, February 1978 and July 1979). Results showed good precision and accuracy (Document IOC-WMO/MAPMOPP-11/12 Add. 1. Washington D.C. February 1978).

Tar on beaches: three strips, 2 metres wide, running from the shoreline (in calm sea conditions) to the inner wave limit, were selected for each area, depths were as follows: Anchor Bay, 3 m.; Qawra, 5 m.; and Marsaxlokk, 5m.

Each zone was thoroughly cleaned and staked out in April 1977. Sampling commenced after 14 days, and was continued at 14-15 day intervals.

The total amount of tar in each zone was weighed. In cases where the tar balls were coated (totally or partially) with Posidonia, this was removed prior to weighing.

RESULTS AND THEIR INTERPRETATION

Oil slicks: the observations are given in Table I. Observed oil slicks were small; the number of oil spills reported is relatively small and there are doubts whether most of the spills reaching the Maltese coast were reported to us.

Dissolved/dispersed hydrocarbons: Results are shown in Table II. The most striking features of the results obtained so far are the low levels as well as the large variability (indicated by the standard deviation) in the results from samples collected at the same time and place. The levels indicate minimal presence of dispersed/dissolved hydrocarbons in the coastal waters round Malta. Oil films on the water surface were never encountered at any of the sampling sites. It should be noted that samples from Grand Harbour contained 3.4 µg/l of dispersed/dissolved hydrocarbons.

The large variations could be due to uneven distribution of dissolved/ dispersed oil in the water column. A statistically significant temporal and spatial variation in the levels of dispersed/dissolved hydrocarbons in sea-water round the coast of Malta is not apparent in view of the variability in sets of results.

A typical emission spectrum of the water extracts, compared to chrysene, shows a maximum at around 340nm whereas chrysene has a maximum in the 380nm region (excitation 310nm), which indicates that the dispersed/dissolved oil is not of a heavy type (e.g., crude oil or bunker oil) but rather a lighter type of oil such as diesel oil or a light fuel oil. However, fractionation of the oil due to preferential solubilization of certain oil fractions cannot be excluded.

Tar on beaches: Results for the three sites are shown in Tables III - V, and Figures 2 - 4. The weight of tar has been calculated on the basis of daily accumulation, since it has not always been possible to sample on the same day of each month. The relatively high standard deviation of the weight of tar collected on the same day from three strips at the same site indicates an uneven accumulation of tar on the beach. This variation could be due to the geographical characteristics of the beach as well as to the quality (size) of tar balls on each strip. Large tar balls (up to 20 kg) were sometimes seen at Anchor Bay but these tar balls were outside the sampling strip. The tar balls found are of various sizes varying from oil films to individual tar balls some 20 cm in diameter. The quality of the tar is mostly of the non-sandy and sandy types, with very little coquina being found. Preliminary tests have shown that the water content of the tar can be up to 19.5 per cent (w/w) and the debris 31 per cent (w/w).

There seems to be correlation between the prevailing wind direction and tar accumulation on beaches. The highest accumulation of tar was at Anchor Bay, which is exposed to prevailing westerly winds, whereas at Qawra and Marsaxlokk, where the wind is generally offshore, the quantity of tar was much lower, and in many instances no tar was deposited on the beach. More was deposited at Anchor Bay in autumn and winter than in spring and summer.

At Marsaxlokk Bay higher levels were found in June/July 1977 and January/February 1978. In the former two months this correlated with prevailing winds in the onshore direction. The tar accumulation for January/February 1978 (joint results) may not be representative of the whole beach, since at two strips no tar was found, while two large tar balls were found on the third strip. At Qawra there has been a consistent decrease in tar since July 1977 and tar has been found only once since December 1977.

CONCLUSIONS

Very few oil spills have been sighted round the coast of Malta and it is possible that a majority of oily residues are discharged at a fair distance from the Island and reach shore in the form of tar balls. The accumulation of tar on beaches seems dependent on the prevailing wind which in Malta is north-westerly. However, knowledge of surface water currents particularly in inshore waters and bays, could provide useful information on the transport of tar balls, particularly in view of the uneven distribution of tar on the beaches being sampled.

In our opinion, this exercise is only providing an indication of the deposition of tar on beaches, since wave action may wash back some of the tar balls; an unknown amount of water and debris are included in the estimation of tar, and the sampling zones may not be representative of the whole beach.

The levels of dispersed/dissolved hydrocarbons (expressed as chrysene units) around the coast of Malta are low (generally 0.1 µg/l) compared with those of other areas in the Mediterranean where concentrations between 1 and 10 µg/l have been reported, using the same analytical technique. Although chrysene may be a useful standard which would enable better comparison of results from different regions, it is considered doubtful whether chrysene allows a good estimation of dispersed/ dissolved oil when its emission spectrum is so different from that of the water extracts.

Figure 1. Map of Malta showing sampling sites for MED I

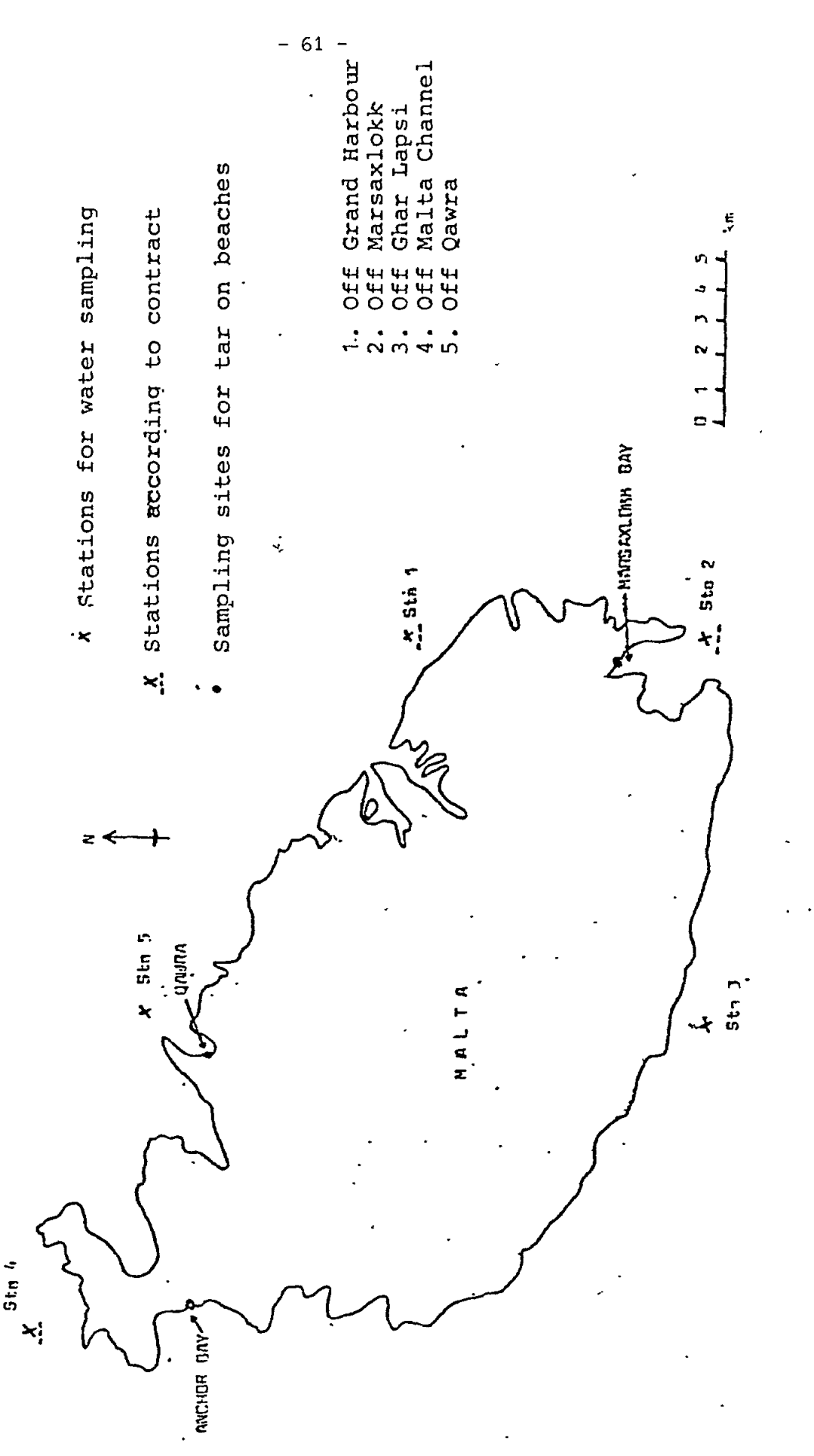

Fig. 2. Tar on Beaches (MALTA)

ANCHOR BAY

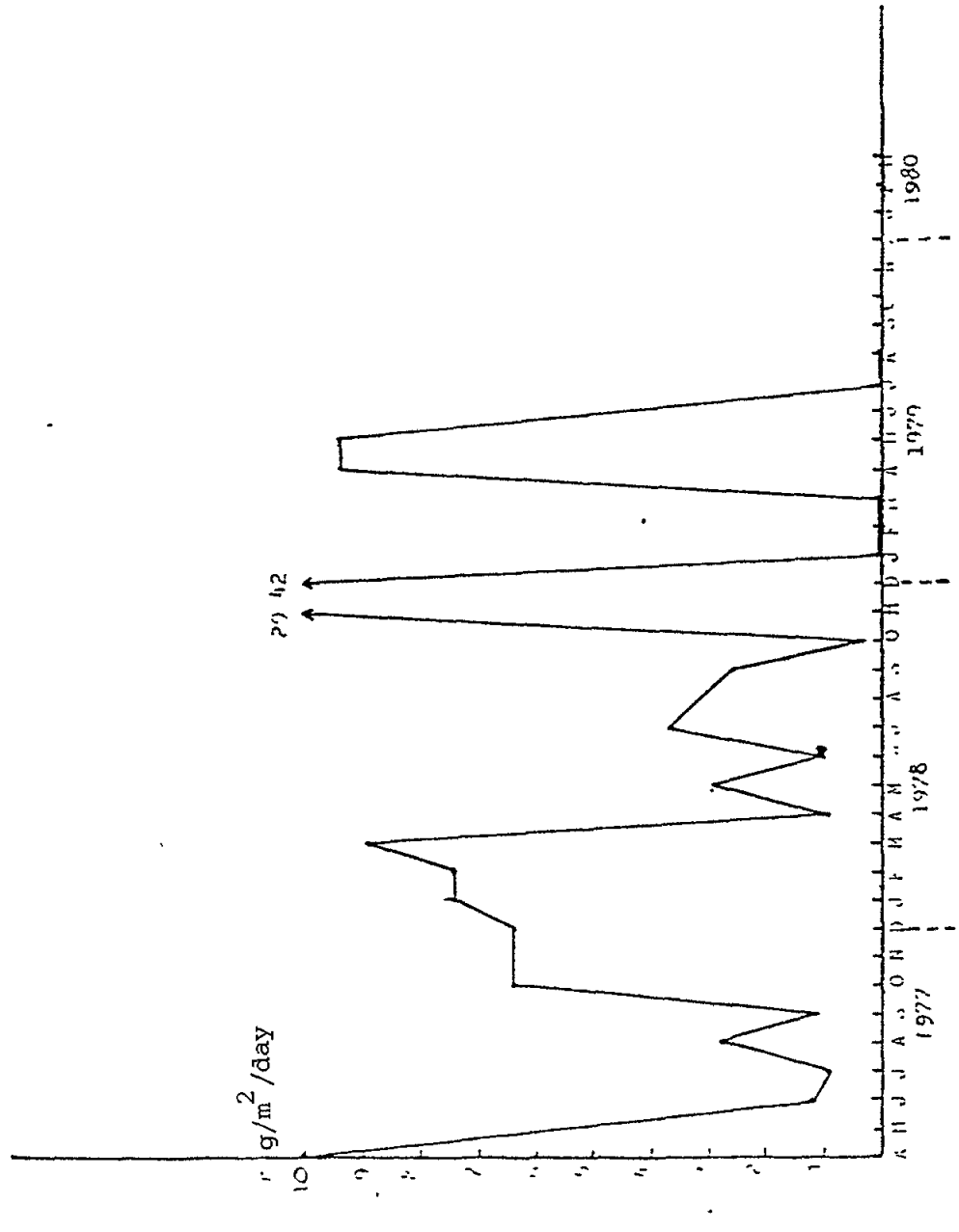

Fig. 3. Tar on Beaches (MALTA)

MARSAXLOKK BAY

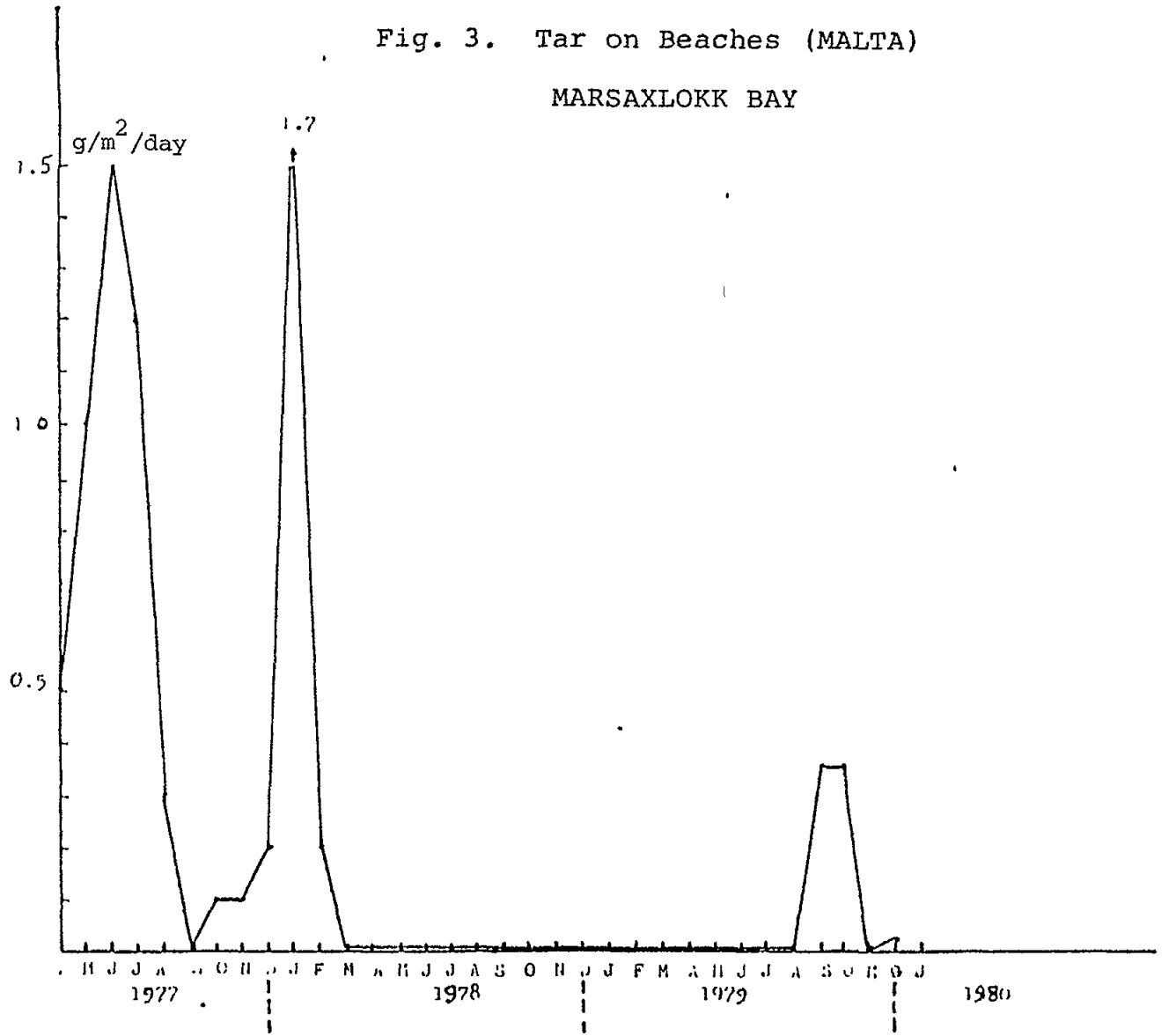

Fig. 4. Tar on Beaches (MALTA)

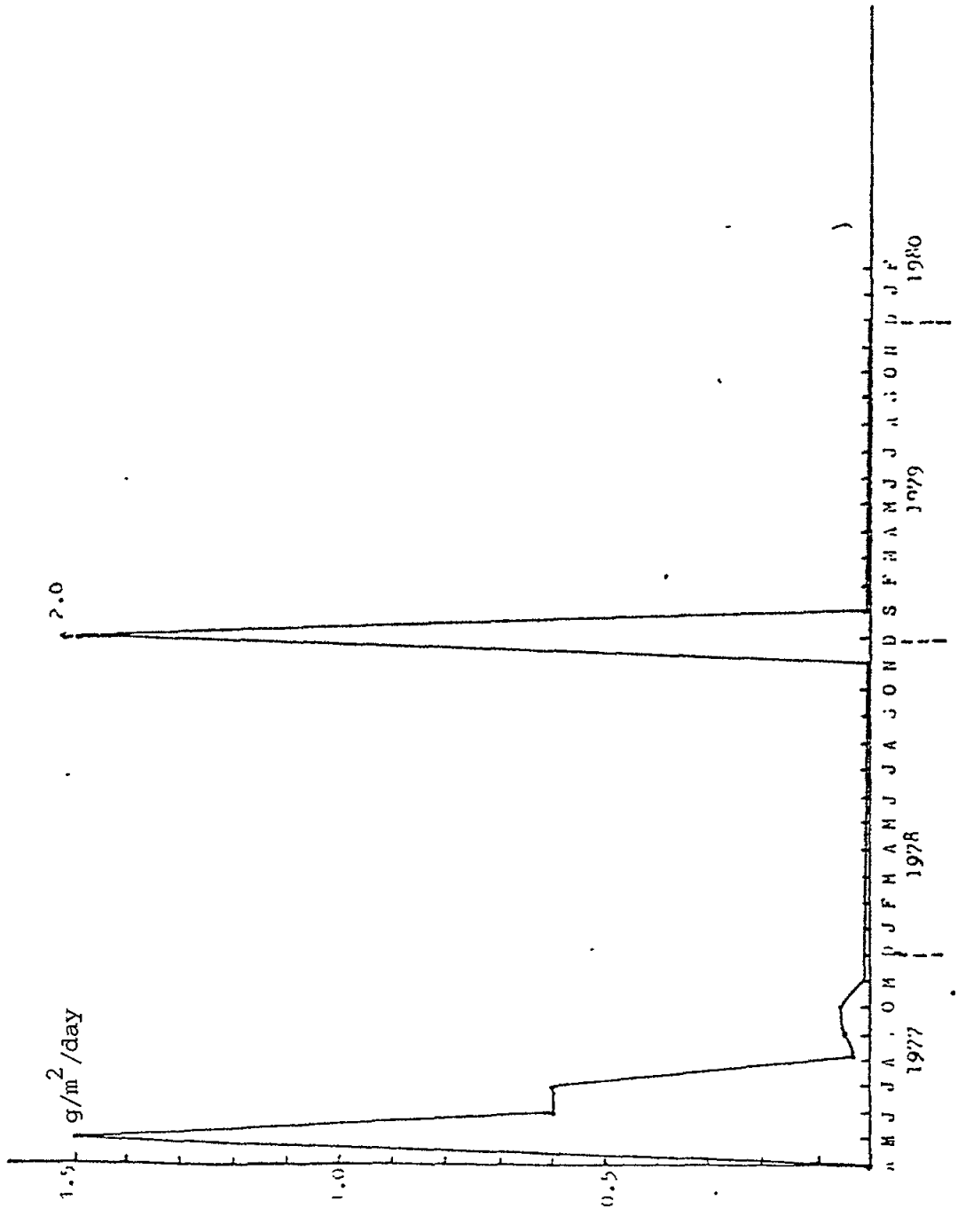

Table I. Observations of oil spills

Date	Position	Size	Action Taken	Remarks
3.6.76	RTCI*	50ft sqr	mechanical removal and dispersion.	-
24.7.76	RTCI*	200 gallons	mechanical removal and dispersion.	-
19.1.78	33°57'N 15°31'E	Unspecified	None	Oil slick reported by an aircraft of RAF (Malta).
13.2.78	13 miles NNW of Luqa (Malta)	2sqr miles	Oil slick dispersed by Maltese authorities	Oil slick reported by an aircraft of RAF (Malta)
4.12.79	Northern side of Maltese coast Grand Harbour Mellieha Bay	Approx. 120 tons heavy "Chocolate Mousse" patches	Oil spill cleaned by Maltese authorities	Origin of spill unknown

* Ricasoli tank cleaning installation.

(No oil slicks were ever observed during sampling trips).

No records of small oil spills that occur in harbours (Grand Harbour, Marsaxlokk Bay, Marsamxett, St. Paul's Bay) are available.

Table II. Dispersed/dissolved hydrocarbons in the coastal waters of Malta

Levels expressed as µg/l as chrysene equivalents

Date	Station 1 Off Grand Harbour		Station 2 Off Marsaxlokk		Station 3 Off Ghar Lapsi	
	$\bar{x}$	S.D.	$\bar{x}$	S.D.	$\bar{x}$	S.D.
14/10/77	0.160	0.111	0.053	0.056		
11/11/77	0.064	0.02	0.078	0.023	0.070	0.043
29/12/77	0.097	0.047				
13/ 1/77	0.095	0.065				
6/ 3/78	0.048	0.002	0.292	0.201	0.256	0.290
30/ 3/78	0.038	0.040				
11/ 4/78	0.041	0.016	0.025	0.009	0.046	0.009
16/ 5/78	0.031	0.012	0.026	0.006	0.021	0.008
11/ 7/78	0.042	0.008	0.065	0.014	0.027	0.008
20/ 9/78	0.032	0.010	0.050	0.027	0.116	0.113
23/11/78	0.065	0.013	0.071	0.017	0.026	0.006
9/ 3/79	0.085	0.007	0.082	0.014	0.065	0.008
17/ 5/79	0.035	0.013	0.038	0.003	0.011	0.006
17/ 7/79	0.011	0.004	0.051	0.004	Sampling not possible	
11/ 9/79	0.021	0.004	0.037	0.008		

Date	Station 4 Malta Channel		Station 5 Off Qawra	
	$\bar{x}$	S.D.	$\bar{x}$	S.D.
14/10/77	0.158	0.084		
11/11/77	0.074	0.02		
29/12/77				
13/ 1/78				
6/ 3/78	0.050	0.019	0.216	0.276
30/ 3/78				
11/ 4/78	0.037	0.031	0.052	0.017
16/ 5/78				
11/ 7/78	0.039	0.006	0.032	0.009
20/ 9/78	0.023	0.006	0.022	0.004
23/11/78	0.057	0.013	0.040	0.006
9/ 3/79	0.079	0.011	0.052	0.007
17/ 5/79	0.011	0.006	0.027	0.009
17/ 7/79	0.010	0.003	0.015	0.003
11/ 9/79	0.012	0.004	0.022	0.005

Inside Grand Harbour

14/10/77	3.424	0.396

$$\frac{\text{Chrysene used}}{\text{Chrysene in Intercomparison Exercises}} = 0.98$$

$\bar{x}$, Arithmetic mean of triplicate samples

S.D., Standard deviation

Table III. Tar on a beach in Anchor Bay

Sampling Date	Predominant Wind Direction	g/m^2	S.D.	g/m^2/day	S.D.
13/ 4/77	On shore	150	103	10.0	6.9
A 27/ 4/77	On shore	64	18	4.6	1.3
M 13/ 6/77	Off shore	54	27	1.2	0.6
J/J 10/ 8/77	Off shore	37	26	0.9	0.6
A 30/ 8/77	On shore	55	31	2.8	1.6
S 5/10/77	On shore	40	23	1.1	0.6
O/N 6/12/77	On shore	219	173	6.4	5.1
D 3/ 1/78	On shore	198	134	6.4	4.3
J/F 20/ 2/78	On shore	356	210	7.4	4.4
M 10/ 4/78	On shore	436	132	8.9	2.7
A 11/ 5/78	On shore	26	23	0.9	0.8
M 8/ 6/78	On shore	78	8	2.9	0.3
J 6/ 7/78	On shore	28	8	1.0	0.3
J 8/ 8/78	On shore	116	143	5.7	4.6
A 12/ 9/78	On shore	*1	-	*1	-
S 20/10/78	On shore	74	64	2.6	2.2
O 14/11/78	On shore Partly off shore	7.5	5	0.3	0.2
N 12/12/78	On shore Partly off shore	812	336	29	12
D 11/ 1/79	On shore	1260	-	42	-
J 16/ 2/79	On shore	0	-	0	-
F/M 10/ 4/79	On shore Partly off shore	0	-	0	
A/M 21/ 5/79	On shore	377	309	9.4	7.7
J 5/ 7/79	On shore	184	141	4.2	3.2
J 6/ 8/79	On shore	0	-	0	-
A 11/ 9/79	On shore	0	-	0	-

*1 Fresh tar mixed with seaweed; could not be collected.
S.D., Standard deviation

No further sampling could be carried out at this site after September 1978 because of construction work in progress.

Table IV. Tar on a beach in Marsaxlokk Bay

Sampling Date	Predominant Wind Direction	g/m^2	S.D.	g/m^2/day	S.D.
18/ 4/77	Off shore	6	7	0.4	0.5
A 2/ 5/77	Off shore	7	11	0.5	0.7
M 13/ 6/77	On shore	42	15	1.0	0.4
J 8/ 7/77	On shore	37	8	1.5	0.3
J 8/ 8/77	On shore	37	19	1.2	0.6
A 1/ 9/77	Partly on (rest off)	6	7	0.3	0.4
S 5/10/77	Off shore	0	-	0	-
O 14/11/77	Off shore	5	4	0.1	0.09
N 6/12/77	Off shore	3	0.7	0.1	0.02
D 3/ 1/78	Off shore	5	4	0.2	0.16
J/F 20/ 2/78	Off shore	83	143	1.7	2.9
M 10/ 4/78	Off shore	10	17	0.2	0.3
A 11/ 5/78	Off shore	0	-	0	-
M 8/ 6/78	Off shore	0	-	0	-
J 6/ 7/78	Off shore	0	-	0	-
J 8/ 8/78	Off shore	0	-	0	-
A 12/ 9/78	Off shore	0	-	0	-
S 20/10/78	Off shore	0	-	0	-
O 14/11/78	Off shore	0	-	0	-
N 12/12/78	Off shore	0	-	0	-
D 11/ 1/79	Off shore	0	-	0	-
J 16/ 2/79	Off shore	0	-	0	-
F/M 10/ 4/79	Off shore	0	-	0	-
A/M 21/ 5/79	Off shore	0	-	0	-
J 5/ 7/79	Off shore	0	-	0	-
J 6/ 8/79	Off shore	0	-	0	-
A 11/ 9/79	Off shore	0	-	0	-
S/O 24/10/79	On shore	14.8	25.6	0.35	0.61
N 22/11/79	Off shore	0	-	0	-
D 11/ 1/80	Off shore (Partly along shore)	7.0	3.5	0.04	0.07

Table V. Tar on a beach at Qawra

Sampling Date	Predominant Wind Direction	g/m^2	S.D.	g/m^2/day	S.D.
18/ 4/77	Off shore	0	-	0	-
A 2/ 5/77	Off shore	0	-	0	-
M 16/ 6/77	On shore	68	47	1.5	1.0
J 5/ 7/77	Along shore	12	10	0.6	0.5
J 5/ 8/77	Along shore	17	10	0.6	0.4
A 30/ 8/77	Off shore	0.8	1.4	0.03	0.6
S 5/10/77	Along shore	2	2	0.05	0.05
O 14/11/77	Off shore	24	20	0.6	0.5
N 6/12/77	Off shore	0	-	0	-
D 3/ 1/78	Off shore	0	-	0	-
J/F 20/ 2/78	Off shore	0	-	0	-
M 10/ 4/78	Off shore	0	-	0	-
A 11/ 5/78	Off shore	0	-	0	-
M 8/ 6/78	Off shore	0	-	0	-
J 6/ 7/78	Off shore	0	-	0	-
J 8/ 8/78	Off shore	0	-	0	-
A 12/ 9/78	Off shore	0	-	0	-
S 20/10/78	Off shore	0	-	0	-
O 14/11/78	Off shore				
	Partly on shore	50	0.93	2.0	3.7
N 12/12/78	Off shore				
	Partly on shore	0	-	0	-
D 11/ 1/79	Off shore	0	-	0	-
J 16/ 2/79	Off shore	0	-	0	-
F/M 10/ 4/79	Off shore	0	-	0	-
A/M 21/ 5/79	Off shore	0	-	0	-
J 5/ 7/79	Off shore	0	-	0	-
J 6/ 8/79	Off shore	0	-	0	-
A 11/ 9/79	Off shore	0	-	0	-
S/O 24/10/79	Off shore	0	-	0	-
N 22/11/79	Off shore	0	-	0	-
D 11/ 1/80	Off shore	0	-	0	-

CENTRO DE INVESTIGACION : Instituto de Investigaciones Pesqueras
CADIZ
España

Investigador Principal : M. CALDERON *

INTRODUCCION

La zona de la Bahía y Puerto de Cádiz ha sido el área estudiada esperando poder ampliar el estudio a otras zonas de la costa gaditana, dentro de los 36° 50' de latitud N y entre los 5° 26' de longitud W.

Las fuentes contaminantes presentes en la zona, predominantemente aguas urbanas residuales no depuradas, procedentes de las poblaciones de Cádiz, Puerto Real, Puerto de Sta. María, Rota y las aguas fluviales, junto con su carga contaminante, del río Guadalete y el río San Pedro, este último, aunque caño, aporta sin embargo agua dulce de los esteros. Los focos más importantes de contaminación industrial son los Astilleros de Matagorda y una fábrica de azúcar cuyos residuos llegan a la Bahía a través del río Guadalete.

Las actividades realizadas, en el Instituto de Investigaciones Pesqueras de Cádiz, sobre la contaminación por hidrocarburos de petróleo comenzaron en 1974.

AREA ESTUDIADA

El Area estudiada es la del Puerto y Bahía de Cádiz, la zona y ubicación de las estaciones se detalla en la figura 1.

El Area posee un clima mediterráneo, sub-húmedo, con veranos cálidos y secos, e inviernos suaves. Presenta una temperatura media anual de 20°C. La presión atmosférica, valor medio, 763 mm. Luminosidad elevada, 2314 horas de sol al año. Lluvias abundantes en primavera y otoño, media anual 546 l/m^2. Durante el invierno y la primavera existen ciclos de vientos de N-ESE-S-Poniente. En el verano los vientos que dominan son : Levante cálido y seco, Sur cálido y húmedo y Poniente fresco. Los vientos son violentos, alcanzan velocidades de 80 km/h y superiores. La oceanografía de las aguas gaditanas, por lo que se refiere a los parámetros de temperatura, salinidad, pigmentos y fosfatos, ha sido ampliamente estudiada por este Laboratorio (Prof. Dr. R. Establier).

Los valores de temperatura y salinidad encontrados en el área oscilan entre los extremos de :

	TEMPERATURA (°C)				SALINIDAD (°/oo)	
	AIRE		AGUA			
Año	Min.	Máx.	Min.	Máx.	Min.	Máx.
1977	9,3	20,0	11,5	19,4	29,523	36,119
1978	12,0	21,3	13,0	19,4	31,719	36,721
1979	10,0	20,0	12,0	19,0	22,820	35,919

* Fallecido

La zona se encuentra poco industrializada, sus fuentes contaminantes principales son las aguas urbanas residuales, no depuradas, procedentes de una población de 300.000 habitantes, que se incrementa a unos 500.000 en verano.

MATERIALES Y METODOS :

Para el estudio de la contaminación por productos petrolíferos se han seleccionado principalmente dos formas de la contaminación :

Hidrocarburos disueltos y/o dispersos en agua de mar.
Residuos sólidos flotantes.

Adicionalmente, se ha realizado, simultáneamente a la toma de muestras, la inspección ocular de la superficie del agua, prestando especial atención a la existencia de películas o manchas de petróleo u otros objetos flotantes.

La toma de muestra de agua fue efectuada en la superficie durante el año 1977, y a 1 m de profundidad a partir del año 1978, en botellas de 1,3 l. La extracción fue hecha inmediatamente en ampollas de decantación de 2 l. de capacidad, con éter de petróleo (2x50 ml), seguida de su concentración, a 1-2 ml, en evaporador rotatorio, a temperatura de 40°C y vacío a la trompa. La aromaticidad fue medida en espectrofluorómetro Perkin-Elmer MOD. MPF-3L.

A partir del año 1.978 se ha seguido el criterio recomendado por el IOC/WMO/UNEP Pilot Project on Baseline Studies and Monitoring of Oil and Petroleum Hydrocarbons in Marine Waters (MED POL I), descrito en el documento de la COI : Manuales y Guias No. 7 suplemento. No obstante se ha introducido una modificación en el método.

Dado que el principal producto contaminante primario en la zona estudiada es el gas-oil marino, la intensidad de la fluorescencia de los extractos se determina a una excitación de 295 nm, en lugar de la recomendada en el método (310 nm) y la fluorescencia en la región de los 330 nm en vez de la de 360 nm.

Se ha utilizado como patrón gas-oil marino, usado como combustible por los barcos y que presenta características espectrofluorimétricas muy semejantes a las muestras estudiadas.

El criseno dadas las características espectrales que hemos empleado no ha sido utilizado como patrón. En los casos de duda y como apoyo se ha utilizado en el análisis la técnica de cromatografía gas-láquido. En anteriores ocasiones, hemos manifestado nuestra opinión, sobre la no conveniencia del patrón de criseno, al menos en nuestro caso, donde la contaminación por productos petrolíferos se debe principalmente a gas-oil marino. (Ver figuras 2 y 3).

No obstante lo anterior, hemos realizado unas curvas de calibrado con soluciones de criseno preparadas por nosotros : - Criseno - (KOCH-LIGHT, RRI 5254 pure); con las soluciones enviadas por el Dr. Adam Zsolnay (criseno 2) y con soluciones del gas-oil marino, utilizado por nosotros como patrón y que presenta unas características espectrales análogas a las de los extractos orgánicos de las muestras estudiadas (Figura 2).

Todo el material utilizado de vidrio o teflón, es cuidadosamente lavado y

posteriormente enjuagado con disolventes antes de ser utilizado. El disolvente empleado es éter de petróleo de punto de ebullición inferior a 40°C, este disolvente ha sido previamente purificado con el tratamiento adecuado para eliminar las trazas de aromaticidad.

El aparato empleado para las mediciones era un espectrofluorómetro Perkin-Elmer, Modelo MPF-3L; rendijas - 4 nm, excitación a 310 nm., emisión a 360 nm., con la sensibilidad apropiada en cada caso.

RESULTADOS Y SU INTERPRETACION

Manchas de petróleo : Jirones o manchas de películas finas de petróleo de color irisado, son observados con relativa frecuencia, procedentes del tráfico marítimo del Puerto; ahora bien debido a su pequeña extensión no deben ser considerados.

Residuos sólidos de petróleo : En el Puerto y Bahía de Cádiz no se observan normalmente residuos sólidos de petróleo particulado flotante. Desde enero de 1.979 hemos realizado, mensualmente, en la Bahía de Cádiz, con la red de neuston, varios recorridos (desde la estación 6 a la estación 2 y desde la estación 3 a la estación 4; figura I) y en ningún caso hemos recogido partículas de petróleo, sólo hemos recogido en la red plancton, macro algas, a veces trozos de corcho, restos de aguas negras, pero no "tar-balls".

Hidrocarburos disueltos y/o dispersos en agua de mar : En los cuadros 1, 2 y 3 se indican los valores medios anuales de las estaciones estudiadas, junto con los estadísticos varianza (S2), desviación normal (S), error de la desviación normal (Sm), e intervalo de confianza (Ic), para los años 1977, 1978 y 1979, respectivamente.

Las estaciones E - 1 a E - 6, presentan unos índices de contaminación mínimos para zonas cercanas a un puerto. Las estaciones E-7 y E-8, dentro del puerto, presentan oscilaciones bruscas en el nivel de contaminación, ésto es lógico dado que depende del mayor o menor tráfico marítimo existente, y, de la apertura o no, de un dique seco situado en las proximidades de la E-7.

Los espectros de fluorescencia que se obtienen de los extractos orgánicos, procedentes de las muestras estudiadas, son análogos a los que presentan los hidrocarburos de petróleo contenidos en los gas-oil marinos envejecidos en mayor o menor grado. Asimismo los cromatogramas de los anteriormente citados extractos orgánicos corresponden a aquellos obtenidos para los gas-oil marinos con mayor o menor grado de envejecimiento (figuras 2 y 3).

De la observación de los datos se deduce que los niveles de contaminación oscilan dentro de límites no alarmantes. Consideramos que el contaminante original es principalmente gas-oil marino acompañado en algunos casos por fuel-oil marino y por aceite de motores quemado, aunque este último en menor proporción que el anterior.

Cuadro I : Nivel medio de contaminación por residuos petrolíferos, en superficie en el Puerto y Bahía de Cádiz. Año 1977. Concentración en µg/l *

Estaciones		Estaciones	
E - 1	n = 22	E - 5	n = 21
	$\bar{x}$ = 12,77		$\bar{x}$ = 25,4
	s2= 135,3		s2= 2368,5
	s = 11,6		s = 48,7
	sm= 2,5		sm= 10,9
	Ic= 7,2		Ic= 30,9
E - 2	n = 22	E - 6	n = 22
	$\bar{x}$ = 15,3		$\bar{x}$ = 15,0
	s2= 132,9		s2= 214,6
	s = 11,5		s = 14,6
	sm= 2,5		sm= 3,2
	Ic= 7,1		Ic= 9,1
E - 3	n = 22	E - 7	n = 22
	$\bar{x}$ = 20,9		$\bar{x}$ = 96,0
	s2= 1149,0		s2=47298,0
	s = 33,9		s = 217,5
	sm= 7,4		sm= 47,5
	Ic= 21,0		Ic= 134,8
E - 4	n = 22	E - 8	n = 22
	$\bar{x}$ = 9,0		$\bar{x}$ = 147,4
	s2= 11,7		s2=48670,0
	s = 3,4		s = 220,6
	sm= 0,7		sm= 48,1
	Ic= 2,1		Ic= 136,7

Ic Intervalo de confianza para el 99%

* Multiplicar por R = 5,52 para transformar los valores en unidades de criseno

Cuadro II : Nivel medio de contaminación por residuos petrolíferos, profundidad 1 m., en el Puerto y Bahía de Cádiz. Año 1978. Concentración en µg/l *

Estaciones			Estaciones		
E - 1	n =	8	E - 5	n =	8
	$\bar{x}$ =	2,6		$\bar{x}$ =	4,2
	s2=	2,3		s2=	6,5
	s =	1,5		s =	2,6
	sm=	0,6		sm=	1,0
	Ic=	1,4		Ic=	2,3
E - 2	n =	8	E - 6	n =	8
	$\bar{x}$ =	3,7		$\bar{x}$ =	3,9
	s2=	5,0		s2=	4,8
	s =	2,2		s =	2,2
	sm=	0,8		sm=	0,8
	Ic=	2,0		Ic=	2,0
E - 3	n =	8	E - 7	n =	7
	$\bar{x}$ =	5,5		$\bar{x}$ =	9,5
	s2=	19,1		s2=	67,8
	s =	4,4		s =	8,2
	sm=	1,7		sm=	3,4
	Ic=	3,9		Ic=	8,2
E - 4	n =	8	E - 8	n =	7
	$\bar{x}$ =	3,8		$\bar{x}$ =	16,2
	s2=	6,5		s2=	677,9
	s =	2,6		s =	26,0
	sm=	1,0		sm=	10,0
	Ic=	1,0		Ic=	26,0

Por causa de fuerza mayor no pudieron realizarse los análisis correspondientes a los meses de marzo-junio.

Ic Intervalo de confianza para el 95%

* Multiplicar por R = 5,52 para transformar los valores en unidades de criseno.

Cuadro III : Nivel medio de contaminación por residuos petrolíferos. Año 1979. Concentración en µg/l *. Puerto y Bahía de Cádiz.

Estaciones			Estaciones		
E - 1	n =	16	E - 5	n =	16
	$\bar{x}$ =	4,0		$\bar{x}$ =	4,6
	s2=	6,9		s2=	15,2
	s =	2,6		s =	3,9
	sm=	0,7		sm=	1,0
	Ic=	1,4		Ic=	2,1
E - 2	n =	16	E - 6	n =	14
	$\bar{x}$ =	5,0		$\bar{x}$ =	6,5
	s2=	15,8		s2=	5,9
	s =	4,0		s =	5,9
	sm=	1,0		sm=	1,6
	Ic=	2,2		Ic=	3,5
E - 3	n =	16	E - 7	n =	16
	$\bar{x}$ =	4,8		$\bar{x}$ =	6,8
	s2=	14,2		s2=	27,6
	s =	3,8		s =	5,3
	sm=	1,0		sm=	1,4
	Ic=	0,1		Ic=	2,9
E - 4	n =	16	E - 8	n =	16
	$\bar{x}$ =	4,5		$\bar{x}$ =	13
	s2=	14,3		s2=	72,2
	s =	3,4		s =	8,5
	sm=	0,9		sm=	2,2
	Ic=	1,9		Ic=	4,7

Ic Intervalo de confianza para el 95%

* Multiplicar por R = 5,52 para transformar los valores en unidades de criseno

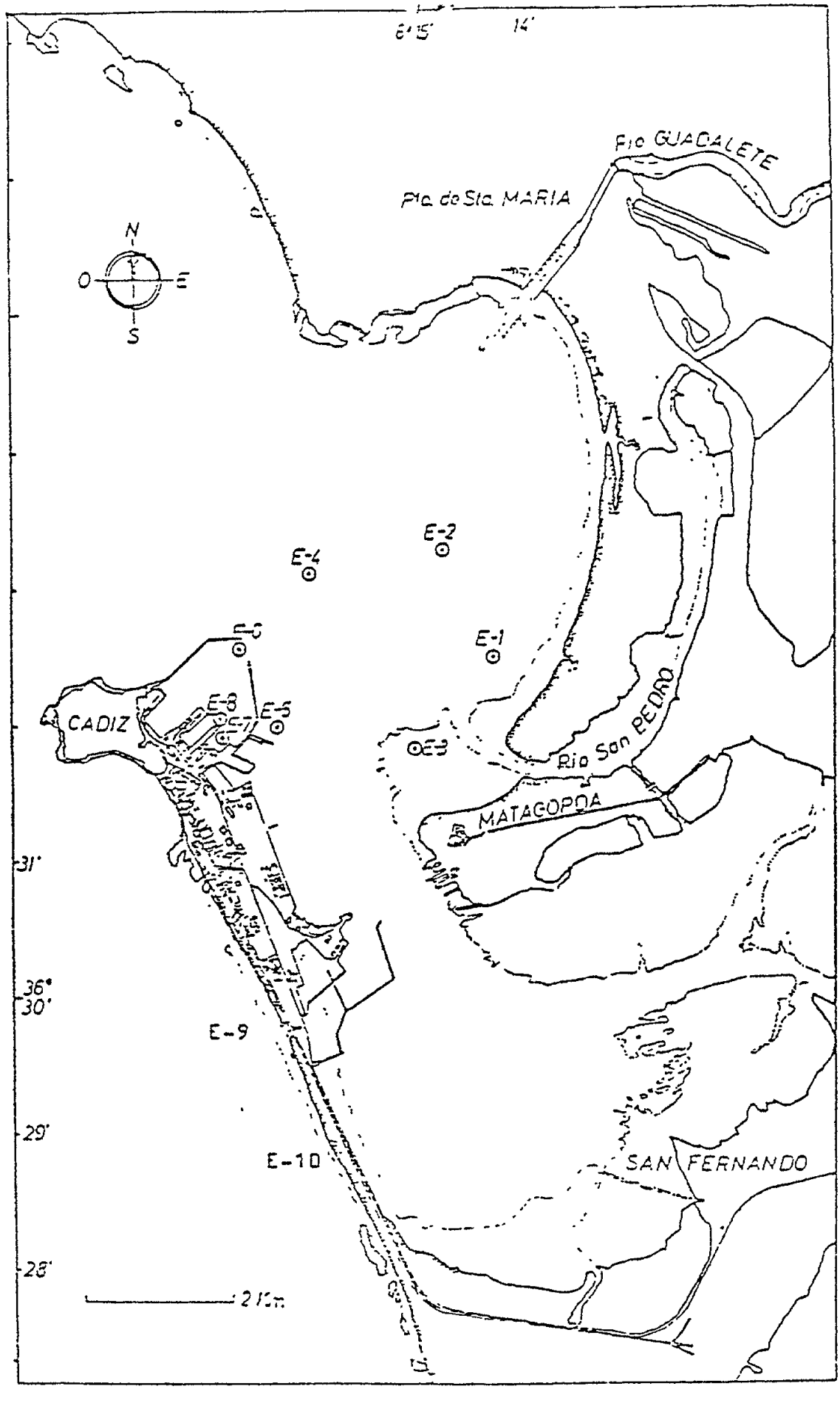

Fig. 1. Mapa de la zona de Cadız, Mostrando las estaciones de noestreo (E1 - E10)

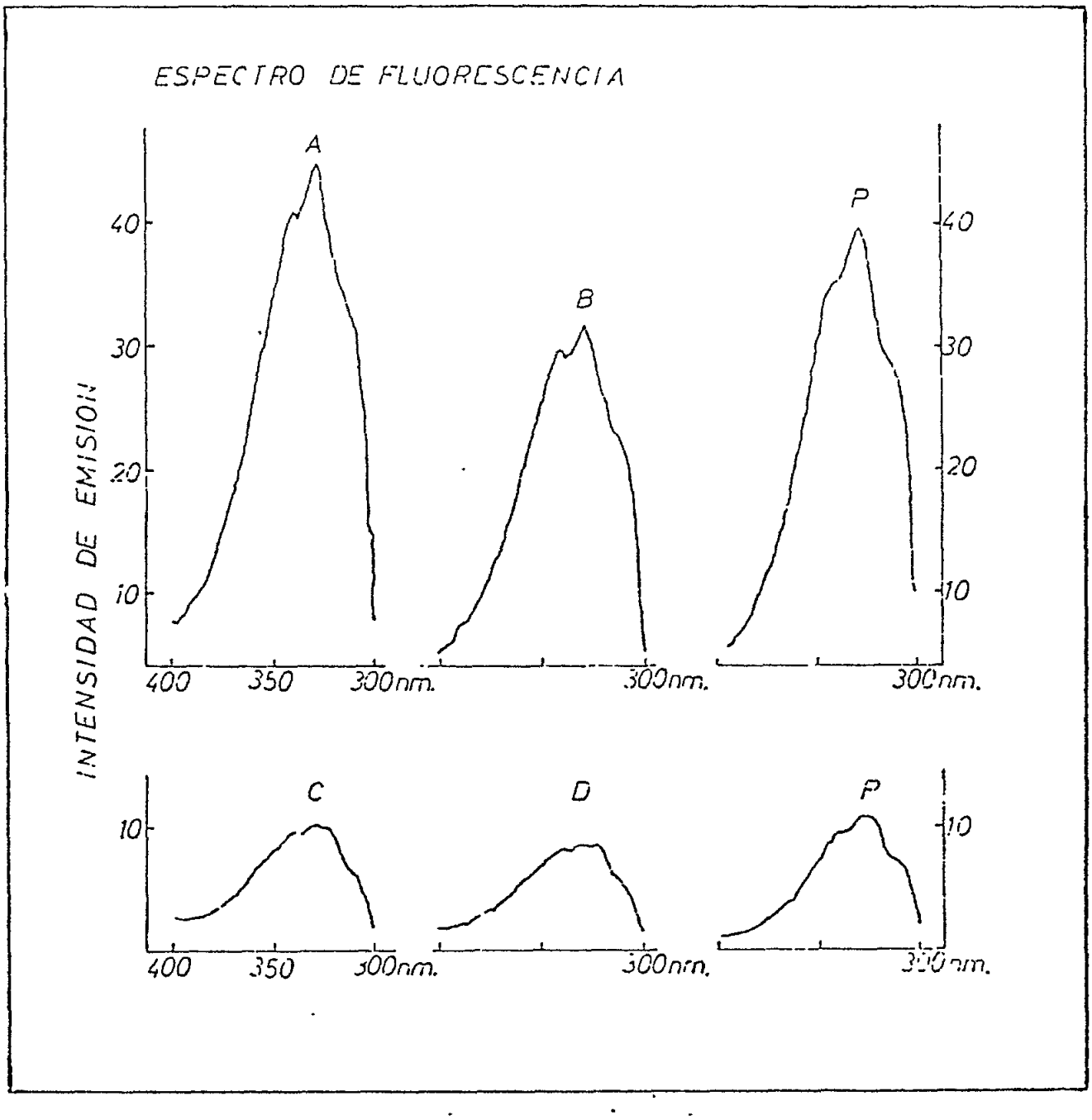

Fig. 2: → A y B, C y D espectros procedentes de muestras , A y B duplicados de la E - 8, y C y D estación E - 1, P Patrón de gas-oil pesado. Longitud de onda de excitación 295 nm rendija de emisión y excitación 4 nm.

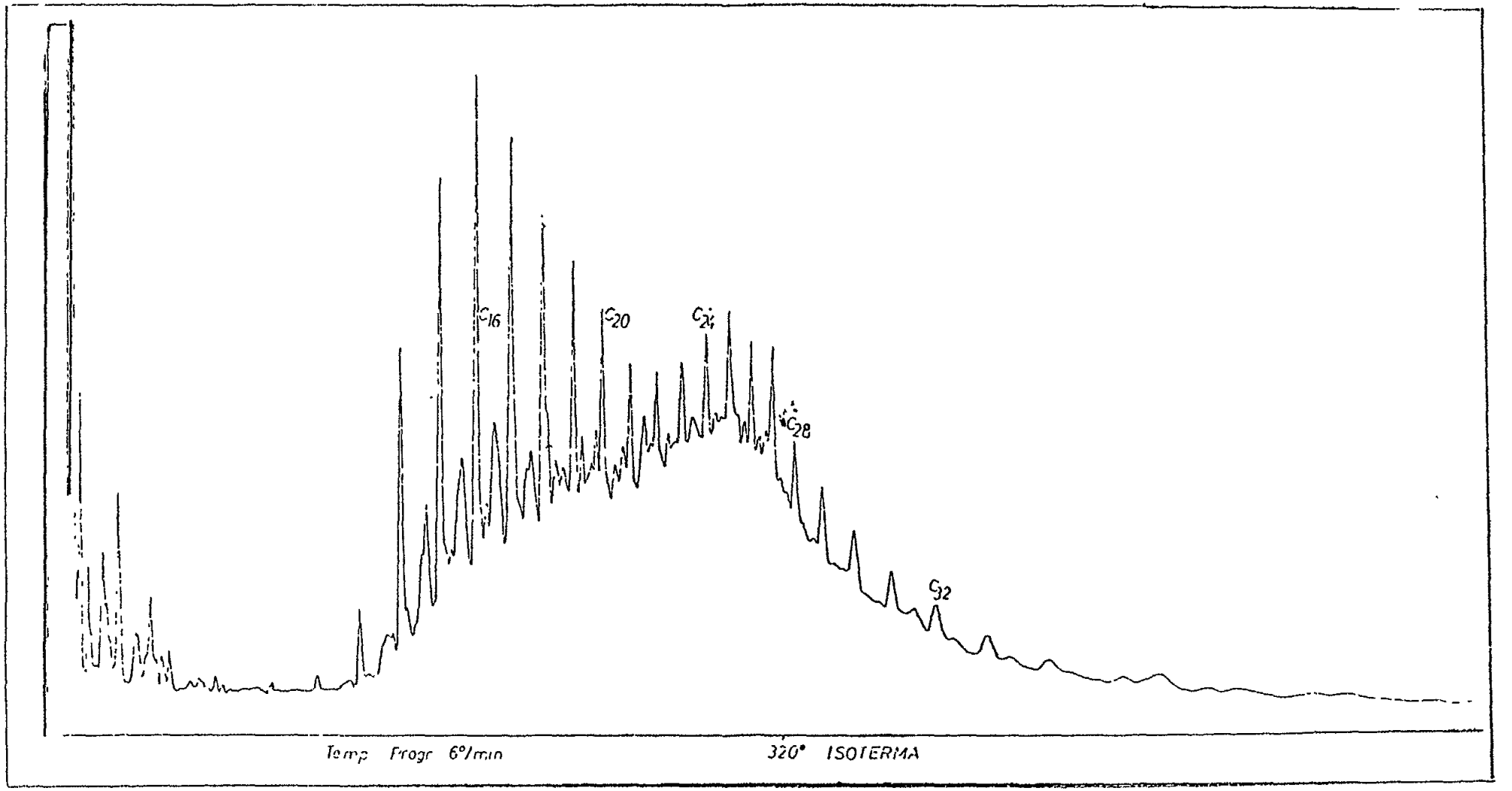

Fig. 3: Cromatograma por cromatografía gaseosa de los productos extraidos de agua de mar. Condiciones: Columna 6'x 1/8'' de UCC-W-982 (un derivado metil-vinil silicona) al 10% sobre Cromosorb, lavado Acido y silanizado. Temperaturas: Detector de ionización de llama 350ºC; Inyector 350ºC, Columna programada de55-320ºC a 8ºC/min. Gas portador: Nitrogeno, flujo de 60 ml/min. Presión de cabeza:2,5 kg/cm^2 Inyección: 1 µl. Atenuación:1x10^2.

Research Centre: Marine Science Department
Middle East Technical University
ERDEMLI-ICEL
Turkey

Principal Investigator: T. I. BALKAS

INTRODUCTION

The Marine Science Department started to participate in the MED POL I pilot project in 1978, but a visual search for oil slicks and statistical measurements of tar balls on beaches was carried out before the signing of the project. Since the project was signed, most emphasis has been given to the determination of dissolved/dispersed petroleum hydrocarbons in sea-water.

The present report includes results up to March 1980.

AREA(s) STUDIED

The area studied is the Cilian basin of the eastern Mediterranean, the region between Mersin and Akkuyu. The approximate locations of the sampling points used for the period June 1977 to July 1978 are shown in Figure 1. In Figure 2 are given the co-ordinates for the sampling sites as used in the period May 1979 to March 1980.

The sea-water temperature varies between 16°C and 30°C and the salinity ranges between 37.8 and 39.2 per cent. Sea-water becomes well mixed during the winter, but thermal stratification usually begins in March.

Winds are mainly classified as high frequency winds (24 hrs), land-sea breezes, and low frequency (3-10 days) winds.

Research on biological parameters started only recently, but nutrient concentrations are very low.

The area studied is in the neighbourhood of a harbour in Mersin which combines an oil refinery and many industrial (textiles, fertilizers etc.) and agro-chemical facilities. Tanker and ship traffic is dense in all seasons of the year.

MATERIAL AND METHODS

Oil Slick observations were made only occasionally.

For the sampling of floating tar balls and sea-water, the principles given in IOC Manuals and Guides No. 7 were followed.

Floating tar balls: Samples were collected (only once) by a neuston net with mesh size 0.500 mm.

Dissolved/dispersed hydrocarbons: Samples were collected with special steel-framed samplers containing 2.5 l glass bottles. Sampling was repeated

every three hours along the ship's track at a distance of approximately 5 km from the shore. Samples were taken at 1m depth. After the samples were taken, 25 ml of carbon tetrachloride were added to each sample, to avoid oxidation and degradation.

A Turner ultra-violet spectrofluorimeter Model 430 was used to analyse the samples, using the wavelengths of 310 nm and 360 nm for excitation and emission, respectively.

Turkish crude oil, drilled in South-East Anatolia, was used as a standard to calculate the hydrocarbon content of the samples. The working standards were prepared within the range of 0.02 to 0.50 ppm, from a stock of 10 ppm. The crude oil originally consisted of 2 per cent aromatic hydrocarbon by weight.

For the samples in the second period (after July 1978) of the investigation, chrysene was used as calibration standard.

The Department has not taken part in the intercomparison exercise as the samples have not yet arrived.

Tar balls on beaches: Samples were taken at a beach near the METU campus at Erdemli on 11 June 1977 (nine samples), 23 July 1977 (six samples), 25 June 1978 (seventeen samples), and 18 June 1979 (eight samples), and at Akkuyu on 9 July 1978 (seven samples).

RESULTS AND THEIR INTERPRETATION

Oil slicks: occasional observations from land and sea have not revealed a single oil slick in the vicinity of Erdemli during the course of the project. It is hoped that satellite photographs will be available during the coming year, thus permitting more systematic observation of the sea surface.

Floating tar balls: These were sampled only once during the period covered by this report. The results did not allow for an assessment of the distribution of the tar balls.

In mid-January 1980 a concentrated flow of floating tar balls was observed 2 km from the coast. There was no chance to estimate the concentration of the tar in this locally polluted area; the observation was not reproducible but a few samples were collected for analysis.

Dissolved/dispersed hydrocarbons: The data for the first period (up to July 1978) are summarised in Figure 1. The values are expressed as µg/l crude oil equivalents.

The data for the second period are listed in table I. These data are also expressed as µg/l, but here as chrysene equivelents. The sampling locations are shown in Figure 2.

Most of the work has been devoted to improving techniques and learning how to overcome the difficulties of the measurements.

The laboratory has not participated in the intercomparison exercise and has had some doubts as to the techniques for sampling and analysis. The results are in fact high compared with those of other workers. In Table I are shown

not only the surface water observations but also one series of measurements extending down to 75 m. The results indicate the presence of petroleum hydrocarbons also in these deeper water layers.

Tar on beaches: The data may be summarized as follows:

Station	Date	Range g/m^2	Mean g/m^2
Campus	11.6.77	21.9 - 52.8	34.3
	23.7.77	4.8 - 52.6	27.9
	25.6.78	5.3 - 44.6	17.9
	18.6.79	4.1 - 51.9	28.8
Akkuyu	9.7.78	2.5 - 24.4	12.4

The results show that, during most of the years, the observations varied roughly by a factor of ten. Regarding the mean value for each year, there is no clear tendency of the pollution load for the Campus beach to increase or decrease. As the Akkuyu beach was sampled only once, no comparison between the two beaches can be made.

TABLE I. Dissolved/dispersed petroleum hydrocarbons expressed in mg/l chrysene units, observed since September 1979

Station No.	Sample date	Location	Dist. offshore (km)	Depth (m)	Conc. (µg/l) Chrysene units
1	Sept.2,1979	Mersin	3	1	7.9
1	" "	"	3	1	6.4
2	" "	Cesmeli	5	1	5.4
2	" "	"	5	1	5.0
3	" "	Kocahasanli	2	1	4.4
4	Nov.14,1979	Campus	2	1	5.4
4	" "	"	2	1	5.1
4	" "	"	2	1	4.2
4	" "	"	2	1	5.6
5	" "	"	3	1	4.2
5	" "	"	3	1	4.4
5	" "	"	3	1	4.4
5	" "	"	3	1	4.9
6	Dec.21,1979	"	10	1	5.8
6	" "	"	10	1	4.2
6	" "	"	10	25	5.1
6	" "	"	10	50	5.3
6	" "	"	10	75	1.0
7	Jan.16,1980	"	20	1	0.5
7	" "	"	20	1	1.2
8	Sept.7,1979	Tascucu	15	1	2.0
8	" "	"	15	1	1.6
9	" "	"	20	1	1.9
9	" "	"	20	1	2.6

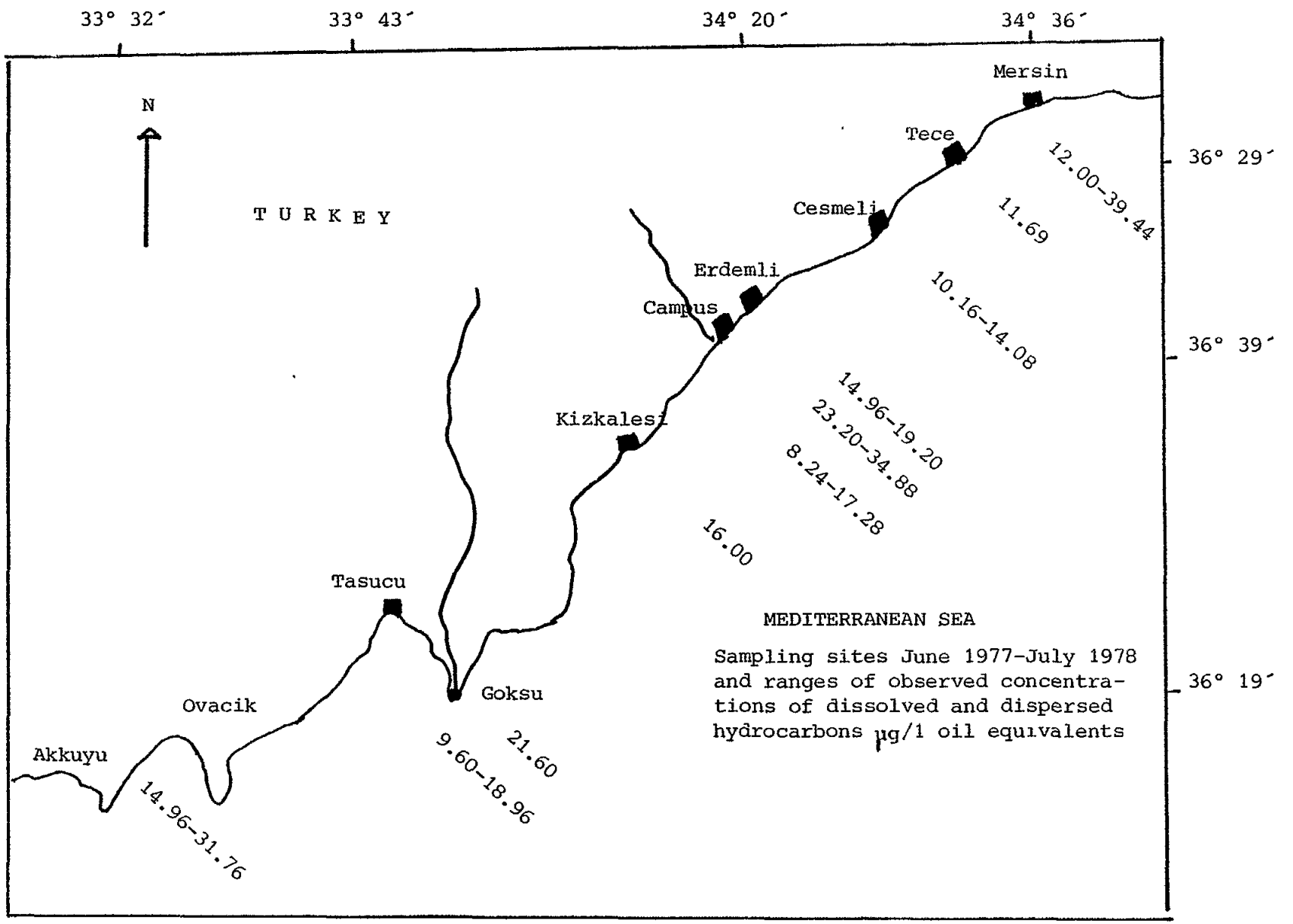
33° 32´
33° 43´
34° 20´
34° 36´
36° 29´
36° 39´
36° 19´
N
TURKEY
Mersin
Tece
Cesmeli
Erdemli
Campus
Kizkalesi
Tasucu
Goksu
Ovacik
Akkuyu
12.00-39.44
11.69
10.16-14.08
14.96-19.20
23.20-34.88
8.24-17.28
16.00
21.60
9.60-18.96
14.96-31.76
MEDITERRANEAN SEA
Sampling sites June 1977-July 1978
and ranges of observed concentra-
tions of dissolved and dispersed
hydrocarbons µg/1 oil equivalents

Figure 1

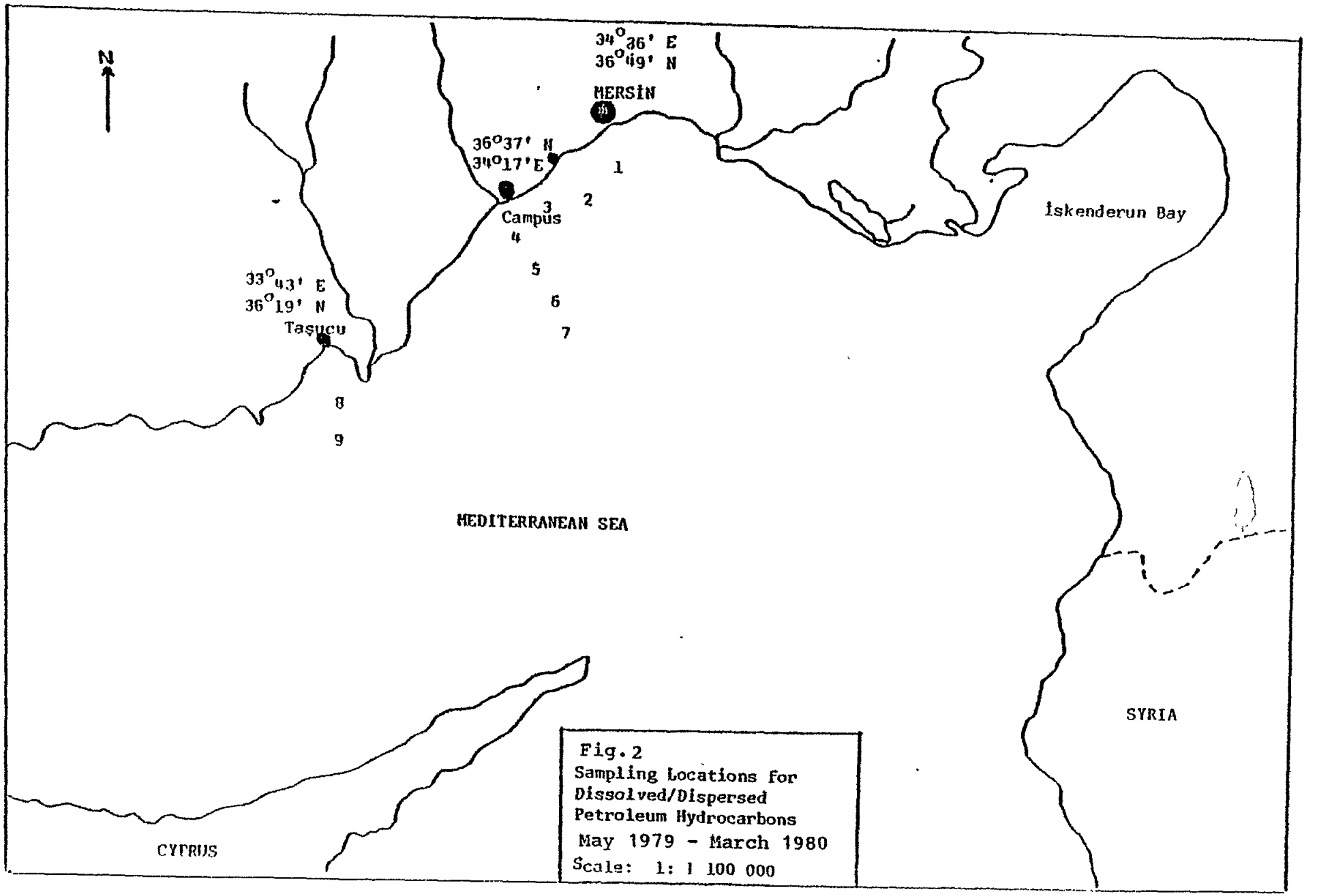

Fig.2
Sampling Locations for
Dissolved/Dispersed
Petroleum Hydrocarbons
May 1979 - March 1980
Scale: 1: 1 100 000

Research Centre: Centre for Marine Research
"Rudjer Boskovic" Institute
ZAGREB, Croatia
Yugoslavia

Principal Investigator: V. PRAVDIC

INTRODUCTION

The Centre started with activities in marine pollution monitoring in 1974, within the framework of the UNDP-sponsored project "Protection of the Human Environment in the Yugoslav Adriatic Region". This project was eventually continued as a national monitoring and research programme. The actual basis for the participation in the MED POL project for the "Rudjer Boskovic" Institute's Centre for Marine Research was the complex environmental impact study of the Rijeka Bay. This project, as a direct continuation of the UNDP activities, was inaugurated by the local authorities in view of the multimillion dollar investment in the Yugoslav deep-water oil terminal and pipeline, as well as a new petrochemical complex. Thus, the site of the MED POL monitoring area coincides with one of the highest-density industrial and urban development areas in the Mediterranean. Competition for land and sea use between urban and industrial development, and fisheries and recreational activities has made this area into one for which environmentally compatible future planning has become of utmost importance.

This project is using the same cruises and some of the same stations for sampling as the IOC/UNEP pilot project on Problems of Coastal Transport of Pollutants (MED POL VI).

AREA(S) STUDIED

The investigated area is the Bay of Rijeka (Figure 1). Figure 1 indicates the approximate locations and the distribution of sampling stations.

The area of the Rijeka Bay has been described in extenso in the report on the MED POL VI pilot project, giving all the pertinent details on geography, climate and currents.

MATERIAL AND METHODS

Oil slicks and other floating pollutants: Observations were made at random in the Bay of Rijeka during cruises and/or beach-tar sampling.

Dissolved/dispersed hydrocarbons: Experimental procedures conformed with the instructions given in document IOC Manuals and Guides No. 7 suppl.

For the samples taken on four cruises of the R/V Vila Velebita in June, September and December 1976, and March 1977, the following procedure was used: the sea-water was collected with a 5-litre polyvinyl-chloride Van Dorn sampler. Bottom samples were collected at every station about 1 m above the bottom. Composite samples were obtained from three depths (at surface, 10-15 m, and 25-30 m); the sea-water was transferred to well rinsed 1-litre glass bottles for transportation to the laboratory; samples were conserved with

copper sulphate solution. Maximum temperature of samples during transportation did not exceed 15°C. The time between sampling and extraction varied from 24 to 36 hours.

As a solvent for the extraction, n-hexane of UV-spectrophotometric grade (Merck, Federal Republic of Germany) was used. A sample of crude oil of Yugoslav origin with known concentrations of aromatic and aliphatic hydrocarbons was used for calibration purposes.

Half-litre samples of sea-water were extracted twice with 10 ml of n-hexane. For fluorescence measurements the aliquots of combined extracts were transferred into 1-cm quartz cells. Fluorescence measurements were performed on a Farrand MK-1 fluorescence spectrophotometer. With excitation at 310 nm and emission at 365 mn, the response was linear for concentrations ranging from 0.001 to 1 µg/ml.

Calibration of the UV-spectrofluorimeter was done using chrysene "zur Synthese", Merck Darmstadt, Federal Republic of Germany, (Cat. No. 820 348), for the samples taken on cruise RIZA 7/77 (9-20 September 1977). The calibration factor was found to be R=6.25.

The Centre did not receive the chrysene samples needed for the intercomparison exercise and, consequently, did not participate in it.

Most of the samples were also analysed with the infra-red spectrophotometric technique. The samples were extracted with carbon tetrachloride and measurements were taken before (IR tot) and after (IR nonpol) running the extract through a column with chromatographic-grade aluminium oxide.

Tar on beaches: In the Bay of Rijeka it is difficult to chose a representative location for sampling; there is no real sandy beach in the whole bay, so a pebbled beach near Jelenscica had to be chosen. The slope of the beach changes under the combined action of wind and waves. On one side of the bay a town of approximately 200,000 inhabitants is located, and on the other an inaccessible island. Prevailing winds are onshore and accumulation of tar, if any, should be expected there. The beach is located downwind, with respect to the prevailing winds, some 22 miles from the major refinery and the deep-water port in Omisalj Bay. The beach was sampled ten times between 12 December 1977 and 9 April 1978.

RESULTS AND THEIR INTERPRETATIONS

Oil slicks and other floating pollutants: The observations of oil slicks have been continuous, relying on the spontaneous reporting by local authorities and ships. During the period of work there were no major oil spills in the area. Minor spills have been observed, but no data are available on their extent. The oil spill clean-up vessel "Jastog" has not been put into action since no need arose.

Dissolved/dispersed hydrocarbons: Tables I -III show the values obtained for the composite (C) and the bottom (B) samples taken at each station, for the concentration (mg/l = 10^3 µg/l) of dissolved/dispersed hydrocarbons, determined by the ultra-violet fluorescence (UVF) method, and, with the exception of the samples taken on cruise RIZA 7/77, by infra-red spectrophotometry. The data given in Tables I and II are also presented in Figures 2 and 3.

The observed differences for the five cruises for which the data are given in Tables I - III should be taken with some caution, since they are based on a rather small number of samples. No conclusion can be reached with regard to seasonal variation.

The results indicate that no significant differences exist between composite and bottom samples. The investigated area is relatively shallow, and mixing of surface water with deeper water should be a fast process, compared with the open sea. However, we consider that this "homogeneity" is rather the result of an unsuitable sampling method than a real state of homogeneity. In our sampling, special attention was paid to avoiding contamination of samples by oils from the ship, but it is possible that certain amounts of dispersed, particulate oil were adsorbed on the walls of the sampler when it passed from the surface to deeper water.

Tar on beaches: Only two samples out of ten, taken at 14-day intervals between December 1977 and April 1978, produced tar on the beach at Jelenscica; the values were 8.6 and 0.5 g/m^2.

The results for the Rijeka Bay show that it is a comparatively clean area not yet polluted by hydrocarbons. The data indicate a bay in which the combined effects of biodegradation, mixing and transport by currents allow for a high degree of autopurification. There are definitely more polluted areas elsewhere in the Mediterranean Sea. This, of course, is partially due to the comparatively small loads of hydrocarbons being transported into the area. As said before, the operational start of the Yugoslav deep-water oil terminal and the increase in capacity of the oil refinery in the Bay will mark a critical period there. If the operational spills could be contained in the foreseen frame, the situation may not necessarily worsen. However, it is to be seen what conditions will prevail and whether the technology of unloading the very large crude-oil carriers (VLCCs) will be adequate for preventing major spills.

The research work related to the monitoring exercise mentioned above has been concerned with studies of the dynamics of surface films at the sea surface. These films are of a thickness from a fraction of a millimetre down to molecular dimensions. Optical properties of the sea surface (reflectance, absorption of radiation) have been known to be influenced by these. The actual influence of small, sometimes negligibly small quantities of spilt oil and petroleum hydrocarbons, may still influence the exchange of gases and other particulate matter, involved in spray formation at the surface of the sea.

Work with this objective was concerned with laboratory studies of the dynamic surface tension of these films. It has been shown that they are formed after a collapse, or upon surface delivery of oil droplets, in times of 0.2 seconds or less. Thus, there is a high probability that films of petroleum hydrocarbons do influence the exchange of matter at almost all times.

Sediments were sampled at several stations in the Rijeka Bay area. Extensive studies of its properties have been made. The concentrations of petroleum hydrocarbons in the sediments were correlated with the heats of adsorption, determined using batch microcalorimetry. It has been found that the sediments of

Rijeka Bay have a specific surface area of 10 m^2/g. The interaction energy with petroleum hydrocarbons is largely dependent on the organic matter of natural origin (proteinaceous matter, mucopolysaccharides etc.). The organic coating decreases the affinity of the mineral material for water (makes it less hydrophilic), and increases the affinity for hydrocarbons. The results obtained so far suggest that because of the high intensity of bioturbation at the bottom, the sediments cannot be considered as an ultimate depository for petroleum hydrocarbons. It is the biodegradation process which will have to account for the ultimate self-purification capacity of the ecosystem.

The following publications were produced partially or completely as a result of work under MED POL I.

M. PICER, M. AHEL and N. PICER (1977): Some remarks on the use of standard spectrophotometric methods for the determination of volatile phenols and mineral oils in seawater, (in Croatian), Nafta 28, 99-102.

M. PICER (1977): Fate and abiotic effects of polluting petroleum in the marine environment, (in Croatian), Pomorski zbornik, 15, 437-470.

M. AHEL and M. PICER: Monitoring of dissolved and dispersed petroleum hydrocarbons in the Rijeka Bay, IVème Journées Etud. CIESM. Antalya, 1978, 99-103.

M. AHEL and M. PICER: Petroleum hydrocarbons in northern Adriatic, (in Croatian), Proc., 2nd Conference on the Protection of the Adriatic Sea, Hvar 1979, Book 11, 397-405.

M. PICER, N. PICER and M. AHEL: The importance of the development of analytical methods for estimating the pollution of the sea by some organic materials, (in Croatian), Proc., of 2nd Conference on Protection of Adriatic Sea, Hvar 1979, Book 11, 387-397.

V. PRAVDIC (1976): The microcalorimetric measurements of interaction of sediments with seawater, Rapp. P.V. Réun. CIESM. 23, 65-66.

V. PRAVDIC and M. VUKOVIC (1976): The Dynamic Surface Tension of Seawater as a Measure of Pollution, Ibid. 23, 39-40.

V. PRAVDIC, M. JURACIC and Dj. DRAGCEVIC: Investigation of some physico-chemical aspects of distribution of pollutants at the seawater/air and the seawater/sediment interface, IVème Journées Etud. Pollutions, CIESM. Antalya 1978, 611-615.

M. JURACIC and V. PRAVDIC: The characterization of the properties of sea sediment in marine pollution research, Ibid. Antalya 1978, 629-634.

Dj. DRAGCEVIC, M. VUKOVIC, D. CUKMAN and V. PRAVDIC (1979): Properties of the seawater/air interface. Dynamic surface tension studies, Limnol Oceanogr., 24, 1022-1030.

Dj. DRAGCEVIC and V. PRAVDIC (1980): Steady-state relaxation times for surractant films at the water/air interface, Croat. Chem. Acta, 53, 1-8.

Four other papers have been submitted or are in press, and one M.Sc. thesis was written partly within the framework of the MED POL I pilot project.

TABLE I

Analyses of samples collected during the cruise in June 1976, by UV spectrofluorimeter and IR spectrophotometry

Analyses of samples collected during the the cruise in September 1976 by UV spectrofluorimeter and IR spectrophotometry

Station*		mg/l			mg/l		
		UVF	IR_{tot}	IR_{nonpol}	UVF	IR_{tot}	IR_{nonpol}
R_1	C	0,050	0,5	0.4	0,004	0,1	< 0,1
	B	0,035	0,9	0.4	0,002	0.3	< 0,1
R_2	C	0,040	1,1	0.5	0.002	< 0,1	< 0.1
	B	0,028	0,8	0,2	0.002	0,2	< 0.1
R_6	C	0,014	0.4	0.3	0,008	0.2	< 0,1
	B	0,012	0.4	0,3	0.006	0,1	< 0,1
R_7	C	0,022	0.4	0,3	0,002	0,5	0.1
	B	0,018	0.4	0.3	0.002	0.2	< 0.1
R_{11}	C	0,023	0.4	0.3	0.016	0.4	< 0.1
	B	0,030	0,3	0,2	0.004	0.4	< 0.1
R_{12}	C	0.036	0,4	0.4	0,010	0,2	< 0,1
	B	0.018	0,3	0.2	0,006	< 0,1	< 0,1
R_{15}	C	0,010	0,3	0.2	0,002	< 0,1	< 0,1
	B	0,012	0,3	0,2	0,004	0,1	< 0,1
R_{17}	C	0,015	0,3	0.2	0.010	0,1	< 0,1
	B	0,013	0,2	0.2	0.002	< 0,1	< 0,1
R_{19}	C	0.010	0,2	0,1	0,010	0,1	< 0.1
	B	0.005	0.1	<0.1	0.001	< 0,1	< 0.1

* See Figure 1. C = composite; B = Bottom.

TABLE II

Analyses of samples collected during the cruise in December 1976, by UV spectrofluorimeter and IR spectrophotometry

Analyses of samples collected during the cruise in March 1977, by UV spectrofluorimeter and IR spectrophotometry

Station		mg/l			mg/l		
		UVF	IR_{tot}	IR_{nonpol}	UVF	IR_{tot}	IR_{nonpol}
R_1	C	0.002	< 0.1	-	< 0.001	0.1	< 0.1
	B	0.008	0.6	-	< 0.001	< 0.1	< 0.1
R_2	C	< 0.001	< 0.1	-	0.001	< 0.1	< 0.1
	B	0.001	0.2	-	< 0.001	0.2	< 0.1
R_6	C	0.002	0.6	-	0.520	0.3	< 0.1
	B	< 0.001	0.2	-	0.290	0.4	< 0.1
R_7	C	0.012	0.5	-	0.155	0.3	< 0.1
	B	0.005	0.4	-	0.001	0.2	< 0.1
R_{11}	C	0.007	0.3	-	< 0.001	0.4	< 0.1
	B	0.004	0.3	-	< 0.001	0.3	< 0.1
R_{12}	C	0.003	< 0.1	-	0.005	0.1	< 0.1
	B	0.002	< 0.1	-	0.001	0.2	< 0.1
R_{15}	C	0.022	< 0.1	-	0.002	< 0.1	< 0.1
	B	0.001	0.1	-	0.001	0.3	< 0.1
R_{17}	C	0.012	< 0.1	-	0.001	< 0.1	< 0.1
	B	0.002	0.2	-	0.001	0.7	< 0.1
R_{19}	C	0.004	22	-	0.720	0.3	< 0.1
	B	0.006	56	-	0.060	0.2	< 0.1

TABLE III

Analyses of samples collected during cruise RIZA 7/77 (9-20 September 1977) by UV spectrofluorimetry

Station	UVF (µg/l)
R_1	3.3 1.7
R_4	1.8 0.5
R_6	0.7 0.1
R_7	0.2 0.1
R_{7a}	0.2 0.2
R_8	0.9 0.2
R_{8a}	0.9 0.2
R_{9a}	0.3 0.2
R_{10}	0.2 0.4
$R10_a$	0.4 0.4
R_{11}	0.1 0.1
R_{12}	0.1 0.1
R_{15}	0.1 0.1
R_{17}	0.4 0.4
R_{18}	0.3 0.3
R_{19}	0.2 0.1
R_{20}	2.5 2.4
R_{20a}	0.6 0.6
R_{22}	0.1 0.1

See figure 1.

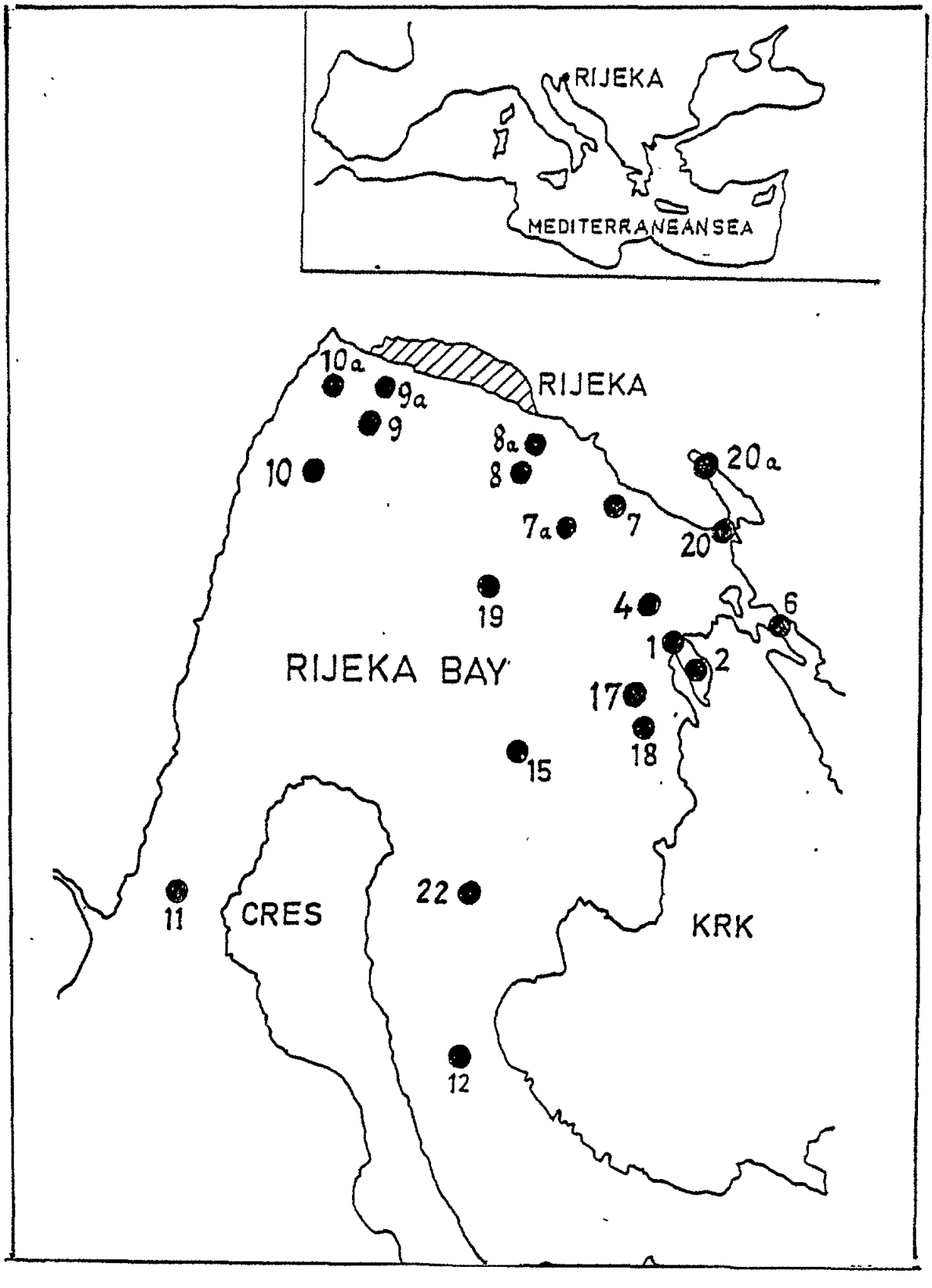

Figure 1. The investigated area

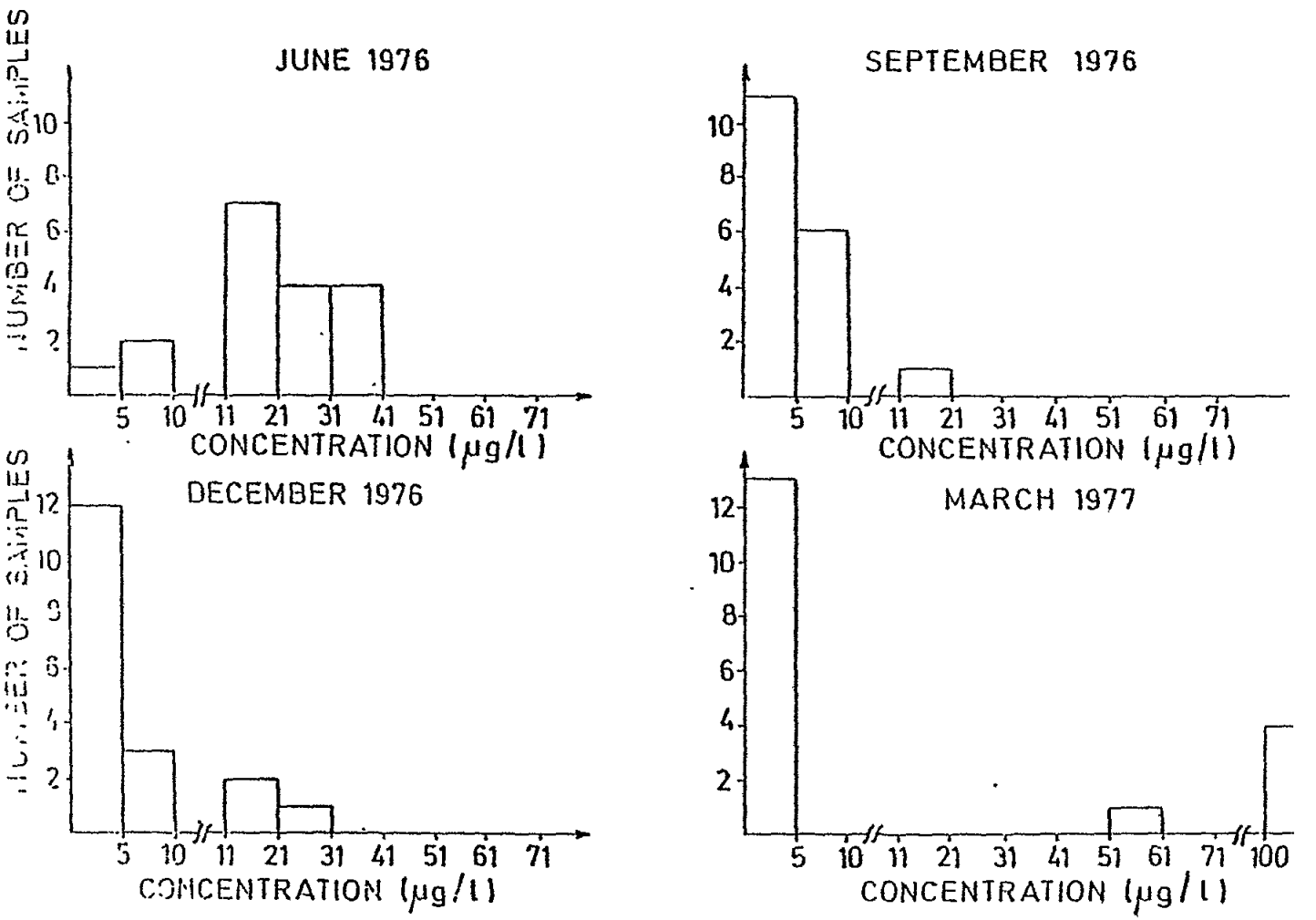

Fig. 2. Histograms of number of samples vs. concentration of dissolved petroleum hydrocarbons in Rijeka Bay in four sampling cruises.

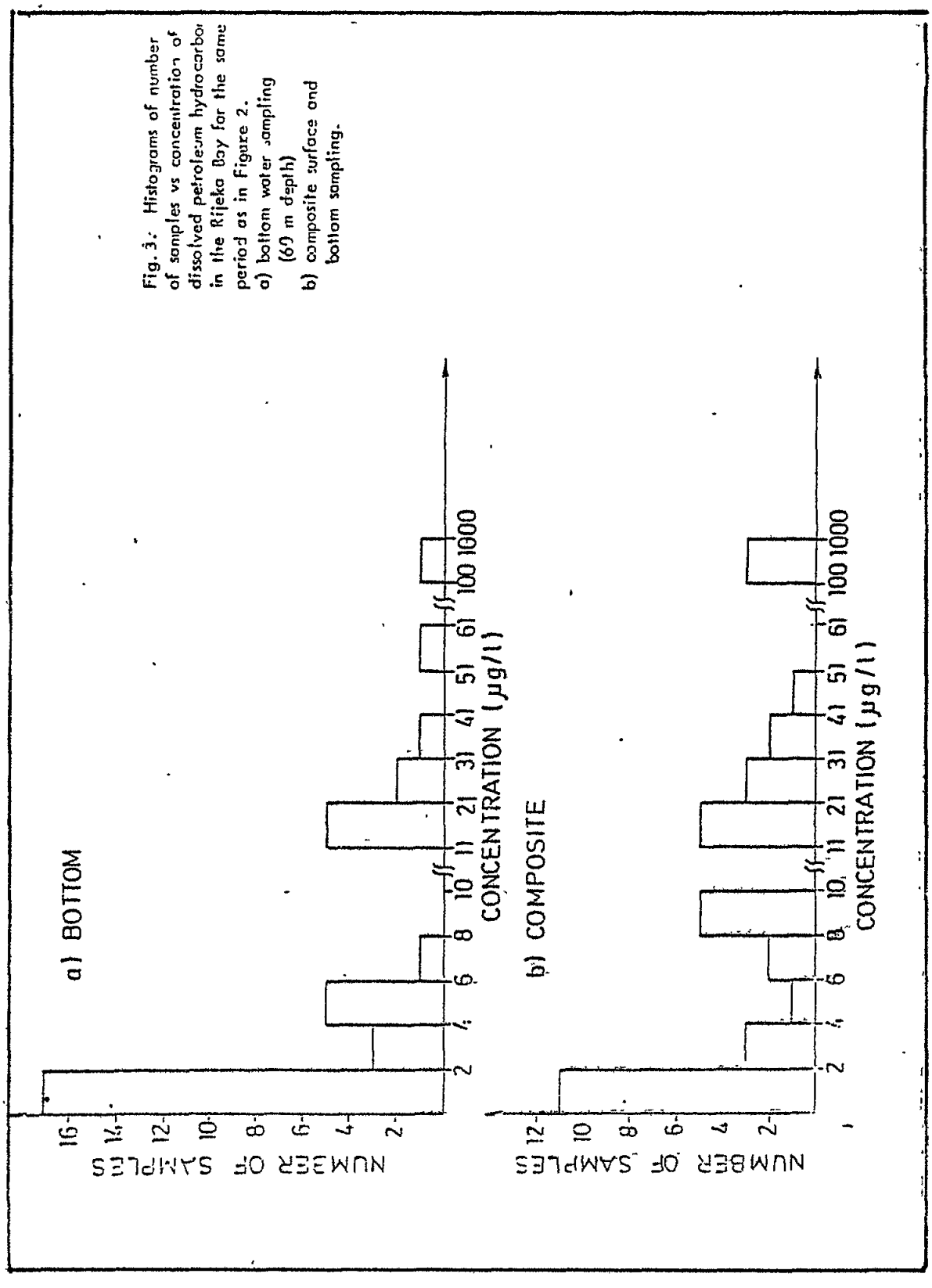

Fig. 3: Histograms of number of samples vs concentration of dissolved petroleum hydrocarbo in the Rijeka Bay for the same period as in Figure 2.
a) bottom water sampling (60 m depth)
b) composite surface and bottom sampling.

Fig. 3. Histograms of number of samples vs. concentration of dissolved petroleum hydrocarbons in the Rijeka Bay for the same period as in Figure 2.
a) bottom water sampling (60 m depth)
b) composite surface and bottom sampling.

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