



MEDITERRANEAN ACTION PLAN

MED POL

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UNITED NATIONS ENVIRONMENT PROGRAMME



FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS  
(GENERAL FISHERIES COUNCIL FOR THE MEDITERRANEAN)

BASELINE STUDIES AND MONITORING OF DDT, PCBs AND OTHER  
CHLORINATED HYDROCARBONS IN MARINE ORGANISMS (MED POL III)

ETUDES DE BASE ET SURVEILLANCE CONTINUE DU DDT, DES PCB ET DES AUTRES  
HYDROCARBURES CHLORES CONTENUS DANS LES ORGANISMES MARINS (MED POL III)

FINAL REPORTS OF PRINCIPAL INVESTIGATORS  
RAPPORTS FINAUX DES CHERCHEURS PRINCIPAUX

MAP Technical Reports Series No. 3

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JNEP

Athens, 1986

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**PNUE/FAO: Etudes de base et surveillance continue du DDT, des PCB et des autres hydrocarbures chlorés contenus dans les organismes marins (MED POL III). MAP Technical Reports Series No.3. UNEP, Athens 1986.**



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This volume is the third 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 troisième 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, WMO, IOC), 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 Agencies 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 DDT, PCBs and Other Chlorinated Hydrocarbons in Marine Organisms (MED POL III)".

## INTRODUCTION

Le Programme des Nations Unies pour l'environnement (PNUE), en coopération avec les organismes spécialisés compétents des Nations Unies (FAO, OMS, OMM, COI), 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).
- Agence 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 DDT, des PCB et des autres hydrocarbures chlorés contenus dans les organismes marins (MED POL III)".



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

Principal Investigators: A. DEMETROPOULOS - L. ATHANASSIADOU

Reporting period: September 1976 - March 1981

#### INTRODUCTION

No substantial work was carried out by this Department relevant to the MED POL project before this programme.

#### METHODOLOGICAL CONSIDERATIONS

##### Selection of the species:

The following species were monitored: Mullus barbatus, Xiphias gladius, Patella coerulea and Arca noae.

##### Pollutants analysed:

Aldrin, dieldrin, DDT, DDD, DDE and PCBs (as Aroclor 1254).

##### Areas studied:

###### (a) Akrotiri Bay (Fig. 1)

Akrotiri Bay is in the south of Cyprus and is bounded on the west side by the Akrotiri peninsula and to the north by the mainland. On the bay is situated Limassol, a town of about 65,000 inhabitants; it has two commercial ports. There are no permanent rivers, only streams which flow during the rainy period. The increasing construction of dams also limits the quantity of water reaching the sea. Surface sea-water temperatures range from 14.5 to 27°C. During the summer the thermocline is formed at 25-30 m depth. Salinity varies from 38.6 to 39.5‰. The content of the dissolved oxygen, during winter, is approximately 5.5 ml/l, reaching a maximum of 5.9 ml/l at the depth of 50-75 m. During summer the content of dissolved oxygen is about 5 ml/l, reaching the same maximum at the same depth.

Analyses for suspended solids show values of 0-400 ppm. The sea bed in the bay is as follows: sand with some single (beach), Posidonia meadows/sand (5 m), Posidonia meadows/muddy sand (10 m), muddy sand with Caulerpa (20 m), mud with Caulerpa (30 m) and mud aphytal (100 m).

###### (b) Episkopi Bay (Fig. 2)

Episkopi Bay lies west of Limassol Bay on the other side of Akrotiri. There is no habitation in close proximity to the sea.

(c) Larnaca Bay (Fig. 3)

Larnaca Bay is situated in the south-east side of the island. The main town is Larnaca having a population of about 35,000 inhabitants. Surface sea-water temperatures reach a maximum of about 28°C and a minimum of about 14.5°C.

The Larnaca area has not been studied to any extent but it appears to be similar to Akrotiri Bay.

(d) Paphos area (Fig. 4)

The Paphos area lies on the west side of the island and has a rather open coast; Paphos is the main town of the area with 13,000 inhabitants. Surface sea-water temperatures reach a maximum of about 27°C and a minimum of about 14°C.

The Paphos area is exposed to westerly winds and, in general, has a rocky bottom. Its fauna and flora are affected by some local upwelling in the summer.

#### METHODOLOGY

Sampling: Mullus barbatus is caught with trammel nets or trawl nets and is obtained from inshore fishermen or trawlermen. Xiphias gladius is caught with floating long-lines in open waters. Special instructions are given to fishermen on the precautions they have to take.

Patella coerulea are collected by detaching them from rocks, near the shore.

The samples are placed in pre-cleaned aluminium foil and then are placed in thermoisolated boxes which are cooled with ice and transferred to the laboratory where they are kept deep-frozen.

Sample preparation of Mullus barbatus: The fork and the total length of the fish is determined and its fresh weight is recorded. The fillet of the fish is separated and the skin is pulled away from the flesh with stainless steel tweezers. The fillet is then removed with a stainless steel knife from the vertebral column and is weighed. The same procedure is followed to remove the second fillet. The fillets are then placed in aluminium foil and are kept deep-frozen or are analyzed immediately.

Pre-treatment: The tissue is first homogenized in the presence of anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then the homogenate is extracted in a Soxhlet extractor with hexane. The extract is finally concentrated and its final volume is made up with hexane.

Different concentrations were then made up and the clean-up and separation procedure was followed for each. (This had to be done as only one extractor was available at the time). A sub-sample was also taken for the determination of lipids as a percentage of fresh weight.

Clean-up and separation: A sub-sample was also taken for the determination of lipids as a percentage of fresh weight.

Clean-up and separation: A sub-sample was then treated with concentrated H<sub>2</sub>SO<sub>4</sub>, shaken vigorously, centrifuged and the upper layer injected into the GC (several injections are performed and also different volumes are used).

Saponification: To a sub-sample of the sample (sample + H<sub>2</sub>SO<sub>4</sub>, upper layer) one pellet of KOH dissolved in ethyl alcohol is added in a centrifuge tube. It is then shaken and centrifuged, and its upper layer is injected into the GC (several injections are performed and also different volumes are used). Chromatograms are then compared with those obtained through the above procedure.

Quantification of chromatograms: Known standards of chlorinated hydrocarbons are injected into the GC (different volumes) and their peaks are matched with the peaks obtained from the samples (retention times, etc.).

Analysis of samples was limited to the standards available.

Results: Results are obtained by measuring peak heights of standards and samples, taking into account injection volumes of standards and samples, concentration of standards, final volume of samples and weight of samples.

Intercalibration exercise:

The research centre participated in the intercalibration exercise for the sample MA-M-1 (oyster tissue homogenate).

## RESULTS

At present, only 4 specimens of Mullus barbatus from 2 areas have been analysed. Therefore, no conclusions can be drawn and results are shown here for reference only.

Chlorinated hydrocarbons in Mullus barbatus:

Episkopi Bay (µg/F.W.):	$\bar{x}$	(n) range
PCB (as Aroclor <sup>R</sup> 1254)	41.3	(1)
DDT	28.9	(3) 10.5-54.7
DDD	6.3	(3) 5.4- 7.6
DDE	41.5	(3) 17.9-73.5
ALD	3.1	(3) 2.2- 3.6
DIE	0.2	(1)

Larnaca Bay (µg/kg F.W.), single values:

PCB (as Aroclor <sup>R</sup> 1254)	11.4
DDT	4.9
DDD	2.7
DDE	10.2
ALD	2.3

## DISCUSSION OF RESULTS

Results obtained cannot be commented upon nor be compared with others, as they are only preliminary and were performed at a time when training was not yet completed.

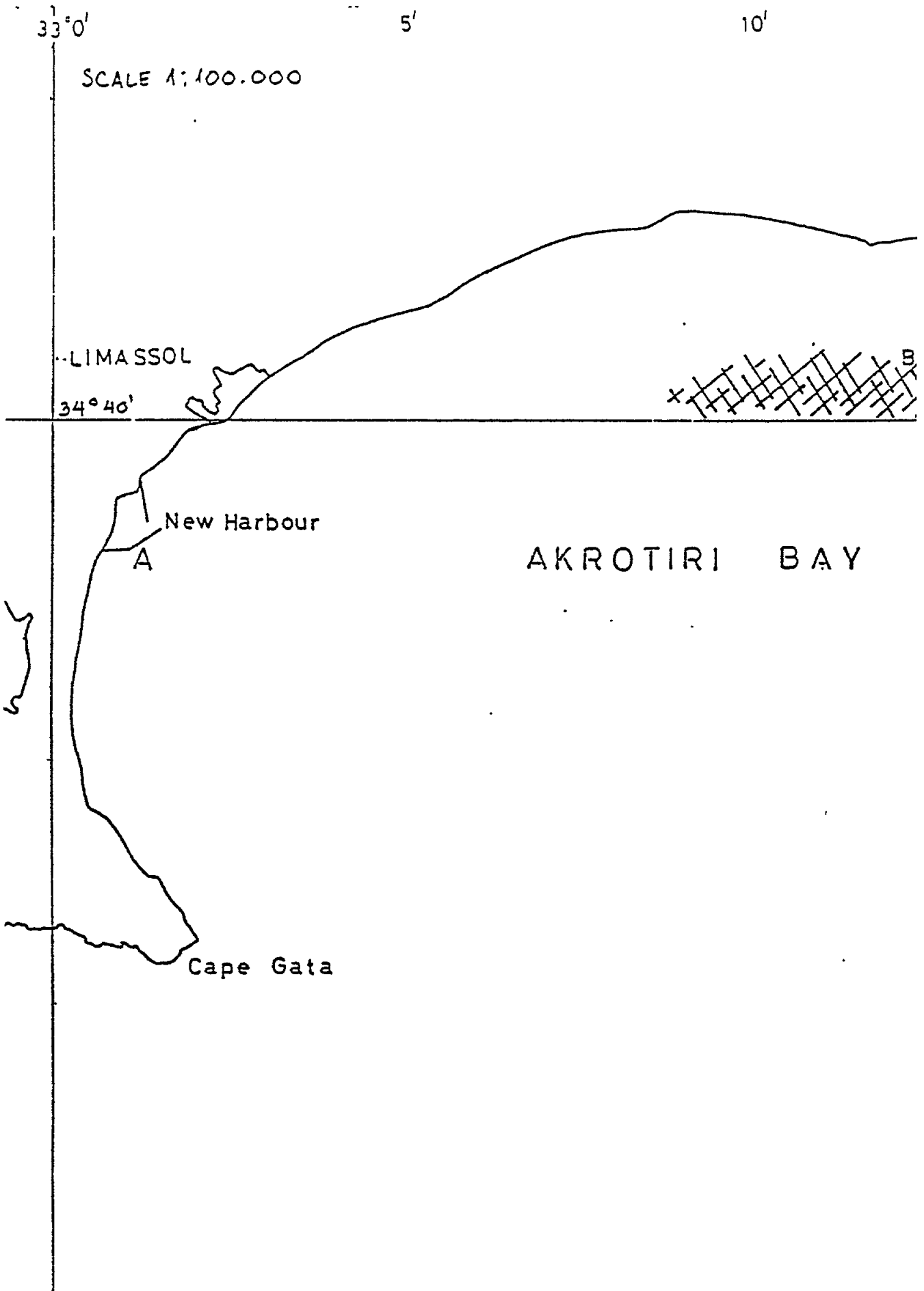


Fig. 1. Sampling stations in Akrotiri Bay

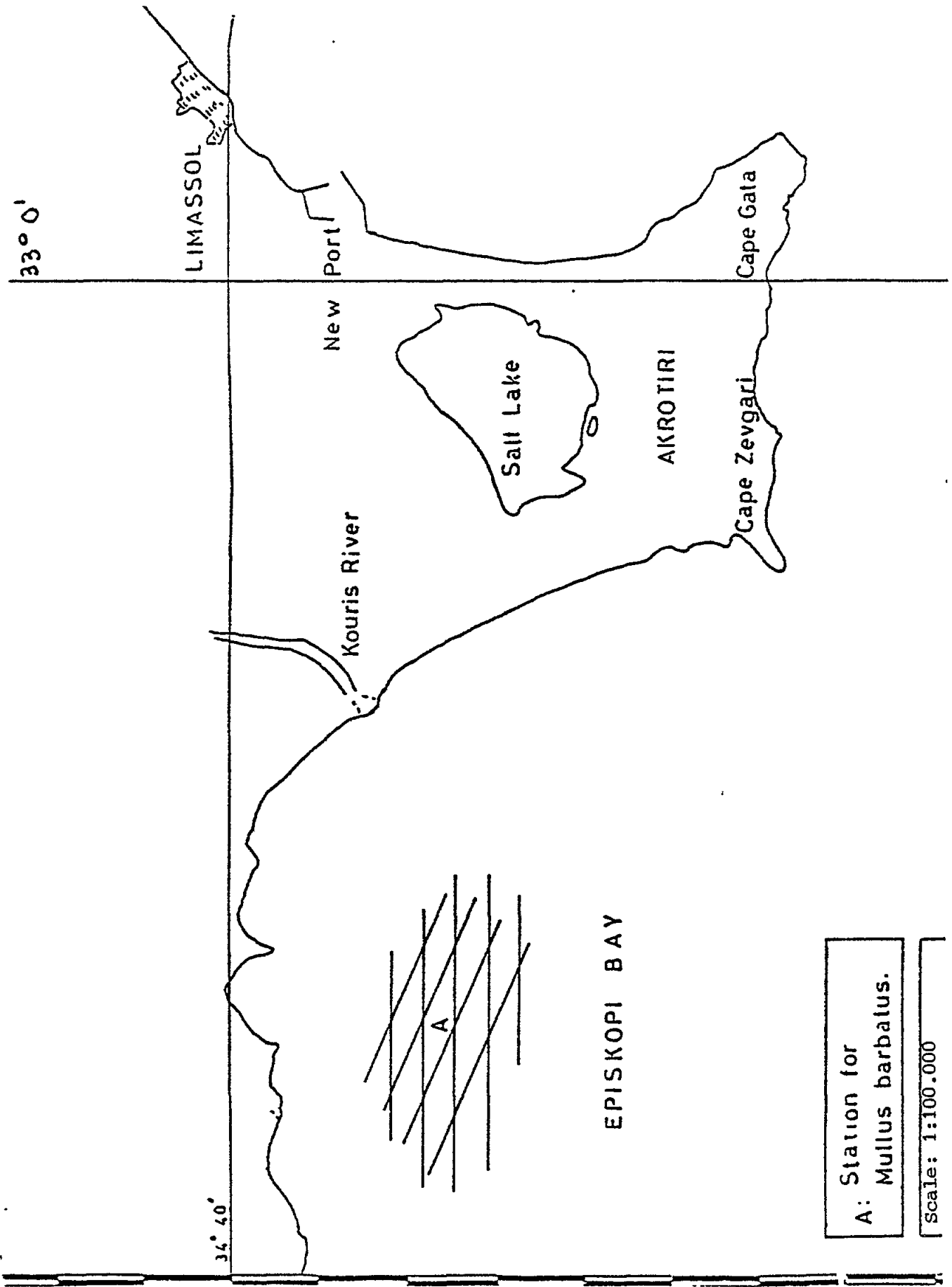


Fig. 2. Sampling stations in Episkopi Bay

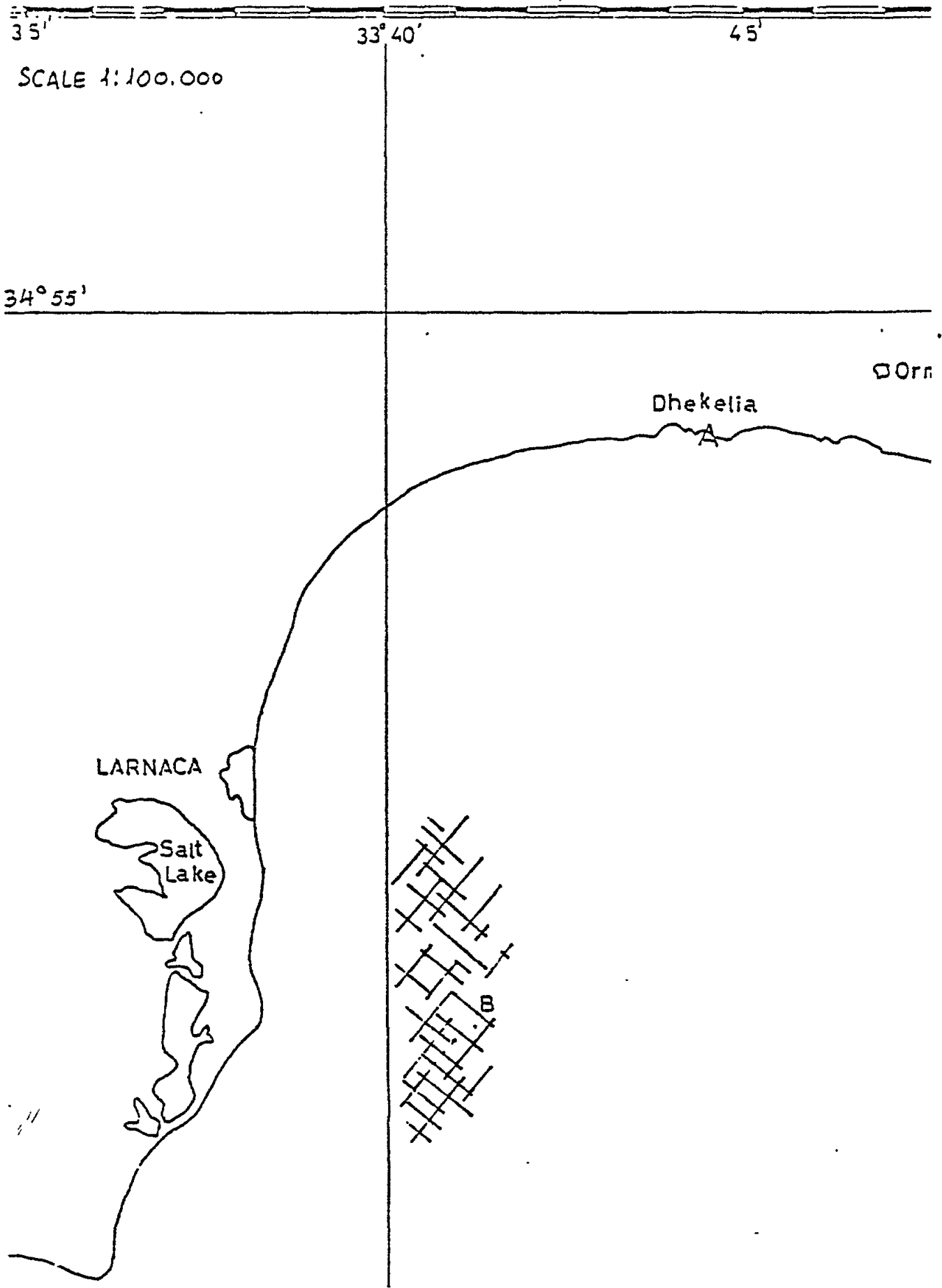


Fig. 3. Sampling stations in Larnaca Bay

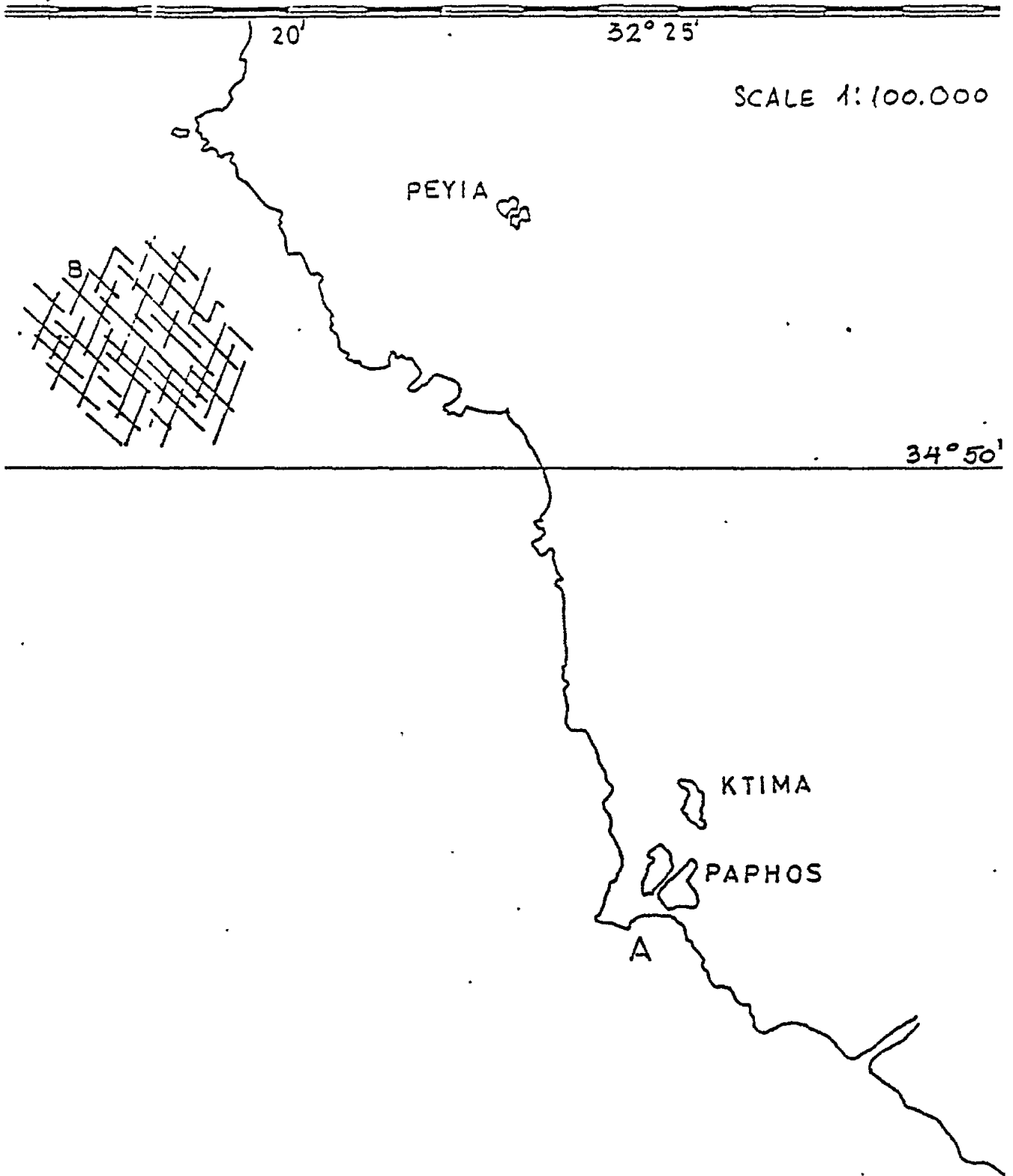


Fig. 4. Sampling stations in Paphos area



Research Centre:           Institute of Oceanography and Fisheries  
                              ALEXANDRIA  
                              Egypt

Principal Investigator:   M. M. ABBAS ALY; H. K. BADAWI (from 1980)

No report on the work performed has been submitted according to the established format. GC was delivered in November 1977 and installed only in January 1979 since the necessary working conditions were not ready before. M. M. Abbas Aly visited the Marine Biology Station at Portoroz and the University of Ljubljana (Yugoslavia) for scientific study during September and October 1977 and W. M. El Sarraf was trained in the Istituto di Biologia Marina CNR (Venezia, Italia) from February to May 1978. Consultants (as well as the maintenance engineer) visited the Institute. The new Principal Investigator started the work in 1980. According to his report, the sampling and analysis of water, biota and sediments were carried out in Lake Burulus. The first results indicated higher levels of DDTs and very low content of PCBs (5% of the total chlorinated hydrocarbons analysed). Further monitoring is necessary to confirm such conclusions.

Research Centre: Centre for Postgraduate Studies and  
Research  
University of Alexandria  
ALEXANDRIA  
Egypt

Principal Investigator: Mr. A. H. EL - SEBAE

No report on activities relevant to MED POL III was submitted by the Principal Investigator.

Centre de Recherche : Institut scientifique et technique des  
Pêches maritimes  
NANTES  
France

Chercheur principal : C. ALZIEU

Période couverte par le rapport : 1978 et 1979

#### Introduction

Parallèlement aux travaux effectués dans le cadre de MED POL, l'ISTPM participe à des programmes de surveillance de la contamination de la faune de l'Atlantique.

#### CONSIDERATIONS METHODOLOGIQUES

##### Sélection des espèces :

Les espèces obligatoires et/ou alternatives n'ont pas été systématiquement échantillonnées pour les raisons suivantes :

-

-Les crevettes et crabes verts sont difficiles à prélever en quantité suffisante pour satisfaire aux besoins de toutes les analyses.

-

-Les prélèvements faits spécialement pour le CGPM n'ont pu être effectués en raison de la mise en place d'une surveillance systématique effectuée sur la côte méditerranéenne dans le cadre d'un programme national. Malheureusement, des difficultés administratives ont retardé le début de ce nouveau programme de sorte que pour l'année 1978, nous disposons seulement d'analyses portant sur des échantillons de moules prélevées dans le golfe de Fos.

Pour l'année 1979, les espèces échantillonnées pour la réalisation du programme MED POL III sont :

moule : Mytilus galloprovincialis

crevette : Crangon crangon

crabe vert : Carcinus maenas

poissons : Boops boops, Maena smaris, Trisopterus minutus capellanus, Solea solea.

##### Polluants analysés :

Tous les polluants obligatoires ont été recherchés : PCB, DDT, DDE, DDD.

##### Zones étudiées :

Les zones de prélèvement de moules ont été étendues à l'ensemble de la côte, soit : Banyuls - Etang de Thau - Golfe de Fos - Golfe de Marseille - Rade de Toulon - Baie de Villefranche et Menton.

## METHODOLOGIE

L'échantillonnage, le traitement et l'analyse des prélèvements ont été décrits en détail dans le premier rapport de mars 1977.

Programme d'intercalibration :

L'ISTPM a effectué les intercalibrations prévues par le programme.

## RESULTATS DES ETUDES

Hydrocarbures chlorés dans Mytilus galloprovincialis :

La contamination de Mytilus galloprovincialis est surtout due aux diphénylpolychlorés (PCB); elle est nettement plus faible en ce qui concerne le DDT et ses produits de dégradation. Les concentrations moyennes les plus élevées en PCB sont relevées chez les moules vivant à proximité de chantiers navals (rade de Toulon) ou d'agglomérations importantes (Marseille, Cannes, Villefranche). Les teneurs moyennes dans la zone industrielle de Fos sont voisines de celles de la rade de Marseille et en nette évolution entre 1978 et 1979. Les gisements de moules de Banyuls, Menton, ainsi que la zone conchylicole de l'étang de Thau sont parmi les zones les moins contaminées par les PCB. La présence de DDT est surtout sensible au niveau de Banyuls du Golfe de Fos et de Villefranche, (voir tableau).

Hydrocarbures chlorés dans les autres organismes marins :

µg/kg poids frais	Teneur moyenne	Déviatiion standard
<u>Solea solea</u> : Etang de Thau		
PCB	468,9	274,1
DDT	101,4	76,2
DDE	72,6	38,8
DDD	120,4	108,0
<u>Trisopterus minutus</u> : Marseille (est)		
PCB	330	145,2
DDT	61,3	15,0
DDE	38,7	8,1
DDD	66,7	41,6
<u>Boops boops</u> : Marseille (est)		
PCB	2537,5	1515
DDT	147,5	78,9
DDE	70	21,6
DDD	55	17,3

## DISCUSSION DES RESULTATS

Les teneurs sont dans leur ensemble assez proches de celles que l'on rencontre habituellement dans les mêmes espèces originaires de côtes françaises tant pour l'Atlantique que pour la Méditerranée.

Tableau 1

Mytilus edulis : Teneurs moyennes et déviation standard (o) en hydrocarbures chlorés (µg/g poids frais)

		P C B		D D T		D D E		D D D	
		o	moyenne	o	moyenne	o	moyenne	o	moyenne
Golfe de Fos	1978	1791,6	1473,0	143,2	186,5	75,9	39,2	138,5	68,7
Golfe de Fos	1979	3001,5	4407,2	282,7	290,6	61,1	96,0	154	42,1
Banyuls	1979	569,8	212	360	317,7	116,7	45,0	96,5	44,7
Thau	1979	624	412,5	193,7	153,2	185,8	77,3	110,9	83,1
Marseille	1979	2966,5	1540,2	165	21,4	68,2	47,8	190,2	149,4
Toulon	1979	9577,3	3727,7	241	250,3	124,6	195,1	195	282,8
Cannes	1979	2184	1405	82,7	84,9	31,7	12,6	73,3	28,9
Villefranche	1979	2014	625,8	284	167,4	47,7	32,2	146,7	119,3
Menton	1979	664,7	414,1	102,3	54,4	30,7	11,0	61,7	33,3

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

Chercheur Principal :                 R. MESTRES

Période couverte par le rapport : 25 mai 1977 - 15 mars 1980

#### INTRODUCTION

Ce travail se situe dans les objectifs de recherche du Laboratoire.

#### CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces :

Mytilus galloprovincialis, Carcinus mediterraneus, Mullus barbatus et zoo-plancton.

Polluants analysés : DPC et pesticides organochlorés persistants.

Zones étudiées :

A partir du point 8 du CNEEXO - Banyuls (Fig. 1)

<u>Mytilus galloprovincialis</u>	Côte Banyuls	42°30' - 3°8'
<u>Mullus barbatus</u>	Station 2	42°30' - 3°9'
Zoo-plancton	Stations 2 et 4	42°30' - 3°9' et 3°15'
<u>Carcinus mediterraneus</u>	Etang de Sigean	43°5' - 3°0'

#### METHODOLOGIE

Echantillonnage : FAO, Document technique sur les pêches n°. 158, pp. 45 à 68.

Analyses : Mestres et coll. - Trav. Soc. Pharmacie Montpellier, 1976, 36, 43-58 et Ann. Fals. Exp. Chim., 1977, 70, 101-111 et 177-188.

Analyses effectuées séparément sur un spécimen et sur la totalité des autres spécimens de chaque lot.

Programme d'intercalibration : MA-A-1 et MA-M-2.

Le centre de recherche a participé dans le programme d'intercalibration en analysant les échantillons : "copepod" (MA-A-1) et "fish" (MA-M-2).

#### RESULTATS DES ETUDES

Note : A l'examen de l'ensemble des résultats, il apparaît que les prélèvements des 17 et 18 octobre 1977 ont été souillés par des DPC et du DDT présents à fortes teneurs dans les crabes. Ces derniers ayant été expédiés en vrac dans le même récipient que les moules, celles-ci ont été fortement contaminées. Les rougets, bien qu'isolés ont subi la même contamination. Les teneurs trouvées dans ces lots seront indiquées, mais de manière séparée.

Mytilus galloprovincialis :

	DP 4	DP 5	Σ DDT	LINDANE
Nombre d'échantillons considérés	8	8	8	10
Pourcentage de résultats positifs	0	100	0	50
Teneur moyenne µg/kg P.F.		341		6,6
σ ±		136		
Teneur dans l'échantillon, N° 17	450	750	190	
Teneur dans l'échantillon, N° 18	65	150	85	

Conclusion : La contamination par le DP 5 est en voie de régression et peut être évaluée à 200 µg/kg de matière fraîche en 1978.

Mullus barbatus :

	DP 5	DDE	DIELDRINE	LINDANE	HCHα
Nombre d'échantillons considérés	10	10	10	12	12
Pourcentage de résultats positifs	100	70	0	66	25
Teneur moyenne µg/kg P.F.	243	27		4,5	2
σ ±	105	9		5	2
		Σ DDT			
Teneur dans l'échantillon, N° 15	8000	115	4	3,5	5
Teneur dans l'échantillon, N° 16	9500	120	5		

Conclusion : Dans les rougets barbets, la teneur en DP 5 a régulièrement diminué avec le temps pour se situer aux environs de 250 µg/kg P.F. en juin 1978. La chair des poissons a toujours renfermé des traces de DDE en 1977, disparues en 1978. Des résidus de dieldrine n'ont été observés que dans les deux échantillons souillés ( N°. 15 et 16) par une pollution d'origine industrielle.

Carcinus mediterraneus :

	DP 4	DP 5	Σ DDT	LINDANE
Nombre d'échantillons considérés	8	8	8	10
Pourcentage de résultats positifs	0	100	0	40
Teneur moyenne µg/kg P.F.		958		19
σ ±		952		14
Teneur dans l'échantillon, N° 19	760	2450	151600	
Teneur dans l'échantillon, N° 20	1100	2500	5400	

Conclusion : L'étang de Sigean où ont été ramassés les crabes est dans un environnement viticole et industriel. Ces essais ont été témoins d'une pollution temporaire localisée, mais la teneur moyenne en DP 5 dans ce lieu peut être considérée comme supérieure à celle observée dans la région de Banyuls, soit entre 300 et 1000 microgrammes par kg de matière fraîche.

Zoo-plancton :

	DP 5	DP 6	Σ DDT
Nombre d'échantillons considérés	4	4	4
Pourcentage de résultats positifs	100	50	100
Teneur moyenne µg/kg P.F.	2075	9750	130
σ ±	816		29

Conclusion : L'analyse du plancton n'a pu être très précise en raison des très faibles prises d'essai qui ont été disponibles, soit 500 mg à 95% d'eau. L'existence de DDT et de DPC dans les échantillons analysés a néanmoins été observée.

DISCUSSION DES RESULTATS

N'ayant pas eu les moyens de procéder aux prélèvements des échantillons, le laboratoire n'a analysé que ceux qui lui ont été expédiés par les services du CNEOX, ce qui a amené à la cessation de cette enquête en juin 1978. Des résultats donnés par les 36 analyses effectuées il ne peut être tiré des conclusions définitives sur l'état de la contamination du milieu marin



étudié. Mis part une pollution locale qui a contaminé des échantillons prélevés au mois d'octobre 1979, compte tenu des incertitudes et imprécisions des techniques applicables, les taux de résidus de DPC et de pesticides organochlorés peuvent être estimés aux valeurs suivantes exprimées en  $\mu\text{g}$  par kg de matière biologique fraîche.

<u>Mytilus galloprovincialis</u>	(origine Banyuls)
DP 5 (Aroclor 1254)	200 $\mu\text{g}/\text{kg}$
<u>Mullus barbatus</u>	(origine : au large de Banyuls)
DP 5 (Aroclor 1254)	200 $\mu\text{g}/\text{kg}$
DDT sous forme de DDE	20 $\mu\text{g}/\text{kg}$
<u>Carcinus mediterraneus</u>	(origine: étang de Sigean)
DP 5 (Aroclor 1254)	300 $\mu\text{g}/\text{kg}$
Zoo-plancton	(origine : au large de Banyuls)
DP 5 (Aroclor 1254)	2000 $\mu\text{g}/\text{kg}$
DDT et métabolites	100 $\mu\text{g}/\text{kg}$

L'expérience a montré que des pollutions temporaires parfois très importantes pouvaient survenir. Ces phénomènes ont été observés dans le cas des crabes récoltés dans une zone lagunaire où les pollutions d'origine agricole et industrielle sont possibles. Il en est résulté des teneurs très élevées : 3 mg/kg pour le DP 5 et jusqu'à 5 et 15 mg/kg pour la somme DDT et ses métabolites.

Comparativement aux chiffres annoncés par d'autres chercheurs, les résultats enregistrés montrent que ce matériel biologique ouest-méditerranéen (région de Banyuls) est moins pollué que des éléments analogues d'autres mers ou d'autres parties de la Méditerranée.

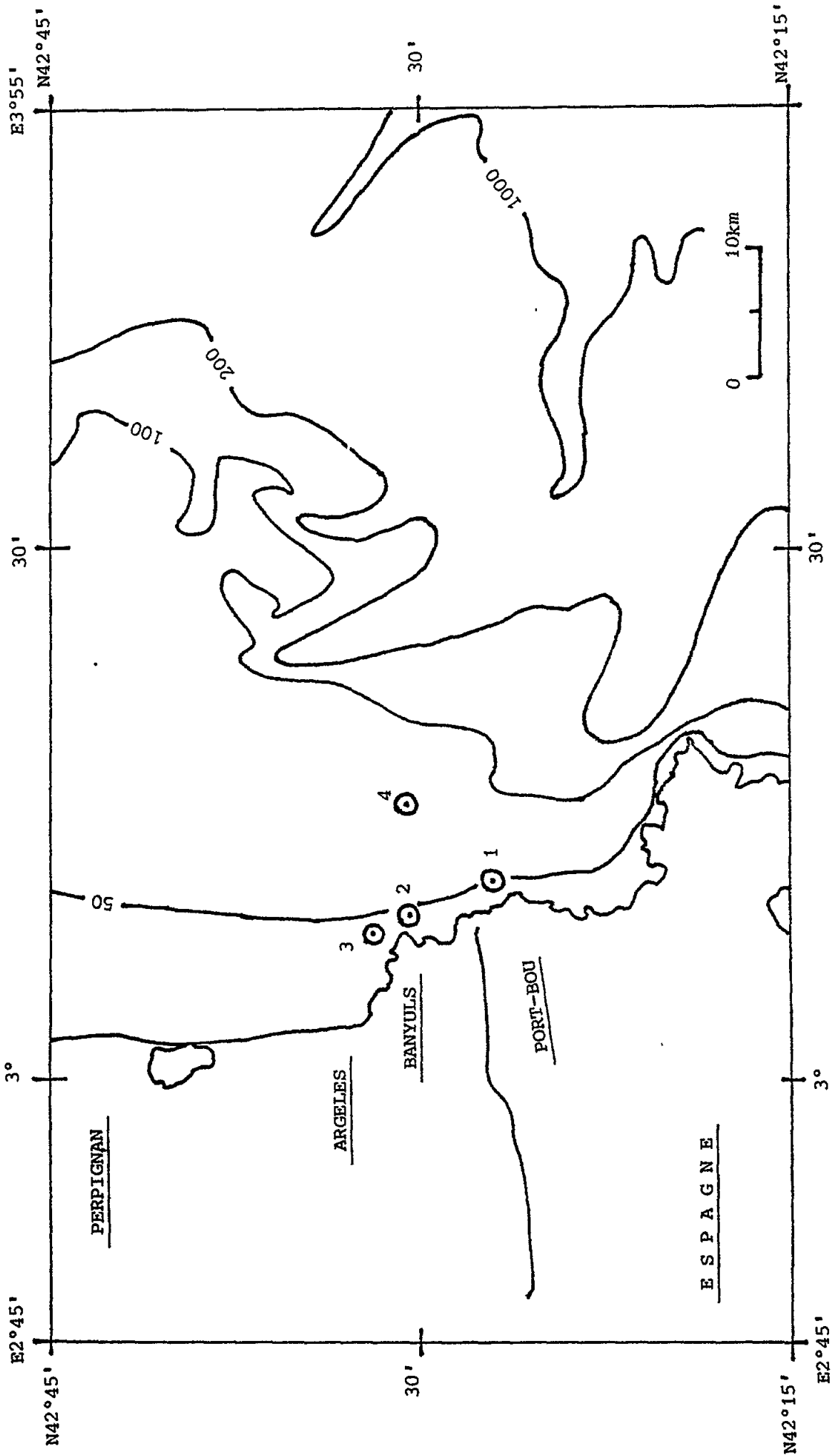


Fig. 1. Zone étudiée

Centre de Recherche : Institut phytopathologique  
Benaki  
ATHENES  
Grèce

Chercheur principal : N. ADAM

Période couverte par le rapport : 1976 - 1978

#### INTRODUCTION

Depuis plusieurs années (1960) l'Institut Benaki a été inquiet sur le sort des pesticides dans la nature.

Pour cette raison beaucoup des travaux ont été orientés afin de décéler la présence des pesticides dans les plantes, le sol, les eaux, les organismes marins et en général dans la nature (analyses des eaux, des poissons, etc.). L'importance de ces travaux est évidente pour l'agriculture aussi bien que pour la pêche.

#### CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces :

Mullus barbatus (Filet en général); Parapenaeus longirostris (Corps sans carapace); Mytilus galloprovincialis (Corps sans coquille).

Polluants analysés :

pp DDE, pp DDD, pp DDT, PCB (Aroclor 1254, 1260, 1242). On n'a pas analysé d'autres hydrocarbures à cause de difficultés techniques.

Zone étudiée :

Golfe de Saronicos. Superficie : 2.900 km sq bornés au Nord par l'Attique et à l'Ouest par le Peloponnèse. Eaux douces : pas de rivières. Stations d'échantillonnage : A-ou AA ouest et est de l'île Salamis près de Pirée), B-sud de l'île Egine (Aiyina), C-nord de l'île St Georges.

Déversements d'eaux polluées : 350.000 m<sup>3</sup> par jour d'eaux polluées urbaines et en plus les déchets de 30 usines installées au bord nord-est du Golfe.

Temps de renouvellement des eaux : 1 - 2 mois pour les eaux du côté nord-est et 2-12 mois pour la côte ouest.

Constatations : En général la vie n'est plus la même et quelques espèces ont disparu.

#### METHODOLOGIE

Echantillonnage : Chalut de fond et congélation à -10°C. L'échantillonnage, l'identification et la préparation des échantillons ont été faits par l'Institute of Oceanography and Fisheries Research (IOFR) selon les instructions de la FAO.

Traitement : Extraction à l'hexane-blender.

Analyse des échantillons et procédés d'évaluation des résultats : Purification des extraits lipidiques à l'aide d'acide sulfurique concentré et ensuite détermination par la chromatographie gazeuse. Confirmation des DDT après saponification.

En général nous avons suivi la méthode de FAO, Document technique sur les pêches N°. 158, p. 95.

Quantification des PCB, pic par pic selon le même Manuel, p. 102.

Programme d'intercalibration :

On a analysé deux échantillons, "oyster" (MA-M-1) et "copepod" (MA-A-1), reçus du Laboratoire de Monaco (IAEA).

#### RESULTATS DES ETUDES

Ces résultats devraient être rapportés comme valeurs moyennes, avec déviation standard et gradient en  $\mu\text{g}/\text{kg}$  poids frais. Toutes les analyses ont été faites sur des échantillons composites. Hydrocarbures chlorés dans Mytilus galloprovincialis. (Tableau I). D'après les résultats des analyses des échantillons que l'Institut Océanographique a pu sélectionner seulement à la zone A, nous pouvons conclure que :

- a) La concentration pour cette espèce pendant les trois ans ne dépasse pas :  

DDT	11	$\mu\text{g}/\text{kg}$	poids frais	$\pm$	4,5
PCB	62	$\mu\text{g}/\text{kg}$	" "	$\pm$	12
- b) Nous n'avons pas trouvé une différence statistiquement significative du niveau de la pollution, pour les trois ans,
- c) non plus, pour les quatre saisons.

Hydrocarbures chlorés dans Mullus barbatus. (Tableau I) :

D'après les résultats des analyses nous pouvons conclure pour DDT et PCB :

- a) Pour les trois ans (1976-77-78) le niveau de la pollution ne dépasse pas :  

DDT	40	$\pm$	23	$\mu\text{g}/\text{kg}$	poids frais
PCB	100	$\pm$	57	"	"
- b) PCB/DDT = 2,5
- c) Une comparaison des trois ans, des trois stations (A-AA, B, C0 et des quatre saisons, présente plus ou moins une variabilité des valeurs moyennes, mais en général ne présente pas une différence statistiquement significative.

Hydrocarbures chlorés dans Parapenaeus longirostris : (Tableau I)

D'après les résultats des analyses on peut conclure :

- a) Niveau de la pollution pour les trois ans :  
DDT =  $3,4 \pm 3,4$  µg/kg poids frais  
PCB =  $11,5 \pm 13$  µg/kg " "
- b) PCB/DDT =  $\sim 10$
- c) Une diminution du niveau de la pollution pour les PCB et DDT se présente (1976-1978).
- d) La station A présente une plus grande pollution (PCB-DDT) par rapport à la station B et aussi la B par rapport à la C.

#### DISCUSSION DES RESULTATS

- a) Mullus barbatus présente une concentration de PCB et DDT plus élevée que les deux autres espèces, Mytilus galloprovincialis et Parapenaeus longirostris. Ces deux espèces ne présentent pas une différence essentielle.
- b) Selon les résultats des analyses de Mullus barbatus on ne trouve pas généralement une diminution de la pollution pendant 1976-77-78.
- c) Les PCB se présentent plus élevés que les DDT : PCB/DDT = 2,5 - 10.
- d) Saisons : Les moyennes donnent l'impression que les polluants sont plus élevés pendant l'hiver vers le printemps. Un nombre d'échantillons plus grand pourrait nous affirmer cette impression. De même pour les différences des trois stations.
- e) Nous croyons qu'une étude plus minutieuse, en choisissant de nouvelles stations et en changeant les dates et la fréquence d'échantillonnage, pourrait nous assurer de meilleurs résultats. Une amélioration de technique d'analyse serait nécessaire.
- f) Après une comparaison de nos résultats avec d'autres obtenus en Méditerranée, on trouve presque les mêmes valeurs et la même variabilité.

Tableau I

Les valeurs moyennes et déviations standard (G)  
des DDT et PCBs dans les trois espèces obtenues dans  
des zones différentes pendant les trois années de surveillance

ESPECES (Echantillons analysés)	Année	DDT's (µg/kg P.F)			Σ PCB's (µg/kg P.F)		
		A et AA	B	C	A et AA	B	C
<u>Mutilus</u> <u>galloprovincialis</u>  ( 7 )	1976	5,5	( - )	( - )	75	( - )	( - )
	1977	12,7 (± 4)	( - )	( - )	59,3 (± 7,2)	( - )	( - )
	1978	14,3 (± 2,4)	( - )	( - )	50 (± 14)	( - )	( - )
<u>Mullus</u> <u>barbatus</u>  (32)	1976	150,3 (± 161,4)	21,3 (± 12,9)	53,7 (± 33,5)	358,3 (± 513,4)	24 (± 41,6)	49,2 (± 44)
	1977	17 (± 4,7)	26 (± 15,7)	33,7 (± 11,9)	32,3 (± 13)	37 (± 21,3)	28 (± 19,1)
	1978	34,4 (± 14,4)	20,5 (± 10,4)	29,6 (± 12,4)	104,2 (± 123,6)	15,7 (± 15,1)	13,4 (± 1,8)
<u>Parapenaeus</u> <u>longirostris</u>  (22)	1976	10,7 (± 4,7)	2	( - )	33,3 (± 16,3)	21	( - )
	1977	2 (± 0,7)	1,9 (± 1,3)	1	8,5 (± 8,3)	5,8 (± 1)	4
	1978	1,2 (± 1,1)	0,6 (± 0,6)	0,5 (± 0,7)	1,7 (± 1,8)	0,8 (± 0,8)	0,5 (± 0,7)

(-) Pas d'échantillons.

Research Centre: Department of Food Hygiene  
Faculty of Veterinary Medicine  
Aristotelian University  
THESSALONIKI  
Greece

Principal Investigator: S.D. KILIKIDIS

Reporting period: March 1977 - December 1980

## INTRODUCTION

The Department is taking part in MED POL III with the aim of improving the knowledge on levels of pollutants in Mediterranean living resources and, accordingly, to produce the necessary information which should enable participating countries to take adequate measures for scientifically justified interventions against pollution. The Institution had no previous activities relevant to MED POL III, except some studies on DDT, PCB's and other chlorinated hydrocarbons which have been investigated since 1971 and, more than 10 papers have already been published, concerning the identification and determination of the above-mentioned substances in foods, human fat, woman's milk and also concerning some experimental effects on animals by these pollutants. This report describes the monitoring of persistent chlorinated hydrocarbons (chlorinated insecticides and PCB's), in several biota species of coastal waters of the North Aegean Sea.

## METHODOLOGICAL CONSIDERATIONS

Selection of the species:

Mytilus galloprovincialis, Mullus barbatus, Thunnus thynnus, Xiphias gladius and Merluccius merluccius.

Pollutants analysed:

Polychlorinated biphenyls (PCB's), chlorinated insecticides: BHC and its isomers, all DDT's, Aldrin, Dieldrin, Heptachlor and Heptachlor epoxide.

Area studied:

The Aegean Sea, especially its northern part (a semi-enclosed formation and a relatively shallow and fairly small water body) belongs to those marine ecosystems whose coastal waters are very good for investigation of chlorinated hydrocarbons. The Department performs studies and monitoring of chlorinated hydrocarbons of fishes and shellfishes of the North Aegean Sea. The area covered corresponds to an anomalous coastline, formed by the oil brought in by five main rivers: Aliakmon, Loudias, Axios, Gallikos and Strymon. From this area three main gulfs have been selected for study: Thermaikos gulf (40°30'N - 21°50'E), Strymonikos gulf (40°50'N - 23°60'E) and Kavala gulf (40°55'N - 24°24'E), Fig. 1.

The water is shallow and provides a very good environment for the cultivation of shellfish. Thermaikos gulf, receives the wastes of the city of

Thessaloniki, industrial wastes (west coast) and agricultural wastes (east coast). The west coast is not suitable for swimming; Strymonikos gulf receives mainly agricultural wastes, while the gulf of Kavala receives the wastes of the city of Kavala and agricultural wastes.

#### METHODOLOGY

The survey of DDT, PCB's and other chlorinated hydrocarbons in marine organisms covers the north coast of the Aegean Sea. Sampling stations are located in the above-mentioned three important, industrial and agricultural, areas of Thermaikos, Strymonikos and Kavala gulfs. For investigation of the pollution of marine organisms, 142 samples (fish and shellfish), were collected by the Laboratory of Zoology, Faculty of Science, University of Thessaloniki, during the period from September 1975 to December 1979. Samples were stored deep-frozen prior to analysis. They were treated with sodium sulphate (anhydrous) and then extracted by Soxhlet apparatus, using petroleum benzine, bp 40-60°C. The extractable organic matter was treated by methods described in Johnson (1965) or Jensen, *et al.*, (1973). In analysing fishes and shellfishes for organochlorine pesticides and PCB's the Gas-Chromatographs used were: Packard, Mod. 7 400 and Varian, Mod. 3 700. The former was equipped with ECD, tritium and the latter with ECD, Ni<sup>63</sup>.

#### Chromatographic Conditions:

In the Packard G.C. a glass column 6' x 1/4'' packed with 15% QF-1 and 10% DC-200 on Chromosorb 80-100 mesh size was used. Oven temperature was 210°C and, inlet and detector temperature were 220°C. Flow rate of the carrier gas (nitrogen), was 100 ml/min. On the other hand, in Varian GC the glass column was 200 cm X 35 mm x 2 mm (i.d) packed with the same liquid phase as the Packard. Inlet and detector temperatures were 300°C and the oven temperature 210°C. Flow rate of the carrier gas (nitrogen), was 14 ml/min.

#### Intercalibration exercise:

The procedure was intercalibrated during the years 1977-78 in an intercalibration exercise organized by the IAEA International Laboratory of Marine Radioactivity, Monaco.

#### RESULTS AND THEIR INTERPRETATION

The average analytical results and ranges for chlorinated hydrocarbons in the five species of fish and shellfish studied are presented in Tables I, II, III, IV and V, together with the necessary supplementary information. The values given in these tables are presented graphically in Figs. 2 and 3. In Fig. 4 the annual variation of the concentrations of chlorinated pesticides and PCB's, in M. galloprovincialis is shown.

Three DDT related compounds (pp'-DDE, pp'-DDT and pp'-DDD) were present in sufficient quantities for reliable determination. No peak corresponding to op'-DDT, dieldrin or heptachlor was observed in any sample. In the case of aldrin in fish, all samples had concentration less than the detection limit (0.01 ng).

From the results obtained (Tables III and V) it is possible to see that the N. Aegean Sea is characterized by a high value of PCB's (406,6 µg/kg F.W. in M. galloprovincialis) while the total DDT in the same organisms is relatively low



(22,9 µg/kg F.W.). Significant concentrations of PCB's were obtained for the organisms from Thermaikos gulf. These are probably due to the presence of local sources of pollution. The concentrations of pesticides (DDT, etc.) in the marine organisms from the polluted areas close to the agriculture outlet (e.g. Kavala gulf) are higher than other areas. Generally, local urban and industrial wastes seems to be the main sources of the pollution by chlorinated insecticides and polychlorinated biphenyls in the areas studied.

There are few results reported for the organochlorinated residues in Mytilus galloprovincialis and M. barbatus from the Mediterranean. The total DDT values reported for Saronikos Bay, and other regions of the Mediterranean are between 3 and 116 µg/kg for Mytilus galloprovincialis and between 8 and 138 µg/kg for M. barbatus, while PCB concentration varied from 300 to 9770 µg/kg, Satsmadjis and Gabrielides (1977), Mestres (1978). Finally, marine organisms from the higher trophic levels (e.g. Thunnus thynnus) were found to be more polluted than the organisms from the lower (e.g. M. galloprovincialis).

It can thus be concluded that an understanding of chlorinated hydrocarbons pollutants regarding their types and concentrations, depends on background information on compounds consumed, their tendency for biomagnification or biodegradation and perhaps seasonal variations. Further studies are still needed to clarify the present picture and to help in predicting the future.

#### PUBLICATIONS

JOHNSON, J.Y. (1965). Collaborative study of a multiple detection method for chlorinated pesticides residues in fatty foods. J.A.O.A.C. 48: 668.

JENSEN, S., RENBERG, L. and WESTLAKE, W.E., (1973). Problems in the quantification of PCB in biological material PCB conference. 2. Publ. Natl. Swed. Environm. Protect. Board (4 E): 7.

SATSMADJIS, J. and GABRIELIDES, G.P., (1977): Chlorinated Hydrocarbons in Striped Mullet (Mullus barbatus) of Saronikos Bay. Thalassographica 1(2): 151.

MESTRES, R., (1978): Baseline Studies and Monitoring of DDT, PCB's and other Chlorinated Hydrocarbons in Marine Organisms, FAO Circ. gen. Fish. Coun. Mediter. 7 May 1978 p. 30.

DUJMOV, J., VUCETIC, T., PICER, M. and PICER, N., (1978). Some results of monitoring of Chlorinated hydrocarbons in organisms from Central Adriatic: Ives J. Etud. Poll. pp 137.

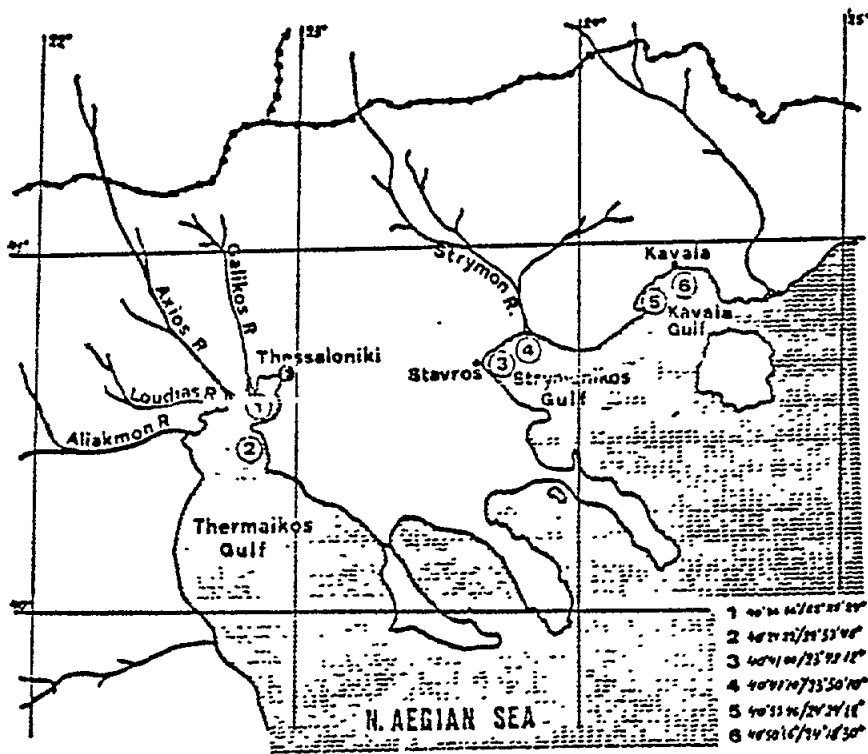


Fig. 1. Areas studied

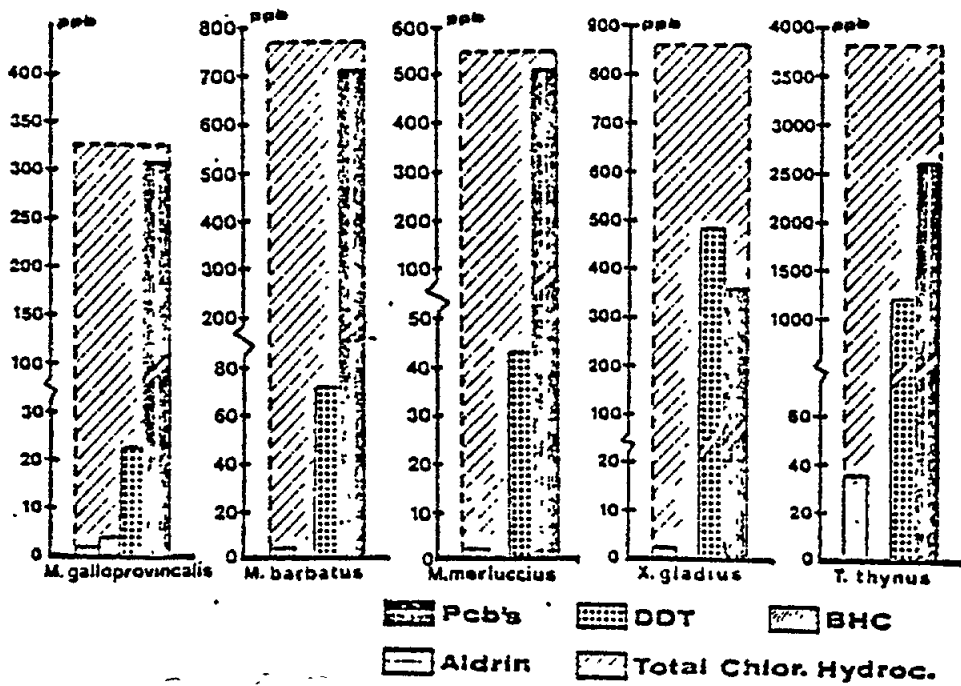


Fig. 2. Results for samples taken at stations indicated in Fig. 1

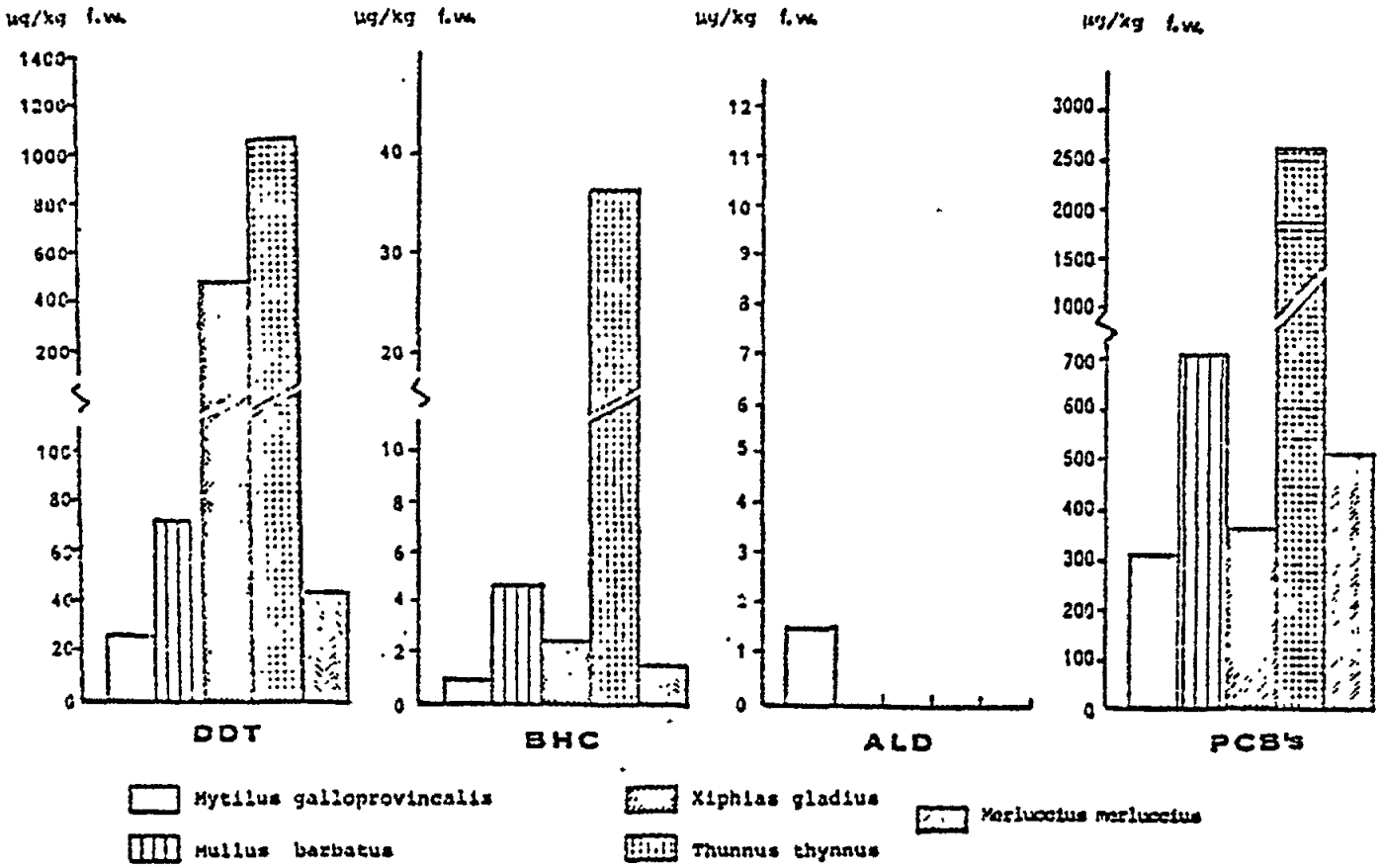


Fig. 3. Results for samples taken at stations indicated in Fig. 1

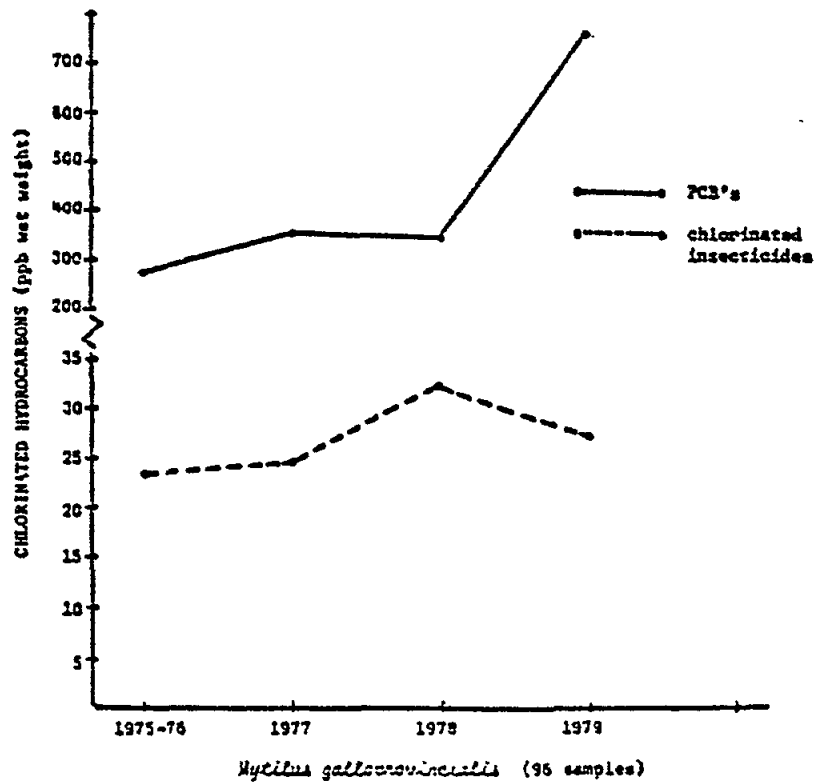


Fig. 4. Annual variation in concentrations

Table I  
Chlorinated Hydrocarbons in Mytilus galloprovincialis (ppb wet weight)

CHLORINATED HYDROCARBONS	THERMAIKOS GULF (40 samples)	STRYMONIKOS GULF (20 samples)	'KAVALA GULF ( 36 samples)
DDE	5.6 (95)*	7,9 (95)	13,6 (97)
DDD	3,5 (87)	7,4 (95)	8,6 (86)
DDT	4,8 (80)	6,3 (90)	11,2 (92)
TOTAL DDT	13,8	21,7	33,5
ALDRIN	0,5 (17)	0,7 (85)	2,8 (38)
BHC	1,3 (47)	1,5 (20)	0,6 (42)
PCB's	340,1 (97)	261,2 (75)	287,7 (97)

Table II  
Chlorinated hydrocarbons in Mullus barbatus (ppb wet weight)

CHLORINATED HYDROCARBONS	THERMAIKOS GULF ( 12 samples)	STRYMONIKOS GULF ( 12 samples)	KAVALA GULF (10 samples)
DDE	29,8 (92)	31,3 (92)	56,6 (100)
DDD	9,0 (83)	10,7 (92)	25,9 (90)
DDT	12,4 (83)	12,2 (92)	33,3 (90)
TOTAL DDT	51,1	54,2	115,8
ALDRIN	∅	∅	∅
BHC	7,5 (75)	2,6 (67)	2,9 (80)
PCB's	229,9 (100)	1613,2 (100)	178,7 (100)

\* Positiveness per cent

T A B L E III

CHLORINATED HYDROCARBONS IN MARINE ORGANISMS FROM N.AEGEAN SEA (ppb wet weight)

CHLORINATED HYDROCARBONS	<i>Mytilus galloprovincialis</i>				<i>Merluccius merluccius</i>		<i>Xiphias gladius</i>		<i>Thunnus Thynnus</i>	
	( 96 samples)	( 34 samples)	( 6 samples )	( 2 samples )	( 4 samples)	( 4 samples)	( 4 samples)	( 4 samples)	( 4 samples)	( 4 samples)
D DE	9,1 ± 10,0	38,2 ± 54,0	17,9	194,5	601,4					
D DD	6,3 ± 6,9	14,6 ± 22,9	9,9	46,4	323,2					
D DD	7,7 ± 8,5	18,5 ± 25,8	15,5	205,3	315,2					
TOTAL DDT	22,9 ± 21,9	71,3 ± 100,0	43,2	446,2	1014,7					
BHC	0,9 ± 1,4	4,4 ± 8,9	1,5	2,4	36,8					
A LDRIN	1,4 ± 3,4	∅	∅	∅	∅					
P C B's	307,5 ± 331,9	703,1 ± 287,3	510,0	363,7	2613,2					

T A B L E IV

ANNUALLY VARIATIONS IN THE LEVELS OF CHLORINATED HYDROCARBONS IN *M.galloprovincialis* AND *M.barbatus*(ppb wet weight)

CHLORINATED HYDROCARBONS	<i>Mytilus galloprovincialis</i>				<i>Mullus barbatus</i>			
	1075-76 (40)	1977 (10)	1978 (23)	1979 (23)	1976 ( 6 )	1977 ( 4 )	1978 (12)	1979 (12)
D DE	9,0	9,3	11,2	8,5	118,2	26,9	29,4	10,9
D DD	3,4	9,3	10,9	6,4	41,2	10,7	10,7	6,4
D DT	7,8	3,5	8,3	10,0	49,1	9,1	16,5	8,2
TOTAL DDT	20,2	22,1	30,4	24,5	208,5	46,7	56,6	25,5
BHC	∅	1,5	1,6	2,1	∅	14,3	5,3	2,3
A LDRIN	3,1	∅	∅	0,8	∅	∅	∅	∅
P C B's	267,1	350,1	341,4	575,3	47,7	4,341,5	227,3	293,5

\* Number of samples

T A B L E V

CHLORINATED HYDROCARBONS IN MARINE ORGANISMS FROM  
NORTH AEGEAN SEA (ppb wet weight) DURING 1980

CHLORINATED HYDROCARBONS	<i>Mytilus</i> <i>galloprovincialis</i> (12 samples)	<i>Mullus</i> <i>barbatus</i> (3 samples)	<i>Merluccius</i> <i>merluccius</i> (3 samples)
DDE	5.2	6.4	10.7
DDD	3.1	4.6	7.9
DDT	5.8	4.3	10.8
Total DDT	14.1	15.3	29.4
BHC	1.3	1.1	1.9
Aldrin	0.5	0.5	Ø
PCB's	406.6	374.3	271.6

Research Centre: Institute of Oceanographic and Fisheries  
Research  
GR- 166 04 Hellinikon,  
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Principal Investigator: J. SATSMADJIS

Reporting period: September 1975 - March 1980

## INTRODUCTION

The beginning of activities related to the analysis of chlorinated hydrocarbons in marine organisms coincided with the Institute's intention to participate in MED POL. This work contributes to the more general effort for the determination of the levels of pollution in the Greek marine environment.

### Area studied:

#### Saronikos Gulf (Fig.1):

Athens and the heavily industrialized area are situated north of the Gulf. Peloponissos lies on the west and the Attiki peninsula on the east. The east-west and north-south dimensions of the Gulf are about 50 km each. Its depth does not exceed 200 m, except in the outer Gulf and the western basin near Epidavros, where it exceeds 400 m. Aegina Island is situated in the centre of the Gulf and Elefsis Bay, an enclosed shallow basin, is formed between Salamis Island and the Attiki mainland in the north.

The Gulf is polluted by the domestic and industrial effluents of the Athens metropolitan area and the Piraeus harbour activities. The effects of pollution are obvious near the sewage outfall and in the Elefsis Bay, where, in summer, dissolved oxygen concentrations may reach zero near the sea bottom. Nutrient concentrations are about four times higher than in the open Gulf, where average values are 2.5  $\mu\text{g-at/l}$  for silicates, 1.5  $\mu\text{g-at/l}$  for inorganic nitrogen ( $\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$ ) and 0.15  $\mu\text{g-at/l}$  for phosphates.

The salinity in the open Gulf is  $38.3 \pm 0.5\text{‰}$  and the oxygen content near saturation. The temperature in the surface layer varies throughout the year from 15 to 25°C, but, near the bottom, where the fish samples were taken, it remains almost constant around 15°C.

## MATERIAL AND METHODS

### Species studied:

Only the obligatory species were used for analysis, i.e. the fish Mullus barbatus, the mussel Mytilus galloprovincialis and the shrimp Parapenaeus longirostris.

### Pollutants analysed:

The multi-residue method was used for analysis and, therefore, apart from the obligatory chlorinated hydrocarbons (PCBs and DDT) and its metabolites (DDE and DDD) and dieldrin, the following have also been included: aldrin, heptachlor, heptachlor epoxide, endrin,  $\alpha$ -BHC and  $\gamma$ -BHC (lindane).

## METHODOLOGY

Mullus barbatus and Parapenaeus longirostris were fished with bottom trawlers. Mytilus galloprovincialis were picked from a single station in Elefsis Bay. All precautions were taken to avoid contamination, especially from plastic materials. The samples were kept in glass jars and deep-frozen until preparation and lyophilization. Sample preparation was carried out according to the procedure outlined in FAO Fisheries Technical Paper No. 158.

The lyophilized material was Soxhlet extracted with N-hexane and the analysis method followed was basically that of Holden and Marsden (1969), J.Chromatog., 44:481-92. An aliquot of the hexane extract was cleaned up by column chromatography on alumina and the chlorinated hydrocarbons were fractionated on a silica column before gas chromatography. The first fraction was eluted with N-hexane and the second with 20% ether in hexane. The GC column used for the first samples was coated with 3% OV-1, but, later, with a mixture of OV-210 (1.95%) and OV-17 (1.5%). The detector was a Ni<sup>63</sup> ECD and the chromatograph was run isothermally at 200°C. The identification and quantification of the constituents was made by comparison with known standards. The quantitative determination of PCBs was carried out by reference to Aroclor 1254 or 1260 (rarely 1242), depending on the chromatogram. The destruction method with concentrated H<sub>2</sub>SO<sub>4</sub> and that of saponification with alcoholic KOH were used for confirmation purposes.

### Intercalibration exercise:

The Institute participated in the intercalibration exercise, analyzing all three samples received.

## RESULTS

As has already been stressed in the progress report of October 1979, the gas chromatograph was out of order for a long time and no analyses were carried out during 1979. In fact, all the data presented here cover the sampling period before and during 1977 and early 1978. All concentrations are given in µg/kg fresh weight.

### Chlorinated hydrocarbons in Mytilus galloprovincialis:

All samples were collected from a single station in Elefsis Bay (Station M).

Constituent	Minimum	Maximum	Mean	Standard deviation
PCBs	41	76	63	15 or 25%
ΣDDT	6,9	18.2	11.4	4.9 or 43%

No conclusions concerning variations by sex, size or season can be drawn.



Chlorinated hydrocarbons in Mullus barbatus:

The table below refers to the Saronikos Gulf as a whole.

Constituent	Minimum	Maximum	Mean	Standard deviation
PCBs	4	1 110	185	248 or 134%
Σ DDT	9	390	96	86 or 90%

Constituent	Station A			Station B			Station C		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
PCBs	63	1110	319	4	90	38	16	124	83
Σ DDT	39	390	136	9	58	30	34	122	78

It is obvious from the above that the concentrations for station A are higher than those for station C, which, in turn, are higher than those for station B.

Chlorinated hydrocarbons in Parapenaeus longirostris:

The table below refers to the Saronikos Gulf as a whole.

Constituent	Minimum	Maximum	Mean	Standard deviation
PCBs	3.3	32	19	8.8 or 46%
Σ DDT	1.7	4.1	3.3	0.8 or 25%

The number of samples is limited and, therefore, no conclusions can be drawn concerning variations by area, size, sex or season.

The averages of all concentrations obtained since starting the project are shown in the attached table.

## DISCUSSION OF RESULTS

The following observations can be made:

- Mullus barbatus exhibits much greater concentrations than the other two species;
- PCBs and  $\Sigma$ DDT predominate in all samples;
- Dieldrin, BHC (all isomers) and endrin were found in small concentrations;
- Aldrin, heptachlor and heptachlor epoxide were not always detected or in very small quantities;
- The area nearest to the sources of pollution presented the highest values.

For the data obtained on Mullus barbatus, which are more numerous than for the other species, the following can also be noted:

- No significant differences were observed between seasons. There is an indication, though, that spring values are the highest;
- For the samples collected near the sewage outfall, there is a perfect relationship between lipids (% EOM) on the one hand, and PCBs, DDE, DDD and  $\Sigma$ DDT on the other;
- The ratios of PCBs to  $\Sigma$ DDT and of DDD to  $\Sigma$ DDT are higher in the area near the sewage outfall than those further away;
- There is an indication that the residue levels increase with the length of the fish and the lipid content;
- Of the three fractions of  $\Sigma$ DDT, DDE was usually the major one and DDD always the smallest.

The concentrations of chlorinated hydrocarbons found can be considered as relatively low, taking into consideration the fact that, in some areas of the world, reported values are one order of magnitude higher. Such high values have been found in the Mediterranean (GFCM Circular No. 7, Report No. 3, May 1978).

The reported results are comparable with those reported from Spain and Yugoslavia.

## PUBLICATIONS

SATSMADJIS, J. and GABRIELIDES, G.P., (1977). Chlorinated hydrocarbons in striped mullet (Mullus barbatus) of Saronikos Bay. *Thalassographica*, 1:151-4

SATSMADJIS, J., and Gabrielides G.P. (1979). Observations on the concentration levels of chlorinated hydrocarbons in a Mediterranean fish. *Marine Pollution Bulletin*, 10(4):109-11

SATSMADJIS, J. and GABRIELIDES, G.P. (1983) Organochlorines in Mussel and Shrimp from the Saronikos Gulf (Greece). *Marine Pollution Bulletin*, 14 (9): 356-358.

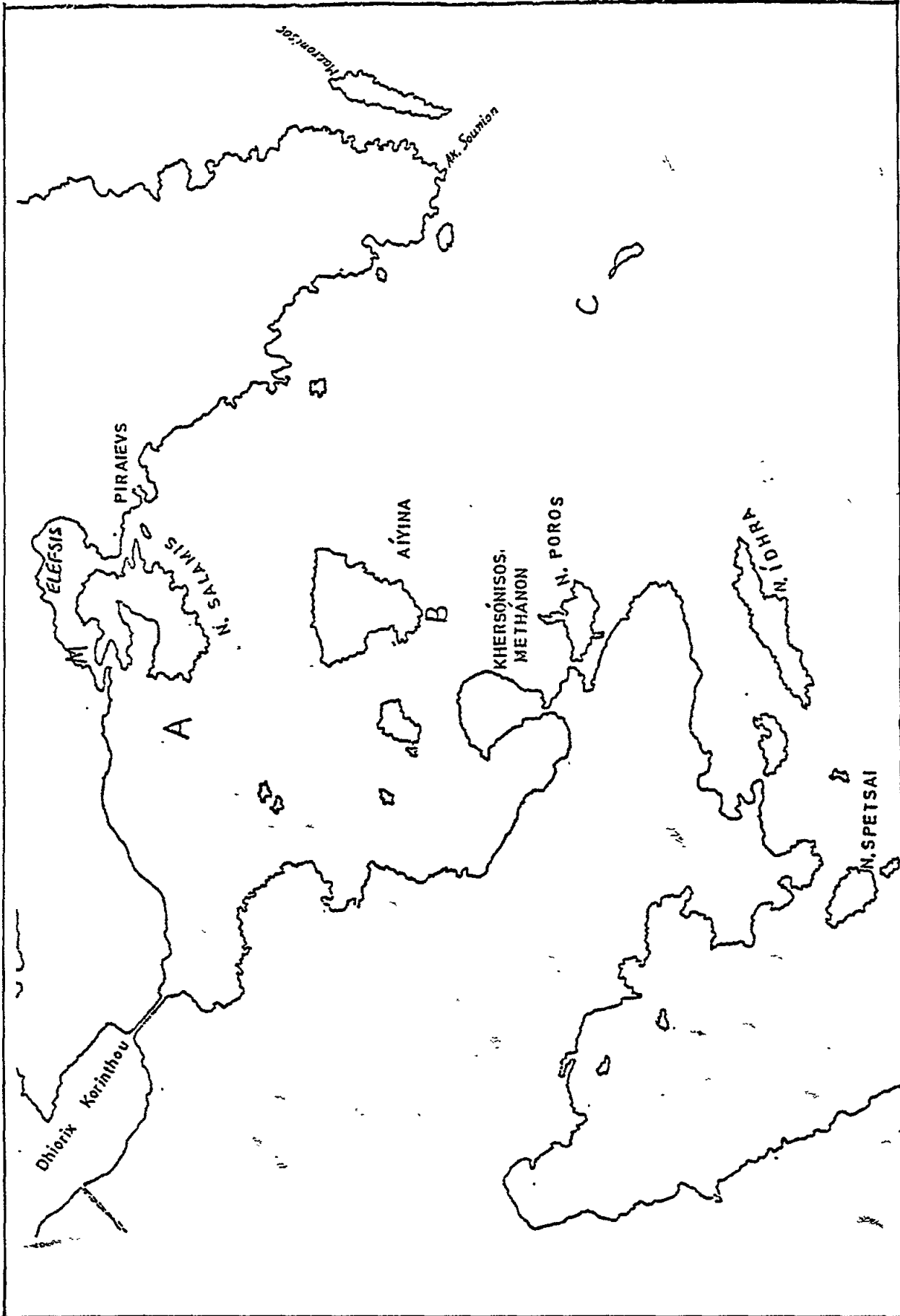


Fig. 1. Map of Saronikos Gulf

Table  
Chlorinated Hydrocarbons Averages  
(ppb/fresh weight)

Mullus barbatus

Stat Or Area	No of Samp	Hexane Extract %	PCB <sub>s</sub>	DDE	DDT	DDD	Σ DDT <sub>s</sub>	Σ HCH <sub>s</sub>	Hept Epoxy	Dieldrin	Endrin
NE	4	4.24	473	72	78	66	217	5.6	0.3	17.0	0.4
NE+NS	5	2.92	175	30	20	12.4	624	5.6	0.3	2.4	1.5
A	5	1.79	29	9.8	5.6	3.1	18.5	1.2	0.2	0.5	0.3
B	7	3.68	39	15.5	9.6	4.4	29.5	5.1	0.3	1.3	1.0
C	9	2.41	70	31.7	25.6	4.1	62.4	2.5	0.5	1.0	1.1

Parapenaeus longirostris

N <sub>3</sub>	2	0.60	25	1.8	0.7	0.2	2.8	0.8	0.2	0.3	0.3
A	7	0.77	10.8	2.3	0.3	0.3	2.9	0.5	0.1	0.2	0.1
B	5	0.72	13.5	1.9	0.4	0.5	2.8	0.4	0.1	0.3	0.2
C	1	0.69	5.3	0.9	0.1	0.4	1.4	0.3	0.0	0.2	0.2

Mytilus galloprovincialis

A	6	1.25	67	5.4	3.3	3.2	11.9	3.0	0.0	1.5	0.7
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Research Centre:            Laboratory of analytical Chemistry  
                                 Faculty of Physics and Mathematics  
                                 University of Thessaloniki  
                                 THESSALONIKI  
                                 Greece

Principal investigator:    G. VASILIKIOTIS

No report has been submitted by the research centre.

f

Research Centre: Israel Oceanographic and Limnological  
Research Ltd.  
HAIFA  
Israel

Principal Investigator: R. RAVID

Reporting period: October 1975 to December 1979

(The final report was not prepared by the Principal Investigator, and the information given below is taken from the previous report (April 1979) and other available information).

#### INTRODUCTION

There is no information about the previous experience of the research centre in the analyses of chlorinated hydrocarbons in marine organisms. Accordingly, it is assumed that the analyses were started with this pilot project.

#### METHODOLOGICAL CONSIDERATIONS

##### Selection of the species:

The most common species of fish from the commercial catches were selected, as well as some species recommended by the project document. The fish examined were: Mullus barbatus, Mullus surmuletus, Upeneus moluccensis, Dentex macrophthalmus, Merluccius merluccius, Pagellus erythrinus, Pagellus acarne, Boops boops, Trachurus mediterraneus, Conger conger, Saurida undosquamis, and the shrimp Parapenaeus longirostris.

##### Pollutants analysed:

DDTs (p-p DDE + p-p DDD + p-p DDT); PCBs (Aroclor 1242 + Aroclor 1254 + Aroclor 1260); BHC ( $\alpha+\gamma$ ) and Aldrin.

##### Areas studied:

The sampling stations are shown in Figure 1.

#### METHODOLOGY

Samples were collected by commercial trawl nets. The methods of collecting and handling followed instructions in FAO Fisheries Technical Paper No. 158. Preparation of the samples for analyses was done according to Erney (1974).

The measurements for the pesticide concentrations were taken on Packard series 14092, with dual Electron Capture Gas Chromatograph. The column was filled with 10 per cent DC-100 on Gas Chrom Q. The temperature of the column was 205°C, temperature of detector 210°C and injector 210°C, N<sub>2</sub> flow - 30 ml/min.

The average recovery of DDTs was 98 per cent, PCBs 96 per cent, BHC ( $\alpha+\gamma$ ) 90 per cent and Aldrin 97 per cent. Standards were injected routinely every day and reagent blank control was processed through the clean-up procedure every

two days. Calibration graphs for appropriate standard solutions were produced daily. The analysis of PCBs given in this paper was obtained by comparing the sum of the peak heights in the sample with the sum of the heights of the corresponding peaks of standard PCBs. Calculations of residue concentrations were based on wet weight of samples.

#### Intercalibration exercise:

The research centre participated in the following exercises: oyster (MA-M-1), copepod (MA-A-1) and fish (MA-M-2).

#### DISCUSSION OF RESULTS

The concentrations of total DDTs (DDE + DDD + DDT), total PCBs (Aroclor 1242 + Aroclor 1254 + 1260), BHC ( $\alpha$ + $\gamma$ ) and Aldrin were determined in the edible parts of the fishes and invertebrate tissues. Mean concentration values in relation to year and area are given in Table I. Ranges and means for each species of the marine organisms for the years 1975-77 are shown in Table II, and for the year 1979 in Table III.

It can be seen from these results that DDTs were found in all the samples investigated and, except for one sample of Mullus barbatus, all samples included PCBs as well. BHC was found in 75 per cent of the samples and Aldrin only in 40 per cent.

Figure 2 illustrates the relationships between the concentrations of DDTs and the length of the organisms. Figure 3 shows the relationships between the concentrations of PCBs and the length of the organisms.

#### Fish:

Mullus barbatus: No changes in the pesticide concentrations in this species were found along the sampling stations (Table I). The relationship between DDT concentrations and the total length of this species for the years 1975-77 shows an increase in the concentration with length (Figure 2). The positive correlation of DDT concentration to total length was significant at the 1 per cent level for 1976 and at the 5 per cent level for 1977. The correlation was not significant for the year 1975 (Figure 2).

The relationship between the PCB concentration and the total length of Mullus barbatus for the years 1975-77 shows a slight increase with length, but the correlation was not significant (Figure 3).

Upeneus moluccensis: From the few data for this species (Table I), the concentrations of pesticides seem to be highest around the Tel Aviv area. Because of the missing data for Ashgelon, no comparison can be made between all sampling stations.

From the results obtained, an inverse relationship was found between DDT and PCB and the total length of the fish. The negative correlation for DDTs was highly significant, and for PCBs was not significant.

Pagellus erythrinus: Concerning the sampling areas, no description or comparison can be made because of absent data (Table I). From Figures 2 and 3, an inverse relationship can be seen between the concentrations of DDTs and PCBs and the total length of the fish, but this was not significant.

Saurida undosquamis: Variations in the pesticide concentrations along all the sampling stations are irregular (Table I). The PCB values in this species are the highest in comparison with the other species (Table I). The relationship between the DDT and PCB concentrations and the total length of Saurida undosquamis is illustrated in Figures 2 and 3. A marked increase in concentration levels can be observed with increase in length. This positive correlation was significant.

Maena maena: From the few data presented in Table II, no conclusions can be drawn regarding this species.

#### Invertebrates:

From the results of pesticide concentrations in Parapenaeus longirostris and Carcinus mediterraneus (Tables I, II and III), it can be observed that the values obtained are much lower than those of the fish. It was noted that in 25 per cent of the Parapenaeus longirostris, no concentrations of pesticides were found. There was no correlation between DDT concentration and body length of the Parapenaeus longirostris, but there was a significant negative correlation between the PCB concentration and the body length (Figures 2 and 3).

The purpose of this preliminary study was to determine the presence of pesticides in marine organisms and their ranges. From the results obtained, it can be seen that the values of pesticides in the invertebrates are much lower than in the fish samples.

The results of pesticides in Mullus barbatus for the year 1976 are compared to results given for other areas in the world (Table IV). It seems that, during this year, the values are slightly higher than those for other regions (FAO, 1977).

There was a decrease in the concentration during 1977, but no data for this year on Mullus barbatus are available for comparison purposes.

To explain the negative and positive correlations between the pesticide concentrations and total lengths of the organisms, a better system of sampling is needed. The samples should represent a wider size range and include many specimens for each species.

#### REFERENCES

BERNHARD, M. (1976). Manual of methods in aquatic environment research. Part 3. Sampling and analysis of biological material. FAO Fish. Tech. Pap., (158):124 p.

ERNEY, D.R. (1974). Rapid screening method for analysis of chlorinated pesticides and polychlorinated biphenyls residues in fish. Journal of the AOAC, 57(3):576-9.

FAO (1975). Manual of methods in aquatic environment research. Part 1. Methods for detection, measurement and monitoring of water pollution. FAO Fish. Tech. Pap., (237):238 p.

FAO (1977). Compilation of progress reports submitted by research centres participating in the pilot projects MED POL II and MED POL III. FIR/PM/77/7, 29 p.

U.S. Department of Health, Education and Welfare, Food and Drug Administration, Pesticide analytical manual, Vol.1.



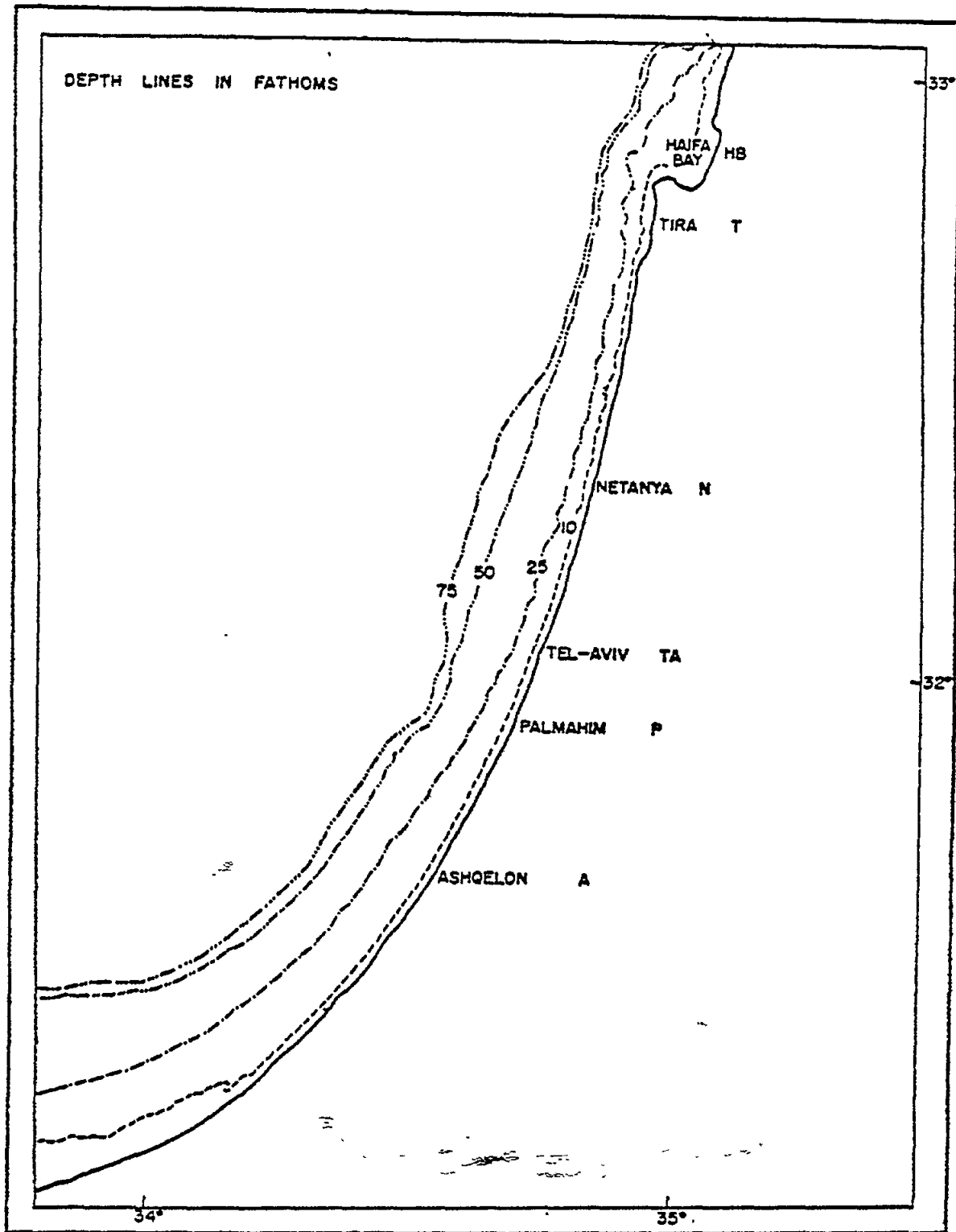


Fig. 1. Sampling stations for MED projects

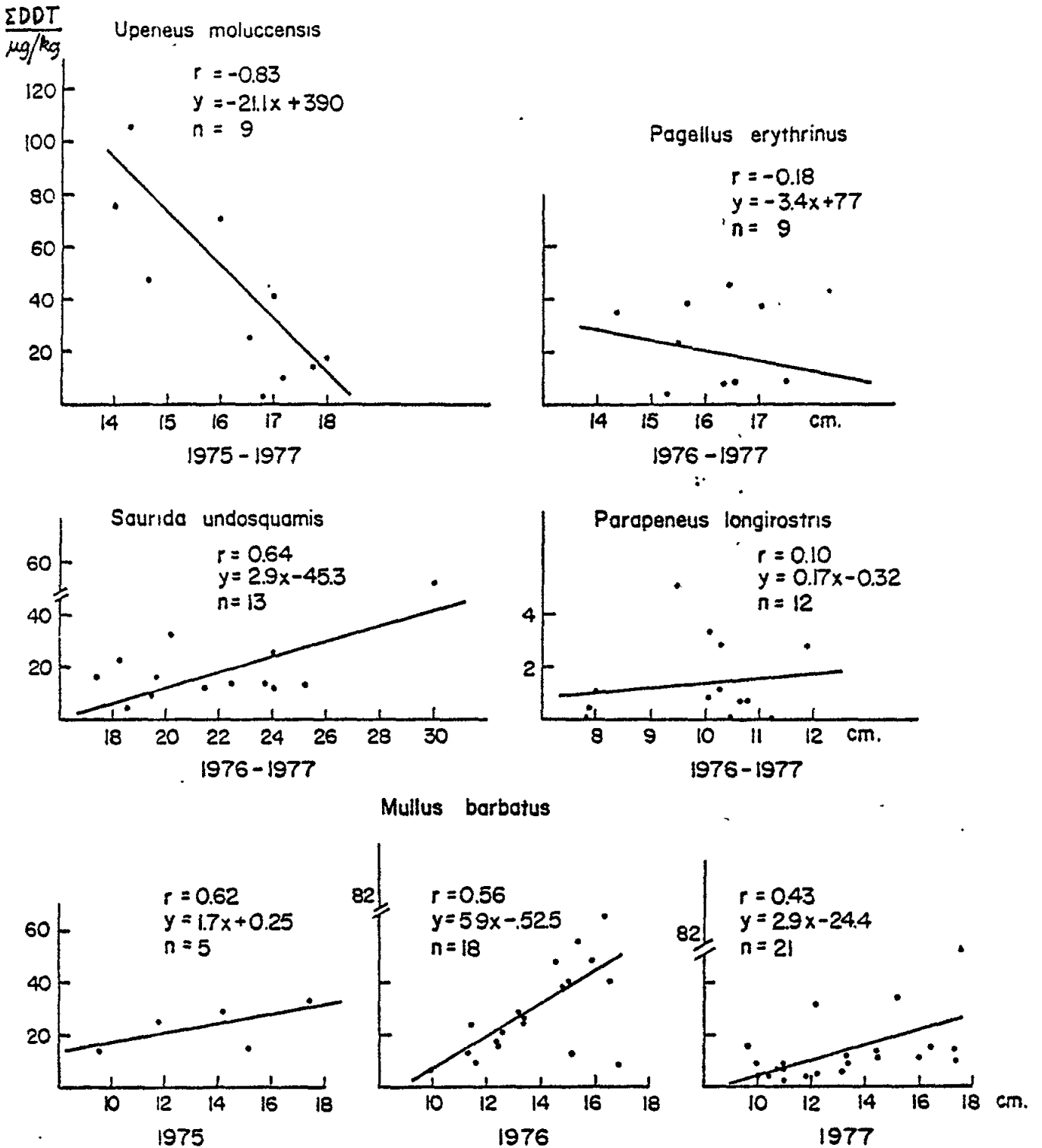
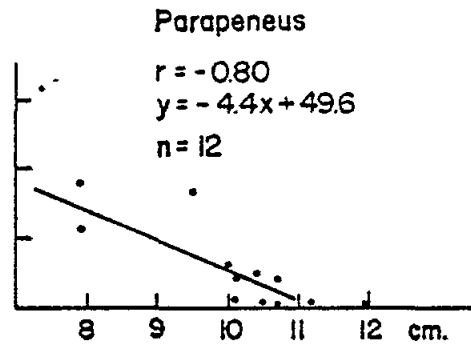
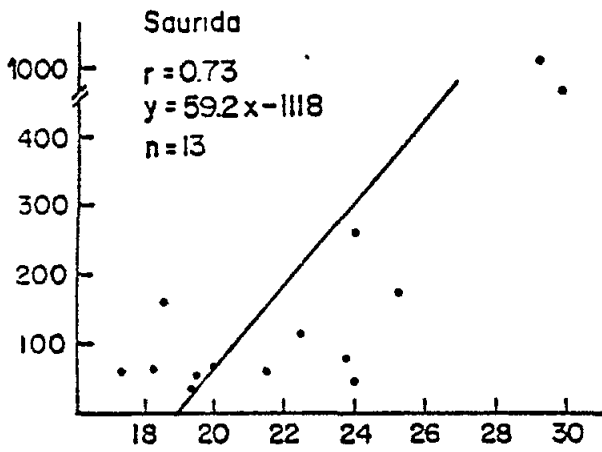
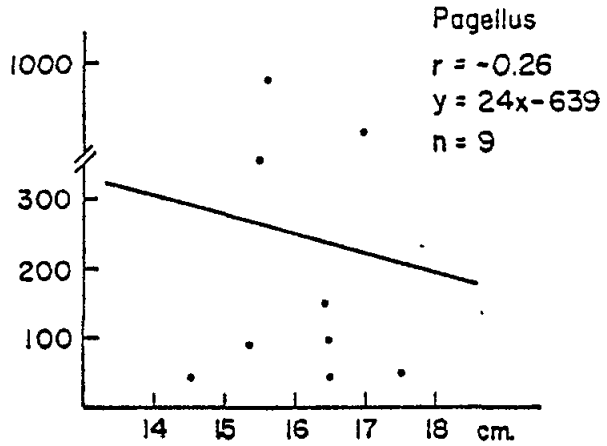
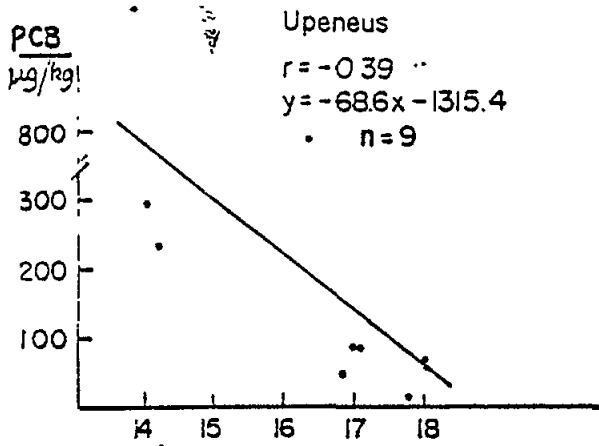


Fig. 2 Relationship between the content of EDDTs and the length of the organism.



Mullus barbatus

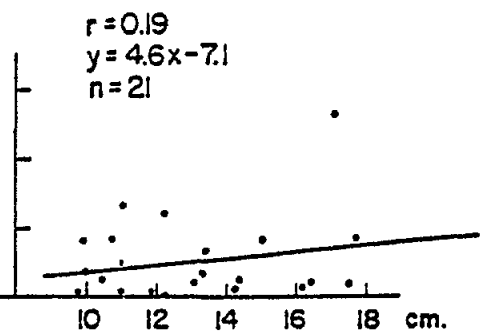
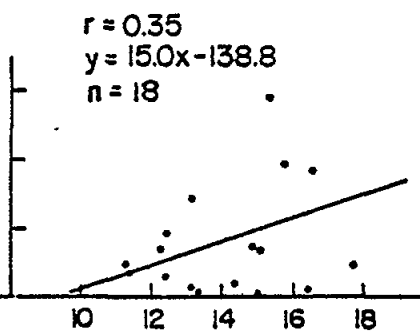
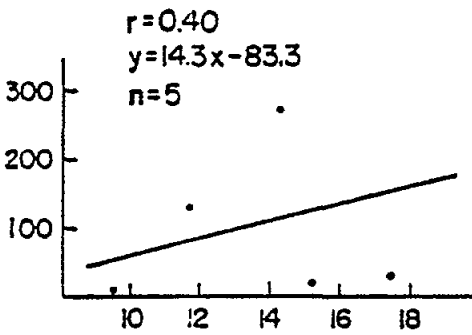


Fig. 3 Relationship between the content of PCBs and the length of the organism.

Table I. Mean concentrations of pesticides in fish and invertebrate samples (ng/g wet weight) along the Mediterranean shore of Israel

Year	T i r a			N o t a n y a			T a l - A v i v			P a l m a h i m			A s h d o d							
	No.	LBHC	EPCU	No.	LBHC	EPCU	No.	LBHC	EPCU	No.	LBHC	EPCU	No.	LBHC	EPCU					
<u>Mullus barbatus</u>																				
1975	10	30.0	7.0	8	16.0	0	17.4	10	29.2	11.3	268.3	-	-	-	9	14.4	0	0		
1976	43	30.23	2.2	31	29.18	4.48	72.58	18	20.5	1.3	92.2	-	-	-	29	33.93	115.86	51.06		
1977	-	-	-	11	16.62	85.60	69.47	105	17.01	3.69	64.79	21	10.39	7.93	31.04	-	-	-		
1979	-	-	-	3	50.9	5.9	67.9	11	27.0	6.7	27.6	-	-	-	-	-	-	-		
<u>Upeneus moluccensis</u>																				
1975	-	-	-	-	-	-	-	10	106.1	23.5	227.8	-	-	-	-	-	-	-		
1976	2	3.1	0	46.8	1	41.3	14.0	87.0	2	75.9	2.4	297.9	-	-	-	-	-	-		
1977	-	-	-	5	25.2	8.3	87.9	5	70.5	183.3	799.6	9	14.43	10.7	33.2	-	-	-		
1979	-	-	-	7	45.8	1.8	96.3	-	-	-	-	4	76.4	12.7	133.1	-	-	-		
<u>Parallus erythrinus</u>																				
1976	4	21.0	145.25	316.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
1977	-	-	-	-	-	-	-	28	20.63	33.28	202.58	7	21.95	2.2	40.75	-	-	-		
1979	-	-	-	-	-	-	-	1	4.3	4.4	35.8	4	18.8	3.3	106.6	-	-	-		
<u>Saurida undouquale</u>																				
1976	2	32.1	143.8	1189.6	-	-	-	1	26.8	2.8	257.0	-	-	-	-	-	-	-		
1977	-	-	-	-	6	11.9	5.9	168.4	8	15.93	3.60	53.17	9	21.85	5.85	156.08	5	14.4	1.37	10.47
1979	-	-	-	-	2	37.5	ND	35.7	-	-	-	3	14.6	0.7	60.0	-	-	-		
<u>Parapeneus longirostris</u>																				
1976	-	-	-	-	69	0.80	3.55	3.55	43	1.72	1.79	0	-	-	-	36	0.90	1.38	3.84	
1977	-	-	-	-	49	4.00	36.01	8.5	34	0.28	5.57	2.64	-	-	-	32	0	3.05	18.56	
1979	-	-	-	-	-	-	-	-	27	9.9	11.4	144.2	45	2.9	11.7	157.3	-	-	-	

\* Total number of specimens in sample.

Table II. Mean values and ranges of chlorinated hydrocarbons in fish and invertebrate samples (ng/g fresh weight) for the years 1975-1977

Species	No. of fish	No. of samples	Mean length (range) (mm)	Σ DDT	PCBs	Aldrin	Σ BHC
<u>Mullus barbatus</u>	306	44	136 (85-180)	23.2 (2.9-82.9)	79.4 (0-283.7)	2.3 (0-28.5)	24.4 (0-572.0)
<u>Upeneus moluccensis</u>	34	9	165 (135-180)	58.0 (3.1-106.1)	189.7 (16.7-799.6)	0.7 (0-1.9)	24.6 (0-183.3)
<u>Pagellus erythrinus</u>	43	9	161 (153-175)	22.3 (4.9-45.0)	293.1 (40.7-993.5)	3.8 (0-22.2)	93.9 (0-282.7)
<u>Saurida undosquamis</u>	33	13	219 (175-298)	24.1 (5.1-67.9)	423.9 (31.4-1189.6)	1.9 (0-19.0)	39.1 (0-143.8)
<u>Contrachanthis maena</u>	14	5	136 (114-155)	19.5 (8.9-40.1)	91.4 (6.9-153.7)	3.6 (0-10.2)	122.0 (0-310.5)
<u>Carcinus mediterraneus</u>	99	7	25/40 (23-26/34-43)	5.8 (1.3-8.2)	54.3 (0-108.5)	1.4 (0-6.5)	45.6 (2.2-167.3)
<u>Parapeneus longirostris</u>	292	12	101 (78-119)	1.3 (0-5.2)	4.5 (0-18.6)	0.41 (0-2.2)	7.9 (0-71.1)

Table III. Mean values and ranges of chlorinated hydrocarbons in marine organisms collected during April and August 1979.  
Results in ng/g fresh weight

Species	No. of fish	No. of samples	Mean length (range) (mm)	Σ DDT	PCBs	Σ BHC
<u>Mullus barbatus</u>	14	9	156 (125-180)	34.9 (7.8-69.9)	41.0 (10.3-139.8)	6.4 (0-12.9)
<u>Mullus surmuletus</u>	3	2	148 (140-155)	13.0 (6.8-19.1)	69.2 (2.2-136.1)	6.8 (5.6-8.0)
<u>Upeneus moluccensis</u>	11	7	151 (120-182)	58.9 (7.9-120.3)	112.1 (36.4-180.2)	6.5 (0-24.2)
<u>Dentex macrophthalmus</u>	4	2	133 (130-140)	76.6 (76.0-77.2)	194.8 (48.5-341.1)	ND
<u>Merluccius merluccius</u>	3	3	213 (165-250)	28.1 (14.2-52.2)	16.4 (0-25.3)	9.6 (3.6-12.9)
<u>Pagellus erythrinus</u>	5	3	159 (145-170)	13.9 (4.3-24.1)	83.0 (35.8-168.3)	3.6 (0-6.5)
<u>Pagellus acarne</u>	1	1	150	20.8	150.6	ND
<u>Boops boops</u>	1	1	165	7.0	74.3	13.9
<u>Trachurus mediterraneus</u>	6	2	141 (125-200)	21.3 (20.8-21.8)	63.3 (26.5-100.0)	1.8 (0-3.5)
<u>Conger conger</u>	1	1	475	58.8	ND	ND
<u>Saurida undosquamis</u>	5	2	252 (240-260)	26.1 (14.6-37.5)	47.9 (35.7-60.0)	0.4 (0-0.7)
<u>Parapeneus longirostris</u>	72	2	104 (100-109)	6.4 (2.9-9.9)	150.8 (144.2-157.3)	11.6 (11.4-11.7)

Table IV . Comparison of pesticide concentrations ( $\mu\text{g}/\text{kg}$  F.W.) in Mullus barbatus on Israeli Mediterranean shores with other Mediterranean areas in 1976

Sampling area	fresh or dry weight basis	DDTs	PCB	BHC
Barcelona	W.W.	243.90	1 291.9	-
Venice	D.W.	89.0	225.8	22.7
Malta	W.W.	18.9	72.2	2.87
Turkey	W.W.	5.44	0.40	-
Israel	W.W.	30.9	71.5	53.43

Research Centre: Istituto di Biologia del Mare  
CNR  
VENEZIA  
Italia

Principal Investigator: V. U. FOSSATO

Reporting period: June 1976 to December 1980

## INTRODUCTION

As from 1972, the Institute has had a laboratory equipped for gas chromatographic analysis of organic pollutants in marine waters and organisms.

At first, the field of research was limited to control the levels of oil pollution in the Laguna Veneta and to study the effects of hydrocarbons on selected organisms. In the second half of 1975, the activities were extended to include the analysis of chlorinated hydrocarbons in organisms collected from the Adriatic Sea in the framework of the FAO (GFCM)/UNEP Joint Co-ordinated Project (MED POL III). At the same time, the Institute was participating in a national programme for monitoring of chlorinated hydrocarbons in edible organisms collected along the Italian coasts. The data accumulated by these activities are considered of relevant interest by national authorities in evaluating the levels of marine pollution and the health risk associated with consumption of fishery products.

## MATERIAL AND METHODS

The work was executed according to the general methodology outlined in the Operational Document developed at the FAO (GFCM)/UNEP Expert Consultation (FAO/UNEP 1975).

### Species selected:

Mussels (Mytilus galloprovincialis), striped mullets (Mullus barbatus), and Mediterranean shore crabs (Carcinus mediterraneus).

Other species analysed: Engraulis encrasicolus, Sardina pilchardus, and Penaeus kerathurus.

Chlorinated hydrocarbons analyzed: Polychlorinated biphenyls (PCB), Dichloro-diphenyl-trichloroethane (DDT), Dichloro-diphenyl-dichloroethane (DDD), Dichloro-diphenyl-dichloroethene (DDE),  $\alpha$ ,  $\beta$  and  $\gamma$  isomers of the Hexachlorocyclohexane (BHC), aldrin, dieldrin.

### Sampling areas:

Two sampling areas were chosen in the Adriatic Sea far from direct pollution sources: the first is located in the Gulf of Venice (northern Adriatic), the second is in the central Adriatic Sea near Ancona (Fig.1).

In the Gulf of Venice the annual variation of temperature, related to the shallow depth, was between 6.5° to 26.1°C. The salinity, which varied between 29.8‰ and 38.2‰, is influenced by the thermal stratification and the



inflow of rivers (Franco, 1967; Cioce, et al, 1979). The second sampling area was selected about twelve miles south-east of Ancona, three miles from the coast, where an artificial park has been in existence for some years now. Although this area is far from industrial areas and the inflow of rivers, it is influenced by the current descending along the Italian coast, which conveys and dilutes the fresh waters coming from northern Italy; in fact, the salinity varied from 26.7‰ (surface waters) to 37.9‰ (deep waters), while the annual variation of temperature was between 7.5° and 24.5°C (Artegiani, et al, 1979).

#### METHODOLOGY

In the Gulf of Venice the mussels were collected seasonally at a depth of 8-10 m from non-metallic structures of a survey platform about eight miles offshore. The striped mullets and the Mediterranean shore crabs were caught by bottom trawl nets at a depth of 10-15 m in a fishing area near the coast. Mussels and crabs are present in this area throughout the year, while mullets are absent in the cool season. In the central Adriatic near Ancona, the mussels were collected seasonally by divers at depths 8 to 10 m from the concrete blocks of the artificial park, while the mullets were fished with bottom trawl nets in the adjacent area. The crabs were collected from inside the harbour of Ancona, since they are absent either in the open sea or along the coast.

The samples, collected offshore near Venice and Ancona and destined to be used for the analysis of metals, were sent to the Laboratorio per la Contaminazione Marina, CNEN, Fiasherino, which in return sent the samples collected in the Gulf of La Spezia.

For collection, storage and preparation of samples for analysis of chlorinated hydrocarbons, the suggestions listed in the FAO Fisheries Technical Paper No. 158, 1976 were followed. Composite samples were prepared for routine analysis, recording the relevant biometric characteristics of the organisms (length and weight). The flesh obtained from organisms (the soft parts of mussels, the skinned fillets of mullets, the muscle tissue of chelae of crabs) was blended and freeze-dried. The ratio between the wet-weight and the dry-weight (105°-110°C) was determined on an aliquot of flesh of each composite sample.

Extraction of the chlorinated hydrocarbons was accomplished by refluxing about 5 g of the freeze-dried sample in a Soxhlet apparatus for eight hours with n-hexane. The solvent was removed by evaporation under reduced pressure at a temperature not higher than 50°C and the weight of the extractable organic matter (EOM) was determined. Coextracted substances were removed using the general method of partitioning between n-hexane and acetonitrile (FDA, Pesticide Analytical Manual 1971, section 211, 14a), then the clean-up of extracts was completed by elution with n-hexane on a small column of florisil. The separation of PCBs from DDT and its metabolites was then achieved by chromatography on a silicagel column according to the procedure of Snyder and Reinert (1971): the column was washed with n-hexane (40 ml) which elutes the PCBs, followed by benzene (50 ml), which retains DDT, DDD, DDE and other chlorinated pesticides.

Analyses were carried out using a Hewlett-Packard 5750 G gas chromatograph equipped with a Ni<sup>63</sup> electron capture detector. Glass columns, 180 cm long x 0.64 cm o.d., packed with 5% DC 200 (apolar phase) on Gas Chrom Q BW-DMCS

100-120 mesh, were used. In order to separate the dieldrin from DDE, the benzene fraction was also chromatographed on a glass column packed with 5% QF-1 (polar phase) on high performance Chromosorb W AW-DMCS. Quantification was based on measuring peak heights; solutions of pure compounds were used as reference standards. For DDT, DDD and DDE the pp' isomers were utilized, for PCBs the commercial products traded under the name of Aroclor 1254 and Aroclor 1260 (Monsanto Company, USA) were used.

#### Intercalibration programme:

From July 1976 to January, 1977 three samples (oyster, copepod and fish homogenates) were obtained from the IAEA Laboratory, Principality of Monaco, and analysed for chlorinated hydrocarbon content in the framework of the intercalibration exercise.

#### RESULTS AND THEIR INTERPRETATION

Chlorinated hydrocarbon values, presented on fresh weight basis in Table I, were from analyses of organisms sampled between June 1976 and December 1980. Fresh/dry weight ratios and percentages of EOM are also reported to facilitate comparison of our data with other determinations reported in the literature. Results indicate that PCB residues predominate in all species at all stations regardless of season. The PCB Aroclor 1260 was not quantified in Mytilus samples, being only a small percentage of total PCB, but it was present in significant quantities in all other species. In all samples, measurable amounts of DDT, DDD, DDE, BHC and dieldrin were determined, while aldrin was present in minor quantities or in traces.

#### Chlorinated hydrocarbons in Mytilus galloprovincialis:

Chlorinated hydrocarbons and EOM showed considerable fluctuations during the year; maxima occurred in June and September during the active lipid accumulation period, but there was no clear evidence for a significant correlation between pesticide residue concentrations and the EOM of mussels. The  $\sum \text{PCB} / \sum \text{DDT}$  ratio was 3.2 for mussels collected from Venice and Ancona, and 5.7 for those from La Spezia. Of the three fractions of DDT, DDT was usually the major one (40 to 45 per cent), while DDD and DDE were present in approximately equal amounts. On the basis of chlorinated hydrocarbon values of mussels, the following series of increasing pollution levels can be constructed: Venice  $\triangleleft$  Ancona  $\triangleleft$  La Spezia.

#### Chlorinated hydrocarbons in Mullus barbatus:

The major part of chlorinated hydrocarbon values of mullets of the Adriatic Sea were from analyses of organisms collected during summer and autumn, and the number of samples from La Spezia were not enough for reliable conclusions about seasonal variations of pesticide residue content. A moderately significant correlation ( $p \leq 0.05$ ) was obtained between  $\sum \text{BHC}$ ,  $\sum \text{PCB}$  and the EOM of mullets from Venice and La Spezia, while conflicting results were obtained for those of Ancona. The PCBs Aroclor 1254 and Aroclor 1260 were present in approximately equal amounts in Mullus, with minor differences at the three stations. Of the  $\sum \text{DDT}$ , DDD was usually the smallest fraction, while DDT and DDE were present in approximately equal percentages. The  $\sum \text{PCB} / \sum \text{DDT}$  mean ratio was 3.5 and 3.3 for mullets collected from Venice and Ancona, respectively, and 7.7 for those from La Spezia. Results of

supplementary research, which was undertaken to verify the variability of chlorinated hydrocarbon content in single specimens of mullets sampled in the same area at the same date, are synthesized in Table II, and indicate a relatively high variability between individual organisms.

Chlorinated hydrocarbons in Carcinus mediterraneus:

Chlorinated hydrocarbon content showed considerable seasonality: maxima for PCBs and DDT occurred in September and December, minima in March and June. A moderately significant ( $0.05 > p > 0.01$ ) correlation was observed between the concentrations of EOM and PCBs in crabs from the Gulf of Venice; however, there was no evidence for such relationship for crabs from Ancona. PCBs were quantified as Aroclor 1254 and Aroclor 1260, but Aroclor 1260 always represented the smallest fraction (11 to 35 per cent). The  $\Sigma$  PCB/ $\Sigma$  DDT mean ratio was 11.5 and 12.8 for crabs collected from Venice and Ancona, respectively. With exceptions, DDE represented the major fraction (mean: 61 to 67 per cent) of total DDT, followed by DDT and DDD. The chlorinated hydrocarbon levels in crabs from Venice and Ancona are very similar, with the notable exception of PCBs, indicating the presence of local inputs in the harbour of Ancona, where the crabs were collected.

Chlorinated hydrocarbons in Engraulis encrasicolus, Sardina pilchardus and Penaeus kerathurus collected from the Gulf of La Spezia:

The data were insufficient for reliable conclusions to be drawn about seasonal variation of pesticide residue content.

DISCUSSION OF RESULTS

On the basis of all data, it seems that the amounts of organochlorine compounds accumulated by the specimens analysed were related to their lipid (EOM) content; for instance, the following series of increasing levels of chlorinated hydrocarbons (Carcinus/Mytilus/Mullus) reflect the increasing lipid content of the three species. However Engraulis and Sardina from the Gulf of La Spezia showed values comparable to those found in Mullus from the same area, although their lipid content was about half that of Mullus. Evidently, also, the food and the physiology of various organisms highly influence their accumulation capacity. This problem has been specifically studied for mussels of the Laguna Veneta, the conclusion reached being that the capability of mussels to accumulate some organic pollutants, petroleum hydrocarbons and chlorinated hydrocarbons, is highly influenced by lipid content and that the relationship is very complex owing to the different mechanism of accumulation and utilization of lipid reserve in different seasons (Nasci and Fossato, 1979).

In the Adriatic Sea no significant differences were observed between levels of chlorinated hydrocarbons in organisms collected off Venice and Ancona; indeed the current descending along the Italian coast receives and dilutes the fresh waters coming from northern Italy, which are (together with air) the most important carriers of organochlorine residues in this area. A national programme for the monitoring of chlorinated hydrocarbons in edible organisms collected along the Italian coasts began in the autumn of 1976, and represented an extension, on a national scale, of the pilot project MED POL III. Results obtained on five species (Mytilus galloprovincialis, Mullus barbatus, Engraulis encrasicolus, Nephrops norvegicus and Thunnus thynnus thynnus), collected seasonally in six different fishing areas from Trieste to

Ancona, indicate an almost uniform distribution of these compounds along the Italian coast of the Adriatic, with the notable exception of organisms collected inside the lagoons and near the mouths of the Adige and Po rivers (Fossato and Craboledda, 1979; 1979b).

Chlorinated hydrocarbon values reported for similar organisms of the Yugoslav coast of the Adriatic are generally lower, with the exception of those from some areas subjected to local pollution sources (Revelante and Gilmartin, 1975; Nazansky, et al, 1978; Dujmov, et al, 1978; Vilicic, et al, 1978).

Available data on concentrations of chlorinated hydrocarbons in organisms of the Adriatic Sea demonstrate an intermediate degree of contamination when compared to related species from other Mediterranean regions. For instance, organochlorine residue levels determined in specimens sampled in the Gulf of La Spezia were much higher than those collected in Adriatic Sea; moreover, the north-western Mediterranean coast generally seems to be more polluted than the Adriatic basin, while lower values were reported for the Tuscan Archipelago and the Central Mediterranean near the Strait of Messina (Bolognari, et al, 1978).

#### PUBLICATIONS

ARTEGIANI, A., SOLAZZI, A., TOLOMIO, C., MARSOCCHI, M., FAVERO, P. and CAVOLO, F. Parametri fisico-chimici e fitoplancton in una stazione a sud del Monte Conero (zona di ripopolamento). Convegno Scientifico Nazionale del Progetto Finalizzato Oceanografia e Fondi Marini, CNR, Rome, 5-7 March 1979, 107-122.

BERNHARD, M. Manual of Methods in Aquatic Environment Research, Part. 3. Sampling and analyses of biological material (Guidelines for the FAO(GFCM)/UNEP Joint Co-ordinated Project on Pollution in the Mediterranean). FAO Fish. Techn. Pap. 158 (1977) 124 p.

BOLOGNARI, A., FERRO, R., FOSSATO, V.U., PIATELLI, M., RENZONI, A. and VIVIANI, R. Monitorage de l'état de la pollution marine le long des ctes italiennes avec l'emploi des indicateurs biologiques. IV<sup>es</sup> Journées Etud. Pollutions, Antalya, CIESM (1978) 667-669.

CIOCE, F., COMASCHI SCARAMUZZA, A., LOMBARDO, A. and SOCAL, G. Hydrological and biological data from the northern basin of the Venice lagoon. June 1977-June 1978. Atti Ist. veneto Sci. 137 (1978-79) 309-342.

DUJMOV, J., VUCETIC, T., PICER, M. and PICER, N. Some results of the monitoring of chlorinated hydrocarbons in organisms from the Central Adriatic, IV<sup>es</sup> Journées Etud. Pollutions, Antalya, CIESM (1978) 137-141.

FAO/UNEP. Report of the FAO (GFCM)/UNEP Expert Consultation of the Joint Co-ordinated Project on Pollution in the Mediterranean, Rome, 23 June 4 July 1975, Rome, FAO, Access No. H 0975, 42 p.

FDA. Pesticide Analytical Manual, U.S. Department of Health, Education, and Welfare, Food and Drug Administration, Vol. 1 (1971) section 211, 14a.

FOSSATO, V.U. and CRABOLEDDA, L. Chlorinated hydrocarbons in mussels, Mytilus sp., from the Laguna Veneta. Arch. Oceanogr. Limnol. 19 (1979) 169-178.

FOSSATO, V.U. and CRABOLEDDA, L. Idrocarburi clorurati (BHC, DDT, PCB) in organismi marini campionati nell'Adriatico centro-settentrionale fra giugno 1976 e giugno 1978. Convegno Scientifico Nazionale del Progetto Finalizzato Oceanografia e Fondi Marini, CNR, Rome, 5-7 March 1979, 831-844.

FRANCO, P. Condizioni idrologiche e produttività primaria nel Golfo di Venezia. Arch. Oceanogr. Limnol. 15 (1967) 69-83.

NASCI, C and FOSSATO, V.U. Studio sulla fisiologia dei mitili e sulla loro capacità di accumulare idrocarburi e idrocarburi clorurati. Atti Soc. tosc. Sci. nat., Mem., Ser.B, 86 suppl. (1979) 216-218.

NAZANSKY, B., PICER, N., PICER, M. and AHEL, M. Monitoring of chlorinated hydrocarbons in biota of the North and Middle Adriatic coastal waters, IV<sup>es</sup> Journées Etud. Pollutions, Antalya, CIESM (1978) 129-132.

REVELANTE, N. and GILMARTIN, M. DDT, related compounds and PCB, in tissues of 19 species of northern Adriatic commercial fishes, Investigation pesq. 39 (1975) 491-507.

SNYDER, D. and REINERT, R. Rapid separation of polychlorinated biphenyls from DDT and its analogues on silica gel. Bull. Environ. Contam. Toxicol. 6 (1971) 385-390.

VILICIC, D., PICER, N., PICER, M. and NAZANSKY, B. Monitoring of chlorinated hydrocarbons in biota and sediments of South Adriatic coastal waters. VI<sup>es</sup> Journées Etud. Pollutions, Antalya, CIESM (1978) 143-146.

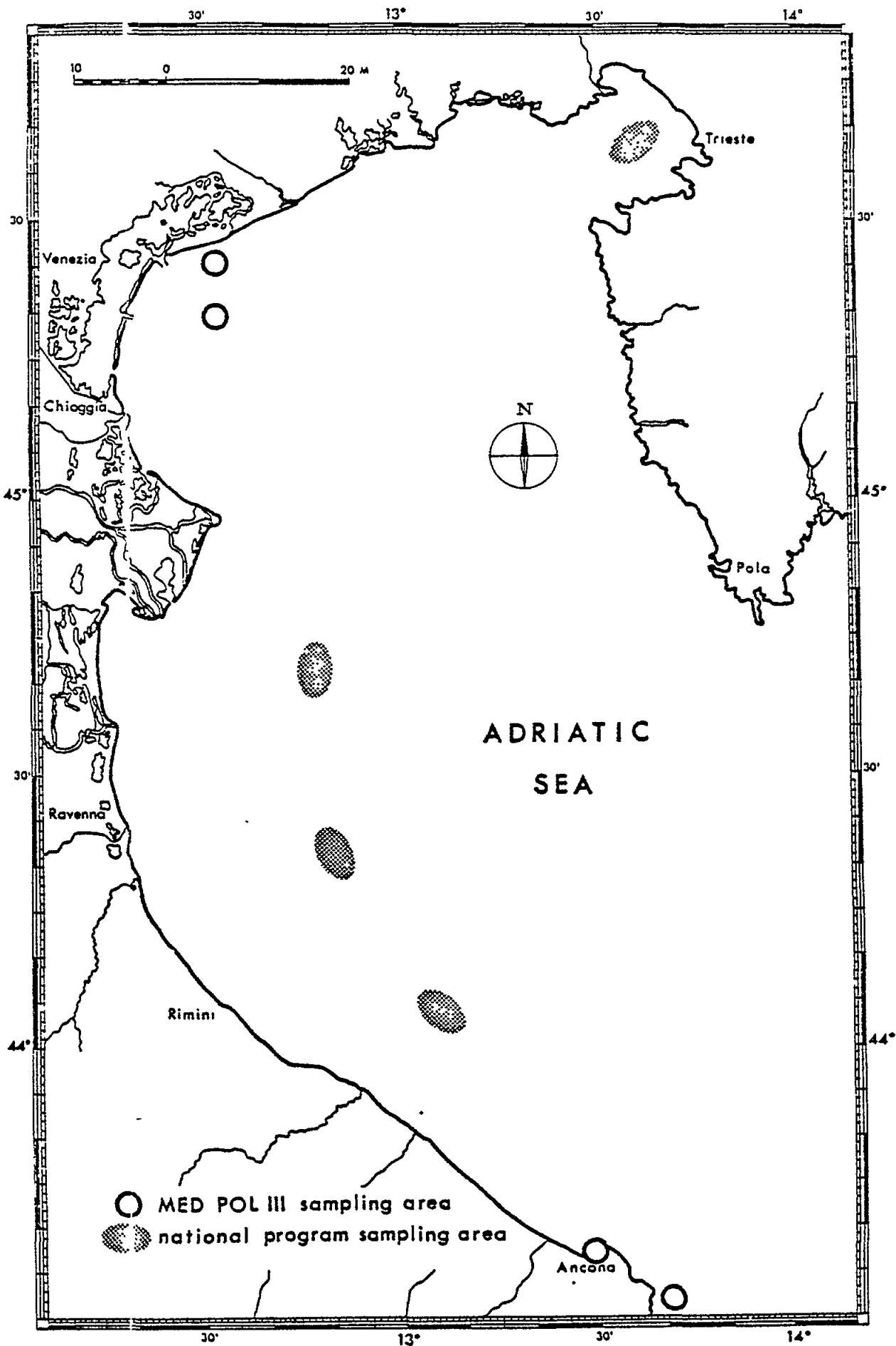


Fig. 1. Sampling areas

Table I. Chlorinated hydrocarbon content (mean  $\pm$  SD,  $\mu\text{g}/\text{kg}$  wet weight) of marine organisms collected near Venice, Ancona and La Spezia from June 1976 to December 1979

<u><i>Mytilus galloprovincialis</i></u>	Venice	Ancona	La Spezia
Samples No.	15	14	9
Wet wt/Dry wt	5.80 $\pm$ 1.08	5.46 $\pm$ 1.21	5.50 $\pm$ 1.48
ECDF <sub>7</sub> wet wt	1.73 $\pm$ 0.58	1.89 $\pm$ 0.66	1.89 $\pm$ 0.64
$\Sigma$ PCB	41 $\pm$ 27	59 $\pm$ 29	150 $\pm$ 123
$\Sigma$ DDT	12.9 $\pm$ 6.9	18.5 $\pm$ 7.8	24.7 $\pm$ 16.9
$\Sigma$ HHC	1.2 $\pm$ 1.0	1.4 $\pm$ 1.3	1.1 $\pm$ 0.7
Dieldrin	0.7 $\pm$ 0.8	0.9 $\pm$ 1.0	1.3 $\pm$ 1.7
<u><i>Mytilus barbatus</i></u>			
Samples No.	9	13	14
Wet wt/Dry wt	3.84 $\pm$ 0.34	3.95 $\pm$ 0.66	4.06 $\pm$ 0.54
ECDF <sub>7</sub> wet wt	5.74 $\pm$ 2.03	5.11 $\pm$ 2.50	4.34 $\pm$ 2.67
$\Sigma$ PCB	122 $\pm$ 49	121 $\pm$ 53	669 $\pm$ 885
$\Sigma$ DDT	39.6 $\pm$ 22.1	42.3 $\pm$ 22.8	94.0 $\pm$ 86.0
$\Sigma$ HHC	4.2 $\pm$ 2.3	3.7 $\pm$ 2.9	2.4 $\pm$ 2.6
Dieldrin	1.0 $\pm$ 1.3	1.6 $\pm$ 1.9	5.2 $\pm$ 9.3
<u><i>Carcinus mediterraneus</i></u>			
Samples No.	14	13	0
Wet wt/Dry wt	4.68 $\pm$ 0.82	4.75 $\pm$ 0.67	
ECDF <sub>7</sub> wet wt	0.33 $\pm$ 0.12	0.32 $\pm$ 0.08	
$\Sigma$ PCB	62 $\pm$ 35	90 $\pm$ 44	
$\Sigma$ DDT	6.6 $\pm$ 3.5	8.7 $\pm$ 6.1	
$\Sigma$ HHC	0.7 $\pm$ 0.5	0.5 $\pm$ 0.5	
Dieldrin	0.5 $\pm$ 0.5	0.5 $\pm$ 0.6	

Table II Biometric data and chlorinated hydrocarbon content (means  $\pm$  SD,  $\mu\text{g}/\text{kg}$  wet weight) in Mullus barbatus samples: (A) eight specimens collected in the Gulf of Venice the 14<sup>th</sup> September 1978; (B) six specimens collected near Ancona the 22<sup>th</sup> September 1978; (C) eight specimens collected in the Gulf of La Spezia the 22<sup>th</sup> November 1979.

	Length mm	Weight g	Wet Wt Dry Wt		EOM %	$\Sigma$ PCB	$\Sigma$ DDT	$\Sigma$ BHC
(A)	106 $\pm$ 4	14.7 $\pm$ 1.7	4.01 $\pm$ 0.27	3.70 $\pm$ 1.79	66 $\pm$ 12	26.2 $\pm$ 15.0	1.1 $\pm$ 0.5	
(B)	158 $\pm$ 17	48.1 $\pm$ 16.3	3.99 $\pm$ 0.44	4.35 $\pm$ 2.30	56 $\pm$ 27	26.6 $\pm$ 17.7	0.9 $\pm$ 0.4	
(C)	111 $\pm$ 12	16.1 $\pm$ 4.5	4.23 $\pm$ 0.31	3.04 $\pm$ 1.88	391 $\pm$ 732	25.0 $\pm$ 16.6	0.2 $\pm$ 0.2	



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#### INTRODUCTION

The work in the field of chlorinated hydrocarbons monitoring started after the signature of the agreement with FAO, with the financial support of the "Progetto Finalizzato Oceanografia e Fondi Marini - Sottoprogetto Inquinamento Marino" of the National Research Council (C.N.R.).

#### METHODOLOGICAL CONSIDERATIONS

##### Selection of the species:

Mytilus galloprovincialis Lamk (blue mussel); Mullus barbatus L. (striped mullet); Nephrops norvegicus L. (Norwegian lobster); Engraulis encrasicolus L. (anchovy); only once : Mullus surmuletus L. (red mullet).

##### Pollutants analysed:

p,p' DDT and its metabolites (p,p' DDD and p,p' DDE); polychlorinated biphenyls (PCBs) were analysed from the beginning and hexachlorobenzene, lindane, heptachlor and heptachlor epoxide, aldrin and dieldrin, during the later period.

##### Area studied:

Northern Tyrrhenian Sea, around the Arcipelago Toscano (figure 1): M. galloprovincialis at sampling stations M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub>; M. barbatus and E. encrasicolus at T<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub>; N. norvegicus at S<sub>1</sub> and S<sub>3</sub>; and M. surmuletus at S<sub>1</sub>.

#### METHODOLOGY

Fish and crustaceans were caught by trawls; mussels by hand. All samples, with the exception of the mussels, were taken to the laboratory at about 4°C and later deep-frozen (-20°C); mussels stayed in clean sea-water, 36 h.

Weight and length were measured according to FAO Fisheries Technical Paper No. 158. Pools were made using about the same weight of each specimen and the tissue analysed was the soft part for mussels and the muscle for the others. All material to be analysed was freeze-dried; sub-samples were used for the determination of the residual water content (24 h at 105-110°C). The concentrations of chlorinated hydrocarbons were expressed as ug/kg, dry basis and then transformed to ug/kg fresh weight using the following values of the ratio fresh weight/dry weight - mussel: 5 (all data normalized), mullet: 4.287; Norwegian lobster: 4.459 and anchovy: 4.100.

A 2-10 g portion of lyophilized material was extracted for about 12 h in a Soxhlet apparatus, using about 200 ml of n-hexane. The solvent was then evaporated under reduced pressure at a temperature not higher than 50°C (Fossato and Craboledda, 1979), until a final volume of 10 ml was reached. An aliquot was used for the complete drying to determine the extractable organic matter (E.O.M.), and the remaining volume was utilized for the clean-up. The first clean-up procedure was performed by the sulphuric acid method introduced by Murphy (1972): very easy, rapid and not expensive, but with complete loss of the dieldrin. This method was then replaced by the partitioning between n-hexane and acetonitrile according to the Pesticide Analytical Manual (1971). The extract obtained was dried over anhydrous sodium sulphate, concentrated to about 5 ml and applied to a small column (15 cm x 0.8 cm, internal diameter) with activated florisisil (1g), and eluted with n-hexane (45 ml).

At this step we can separate the dieldrin, contained in the fraction 46-106 ml, from the others, contained in the first fraction (1-45 ml). The second fraction, concentrated to a small volume, was used for the GLC determination of dieldrin; the first, concentrated to 2-3 ml and transferred to the top of a column (30 cm x 1.0 cm, i.d.) packed under n-hexane with silica-gel activated at 220°C, was eluted with n-hexane and then benzene for the separation of DDT and its metabolites from PCBs and other chlorinated hydrocarbons, according to Snyder and Reinert (1971). The volume was finally adjusted for the GLC analysis.

Analyses were carried out using a Perkin-Elmer F 22 gas chromatograph equipped with a Ni<sup>63</sup> electron capture detector and recorder. Glass columns, 180 cm long x 0.64 cm outer diameter, packed with 10 per cent DC 200 on Gas Chrom Q BW-DMCS 100-120 mesh, were used for routine analyses. Similar glass columns, packed with 5 per cent QF 1 on Chromosorb W AW-DMCS, were used for the qualitative and quantitative controls. The injectors used were "on-column" models. The temperatures of injector, oven and detector were 220, 210 and 240°C for the routine columns and 210, 190 and 240°C for the control columns. The carrier gas was argon with 5 per cent of methane at flow rates of 100 ml/min (first column) and 60 ml/min (second column), including 30% scavenger.

Calculations of the concentrations of the contaminants studied were based on measuring peak heights; solutions of pure compounds were used as reference standards. For DDT and metabolites the para-para isomers were utilized, for PCBs the commercial products traded under the name of Aroclor 1254 and 1260 (Monsanto Company, U.S.A.).

The loss of each compound analysed due to the pre-treatment (extraction, clean-up, separation, various concentrations in the rotary evaporator), was evaluated by the standard addition method (at the beginning of the extraction procedure). Re-extraction tests showed no presence of pesticide or PCBs residues in materials analysed, and also a very low blank level. The error of the entire procedure was under 20 per cent (as coefficient of variation of replicates at the moment of the extraction).

#### Intercalibration exercise:

The research centre participated in the intercalibration exercise (IAEA International Laboratory in Monaco) in analysis of the following sample: oyster (MA-M-1).

## RESULTS

Data obtained do not reveal any seasonal or age variation. The over-all values for each species and for each sampling site are reported in Tables I to V.

### Chlorinated hydrocarbons in Mytilus galloprovincialis:

The concentrations of hexachlorobenzene (HCB), lindane (LIN), heptachlor (HEP) and heptachlor epoxide (HOX), aldrin (ALD) and dieldrin (DIE), are very low and mostly below the detection limits (Table I). Levels of DDE, DDD and DDT are also low, slightly higher at stations M<sub>1</sub> and M<sub>3</sub> (figure 1). Similar patterns, with higher levels, were found for PCBs.

### Chlorinated hydrocarbons in Mullus barbatus:

PCBs show high values, especially in the samples from the northern region of the area studied (Table II).

Values for DDT and its metabolites are low and lower for the other contaminants; for the most part below the detection limits.

### Chlorinated hydrocarbons in Nephrops norvegicus:

All values obtained are very low (Table III), possibly due to the distance of the fishing ground from the coast (and from the pollution sources) and to the low concentration of fatty material in the tissue (muscle) analysed.

### Chlorinated hydrocarbons in Mullus surmuletus:

Taking into account the difference of the E.O.M. levels, the red mullet presents values similar to the Norwegian lobster fished at the same station (Table IV).

### Chlorinated hydrocarbons in Engraulis encrasicolus:

The concentrations of HCB, LIN, HEP, HOX, ALD and DIE are very low. Higher are those of DDE, DDD and DDT; still higher those of PCBs (Table V).

## DISCUSSION OF RESULTS

The values obtained in some marine organisms caught in the Archipelago Toscano area could only give us an idea of the diffusion of the chlorinated hydrocarbons; no rigorous quantification could be advanced at the time. Some conclusions could, however, be drawn:

- (a) chlorinated hydrocarbons, particularly DDT, DDD and DDE, and PCBs are present at a very low level in all material analysed from the areas far from the coast;
- (b) higher values have been found in organisms from the northern stations, located on or near the coast, in front of more developed areas and with higher density of population;
- (c) the concentrations found do not appear to be dangerous for man; a 3-5 years' interval monitoring project should be suggested.

PUBLICATIONS

BACCI, E., FOCARDI, S., LEONZIO, C. and RENZONI, A. (1979). Contaminanti in organismi del Mar Tirreno. Atti del Convegno Scientifico Nazionale del Progetto Finalizzato "Oceanografia e Fondi Marini" (C.N.R.), Roma, 5-6-7 March, 1979.

REFERENCES

FOSSATO, V. and CRABOLEDDA, L. (1979). Chlorinated hydrocarbons in mussels, Mytilus sp., from the Laguna Veneta. Arch. Oceanogr. Limnol., 19, p. 169-178.

MURPHY, P.G. (1972). Sulfuric Acid for the Cleanup of Animal Tissues for Analysis of Acid-Stable Chlorinated Hydrocarbon Residues. Jour. AOAC 55, P. 1360-1362.

Pesticide Analytical Manual (1971). U.S. Dep. of Health, Education, and Welfare, Food and Drug Administration, Vol. I, Section 211. 14a.

SNYDER, D. and REINERT, R. (1971). Rapid separation of polychlorinated biphenyls from DDT and its analogues on silica gel. Bull. Environ. Contam. Toxicol., 6, p. 385-390.

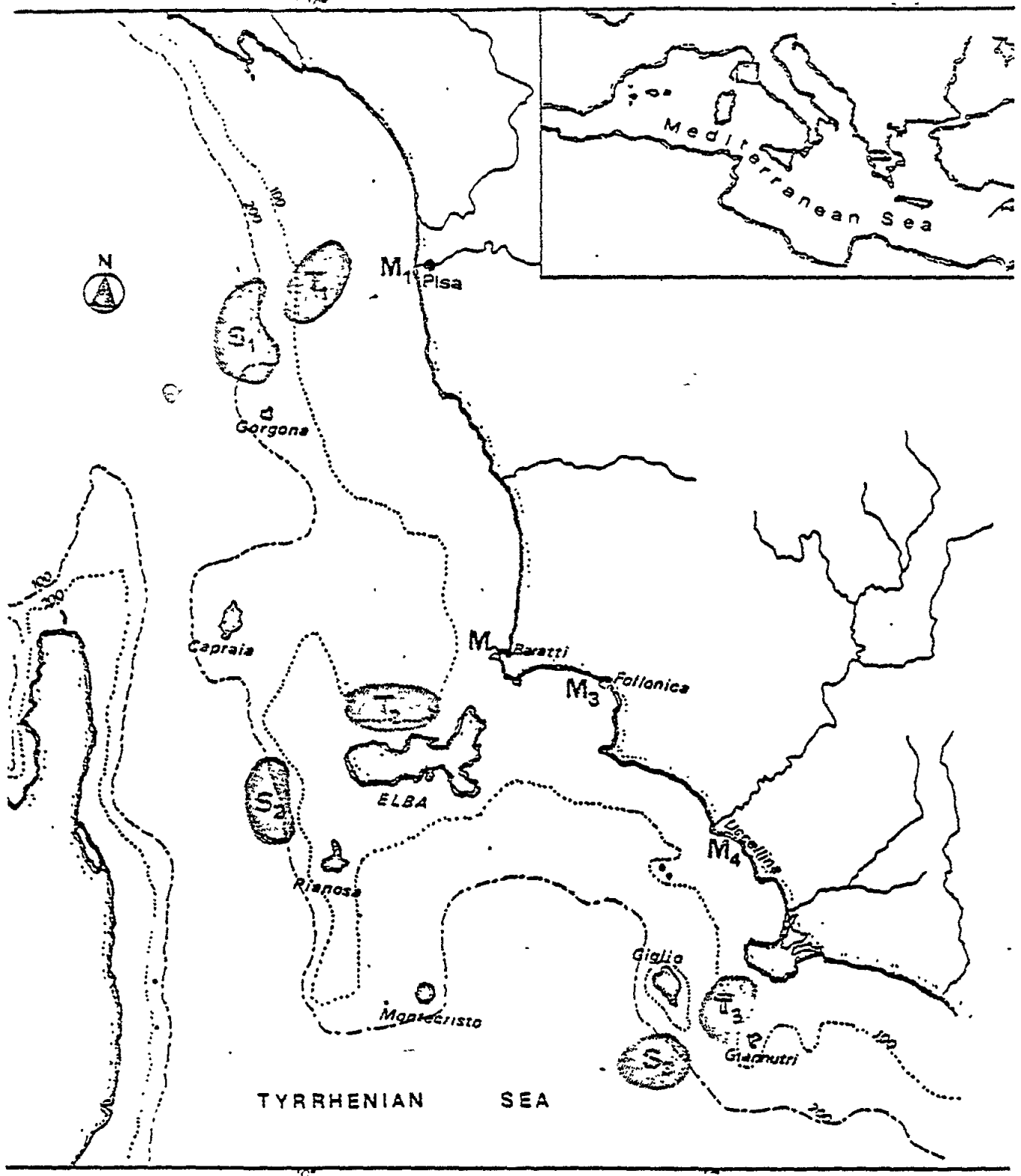


Fig. 1. Sampling area

Tab. I - Chlorinated Hydrocarbons in the mussel *M. galloprovincialis* (soft parts).  
 Concentrations are in  $\mu\text{g}/\text{kg}$ , wet weight, normalized to 80 % water content.  
 $\bar{x}$  = mean; S.D. = standard deviation; n = number of analyses; r = range.

St.	E.O.M. (%)	HCB	LIN	HEP	HOX	ALD	DIE	DDE	DDD	DDT	PCB
M <sub>1</sub>	$\bar{x}$ 1.0	<1	<1	<1	2.5	--	3.5	21	14	17	145
	S.D. 0.34	--	--	--	--	--	--	6.8	5.2	9.2	73.8
	n 7	2	2	2	2	2	2	7	7	7	7
	r 0.8-1.8	<1	<1	<1	1-4	<1-6	1-6	8-27	6-21	6-32	22-230
M <sub>2</sub>	$\bar{x}$ 1.0	<1	--	--	<1	<1	<1	5	--	5	51
	S.D. --	--	--	--	--	--	--	2	--	2.9	23.2
	n 3	2	2	2	2	2	2	.5	.5	5	5
	r 0.7-1.6	<1-1	<1-2	<1-2	<1	<1	<1-1	2-8	<1-5	1-9	12-70
M <sub>3</sub>	$\bar{x}$ 1.2	<1	2.3	--	--	--	5	9	7	9	184
	S.D. 0.32	--	--	--	--	--	--	5.7	4.9	6.1	157.5
	n 5	3	3	3	3	3	3	5	.5	5	5
	r 0.8-1.6	<1	2-3	<1-2	<1-7	<1-5	2-7	4-17	4-16	2-17	21-420
M <sub>4</sub>	$\bar{x}$ 1.2	<1	<1	2	<1	<1	<1	4	--	5	28
	S.D. --	--	--	--	--	--	--	--	--	--	--
	n 3	1	1	1	1	1	1	3	3	3	3
	r 0.8-1.7	--	--	--	--	--	--	2-6	<1-4	1-7	25-32

Tab. II - Chlorinated Hydrocarbons in the striped mullet *M. barbatus* (muscle). Data are in  $\mu\text{g}/\text{kg}$ , wet weight.  $\bar{x}$ , S.D., n and r; see Tab. I.

St.	E.O.M. (%)	HCB	LIN	HEP	HOX	ALD	DIE	DDE	DDD	DDT	PCB
T1	$\bar{x}$ 2.5	--	--	--	--	<1	--	25	18	30	615
	S.D. 1.45	--	--	--	--	--	--	13.1	21.4	40.5	860.9
	n 21	9	9	9	9	9	9	21	21	21	21
	r 1.2-6.2	<1-4	<1-4	<1-1	<1-2	<1	<1-19	11-70	2-90	8-170	80-4050
T2	$\bar{x}$ 2.7	--	--	--	--	--	--	35	10	24	571
	S.D. 1.58	--	--	--	--	--	--	18.0	11.9	17.4	859.1
	n 26	9	9	9	9	9	9	26	26	26	26
	r 1.3-7.0	<1-7	<1-5	<1-5	<1-9	<1-5	<1-12	11-93	4-67	9-89	60-3950
T3	$\bar{x}$ 1.7	--	--	--	--	--	--	26	6	19	130
	S.D. 0.25	--	--	--	--	--	--	15.9	6.6	15.0	58.9
	n 7	--	--	--	--	--	--	7	7	7	7
	r 1.4-2.1	--	--	--	--	--	--	7-56	<1-20	6-49	60-230

Tab. III - Chlorinated Hydrocarbons in the Norwegian lobster *N. norvegicus* (muscle). Concentrations in  $\mu\text{g}/\text{kg}$ , wet weight.  $\bar{x}$ , S.D., n and r; see Tab. I.

St.	E.O.M. (%)	HCB	LIN	HEP	HOX	ALD	DIE	DDE	DDD	DDT	PCB
S1	$\bar{x}$ 0.4	3.6	<1	--	--	£1	--	3	--	--	18
	S.D. 0.06	--	--	--	--	--	--	1.6	--	--	8.6
	n 13	4	4	4	4	4	4	13	13	13	13
	r 0.3-0.5	2-6	<1	<1-3	<1-5	<1-1	<1-2	1-8	<1-2	<1-5	5-35
S3	$\bar{x}$ 0.4	--	<1	<1	<1	<1	£1	4	--	--	30
	S.D. 0.12	--	--	--	--	--	--	1.7	--	--	22.2
	n 15	3	3	3	3	3	3	15	15	15	15
	r 0.2-0.6	<1-4	--	--	--	--	--	2-8	<1-2	<1-6	10-90

Tab. IV - Chlorinated Hydrocarbons in the red mullet M. surmuletus (muscle).  
 Concentrations in ug/kg, wet weight.  
 $\bar{x}$ , S.D., n, r: see Tab. I.

St.	E.O.M. (%)	DDE	DDD	DDT	PCB
$\bar{x}$	1.9	11	2	6	87
S.D.	0.22	3.4	0.4	3.3	18.6
n	6	6	6	6	6
r	1.7-2.3	6-14	1-2	4-13	60-110

Tab. V - Chlorinated Hydrocarbons in the anchovy E. encrasicolus (muscle). Data are  
 in ug/kg, wet weight.  
 $\bar{x}$ , S.D., n, r: see Tab. I.

St.	E.O.M. (%)	HCB	LIN	HEP	HOX	ALD	DIE	DDE	DDD	DDT	PCB
$\bar{x}$	1.5	<1	--	<1	<1	<1	--	46	15	45	385
S.D.	0.50	--	--	--	--	--	--	21.0	11.0	24.2	165.5
n	6	2	2	2	2	2	2	6	6	6	6
r	0.8-2.0	--	<1-2	--	--	--	<1-3	16-63	<1-26	13-72	140-610
$\bar{x}$	2.0	--	7	--	--	1	5	26	15	24	166
S.D.	0.43	--	3.9	--	--	--	3.0	13.4	6.9	11.7	57.1
n	9	4	4	4	4	4	4	9	9	9	9
r	1.4-2.6	<1-5	4-12	<1-2	<1-4	--	1-7	5-50	2-20	2-40	90-260



Research Centre: Marine Research Center  
National Council for Scientific Research  
BEIRUT  
Lebanon

Principal Investigator: H. H. KOUYOUMJIAN

No final report was submitted by the Principal Investigator.

Research Centre: University of Malta  
MSIDA  
Malta

Principal Investigator: J. V. BANNISTER (up to March 1980)  
A. SERRACINO-INGLOTT (from April 1980)

No final report was submitted by the Principal Investigator.

Centre de Recherche : Institut Scientifique des Pêches  
Maritimes (ISPM)  
CASABLANCA  
Maroc

Chercheur principal : H. IDRISSI

Période ouverte par le rapport : Octobre 1977 - Mars 1980

## INTRODUCTION

L'expérience directe de l'ISPM dans ce domaine de recherche est en train de commencer. Jusqu'à présent les analyses effectuées sur les échantillons ont été réalisées dans l'Institut scientifique et technique des pêches maritimes (ISTPM) de Nantes, avec la collaboration des stagiaires de l'ISPM.

## CONSIDERATIONS METHODOLOGIQUES

Sélections des espèces :

L'on a analysé des spécimens appartenant aux espèces suivantes : Mytilus galloprovincialis, Parapenaeus longirostris, Sardina pilchardus, Trachurus trachurus, Scomber scombrus et Merluccius merluccius.

Polluants analysés : DDT, DDD, DDE et PCB.

Zones étudiées :

Les stations de prélèvement des échantillons sont localisées soit sur le littoral atlantique, soit sur la Méditerranée, compris le détroit de Gibraltar (Fig.1).

## METHODOLOGIE

L'échantillonnage se fait manuellement pour les moules, en utilisant les navires de l'ISPM pour les autres espèces. Tous les échantillons recueillis étaient traités suivant les indications de FAO, Document technique sur les pêches N° 158. Les matériels à analyser étaient lyophilisés et conservés à environ -20°C. La méthode d'extraction, de purification et de séparation des hydrocarbures chlorés est celle de l'ISTPM de Nantes.

Programme d'intercalibration :

L'échantillon ("oyster", MA-M-1) reçu a été traité chez ISTPM de Nantes.

## RESULTATS DE L'ETUDE

Mytilus galloprovincialis :

Les PCB sont décelés uniquement dans les échantillons provenant de la Méditerranée. Les taux moyens par PCB, DDT, DDE et DDD obtenus sont :

PCB	: 92,1	µg/kg	P.F.
DDT	: 30,6	µg/kg	P.F.
DDE	: 17,0	µg/kg	P.F.
DDD	: 8,0	µg/kg	P.F.

Les moules prélevées près de l'embouchure de l'Oued Sebou, rivière qui draine une région agricole importante, sont assez contaminées et contiennent tous les résidus recherchés PCB, DDE et DDD.

Parapenaeus longirostris :

Les concentrations en PCB et DDD sont inférieures au seuil de détection de l'appareil. Les spécimens collectés en Méditerranée contiennent du DDE, tandis que ceux recueillis aux environs de l'Oued Sebou contiennent du DDT. Les concentrations moyennes en DDT sont de 93,6 µg/kg P.F.

Sardina pilchardus :

Les échantillons proviennent de la Méditerranée; ils contiennent essentiellement des PCB et du DDE. Les teneurs moyennes obtenues ont été :

PCB : 13,6 µg/kg P.F.  
DDE : 34,0 µg/kg P.F.

Les concentrations en DDE obtenues sont négligeables.

Trachurus trachurus :

Les résidus recherchés ont été les PCB, le DDE, le DDT et le DDD et les moyennes sont respectivement, en ug/kg P.F., 17,0 7,7 0,4 et 0,7.

Les spécimens pris en Méditerranée dénotent une contamination par le DDE et les PCB beaucoup plus importante que celle des échantillons pris en Atlantique.

Scomber scombrus :

Les échantillons traités ont été pêchés au niveau du détroit de Gibraltar. Les concentrations en DDE (20,2) et DDD (9,0) sont relativement élevées. La teneur en PCB est importante (117,1 µg/kg P.F.).

Merluccius merluccius :

Les teneurs sont inférieures au seuil de détection de l'appareil.

Pour l'ensemble des analyses effectuées la fréquence de présence des différents polluants est la suivante :

a) Méditerranée et Détroit de Gibraltar :

PCB	95%
DDE	89%
DDT	44%
DDD	28%

b) Atlantique :	PCB	14%
	DDE	57%
	DDT	43%
	DDD	43%

L'examen des résultats obtenus montre que pour l'ensemble des espèces collectées en Méditerranée pendant les années 1977-1978 et début 1980

contiennent des PCB et du DDE. Ceux récoltés en Atlantique sont moins contaminés. Moins de la moitié des échantillons contiennent du DDT et du DDD. Les concentrations extérieures sont les suivantes :

PCB	213	µg/kg	P.F.	(1977)
DDT	120,4	µg/kg	P.F.	(1977)
DDE	97,8	µg/kg	P.F.	(1978)
DDD	21,5	µg/kg	P.F.	(1978)

#### DISCUSSION DES RESULTATS

Les concentrations moyennes obtenues sont en général plus faibles que celles décelées par certains pays européens. Ces résultats ne reflètent pas l'absence totale de sites industriels le long du littoral méditerranéen marocain. Tous les polluants recherchés sont présents dans tous les échantillons de poissons pélagiques ou démersaux traités et également dans les moules dont le mode de vie est fixe. A l'exception de la plaine de la Moulouya, région agricole importante, l'agriculture extensive et peu développée utilise très peu de pesticides.

En raison de ceci on peut conclure qu'une pollution existe et que cette pollution n'est pas d'origine marocaine.

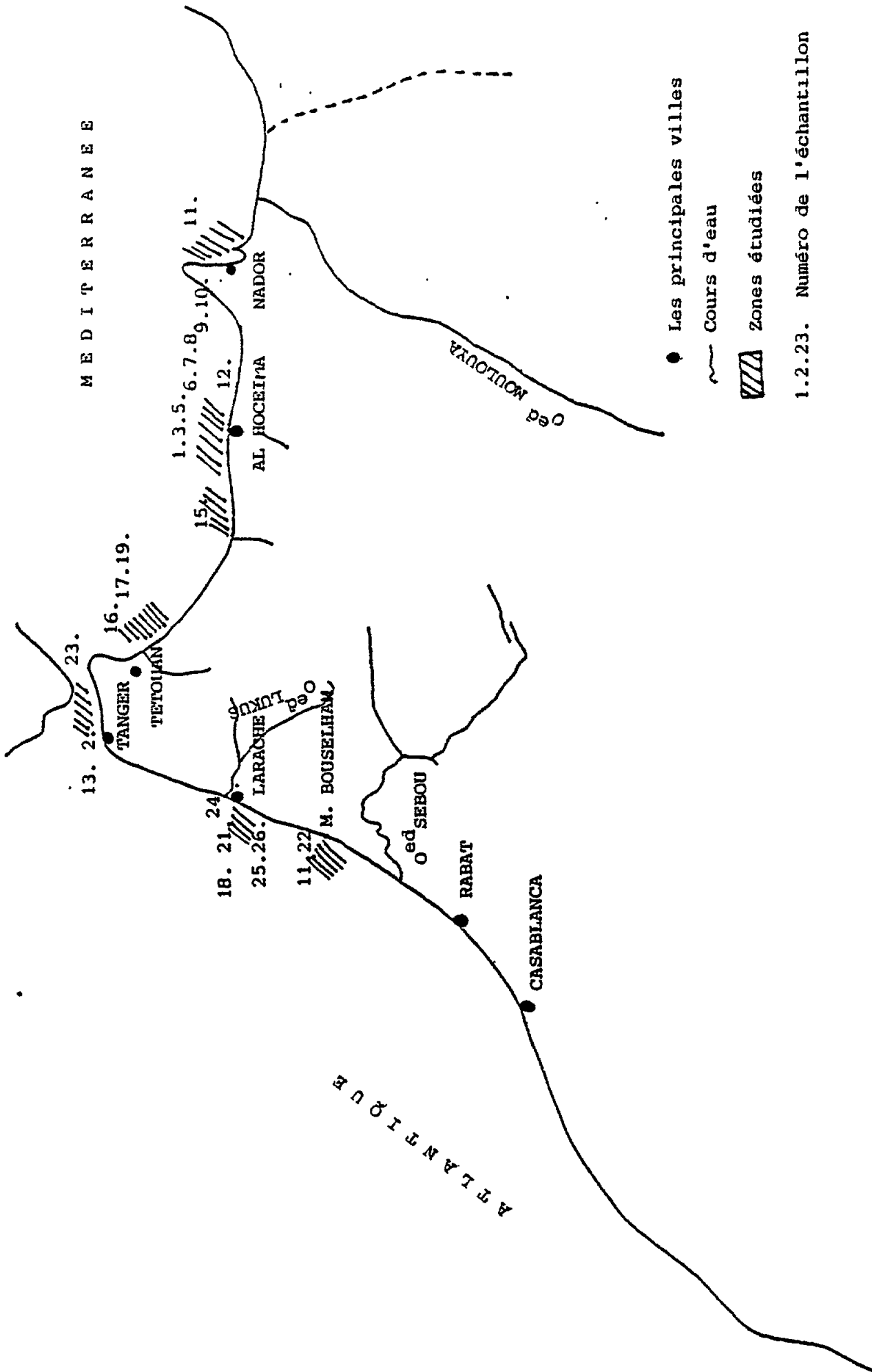


Figure 1. ZONES DE PRELEVEMENTS DES ECHANTILLONS

Centro de investigación: Instituto de Investigaciones Pesqueras  
Barcelona  
España

Investigador principal: A. BALLESTER

El informe final no fué enviado por el Instituto.

Centro de investigación: Instituto Químico de Sarriá,  
BARCELONA  
España

Investigador principal: M. GASSIOT - MATAS

#### INTRODUCCION

En el presente informe se describen las experiencias y análisis realizados desde octubre de 1979 hasta Mayo de 1980. Aunque las relaciones entre FAO/PNUMA y el Instituto Químico de Sarriá se iniciaron en el mes de Mayo y, anteriormente, ya se habían establecido planes de colaboración con el Instituto Español de Oceanografía, los trabajos en el laboratorio no se pudieron iniciar hasta el mes de octubre de 1979 y se han centrado en los siguientes puntos:

- Estudio de la documentación suministrada por FAO y PNUMA para análisis de organoclorados.
- Estudio bibliográfico general de las revistas especializadas.
- Revisión y puesta a punto del detector de captura electrónica E.C.D.
- Preparación de columnas y optimización de las condiciones de trabajo para la separación de PCB's y DDT's.
- Primeras experiencias con muestras reales.
- Análisis de intercalibración.
- Ultimos resultados.

#### CONSIDERACIONES METODOLOGICAS

Condiciones cromatográficas: Después de consultar la documentación a nuestro alcance, se ha optado por utilizar una columna de vidrio de 2m de longitud. El relleno se ha preparado con Gas-Chrom Q. de 80-100 mesh y 1,5% de OV-17 + 1,95% de QF-1 como fase estacionaria, se ajustaron las condiciones de trabajo hasta alcanzar una eficacia de 2500 a 3000 platos teóricos para una mezcla de lindane - aldrin.

Estas condiciones han sido:

- |                              |                                 |
|------------------------------|---------------------------------|
| - Temperatura de la columna  | 200°C                           |
| - Temperatura del inyector   | 350°C                           |
| - Temperatura del detector   | 250°C                           |
| - Temperatura del "manifold" | 350°C                           |
| - Caudal de la columna       | 15 ml/min argon + 5% de metano  |
| - Caudal del "scavenger"     | 100 ml/min argon + 5% de metano |

Es de destacar que fue necesario sustituir los tubos del "manifold" por otros vitrificados interiormente.

También se comprobó el rendimiento del detector (E.C.D.) a través de la determinación del "standing current", lo que permitió comprobar que el



detector estaba en perfectas condiciones de funcionamiento. El valor máximo obtenido fué de  $3,43 \times 10^9$  amperios, valor muy próximo al dado por las especificaciones ( $3,50 \times 10^9$  amperios).

Se ha estudiado el factor de respuesta de varios de los productos organoclorados a determinar y también, los límites de sensibilidad en nuestras condiciones de trabajo:

Lindane  $5 \times 10^{-12}$ g; pp'-DDT  $1 \times 10^{-10}$ g; Aroclor 1254  $5 \times 10^{-11}$ g.

Una expresión de los diferentes factores de sensibilidad se obtiene de las pendientes en el origen, de las curvas de calibración (área/ng):

o-p' DDE 12,6 área/ng; p-p'DDE 17,4 área/ng; p-p' DDD 9,79 área/ng;  
o-p' DDT 7,01 área/ng; p-p'DDT 1,12 área/ng; Aroclor 1254 282,0 área/ng.

Técnicas de extracción y "clean up":

Se ha utilizado el sistema de extracción con Soxhlet por ser más cómodo: se ha comprobado que el rendimiento de extracción es similar al de extracción en frío.

Para el "clean up" se ha utilizado ácido sulfúrico (método de Murphy) y la cromatografía con Florisil. Ambos métodos han dado resultados similares, no obstante, la técnica del Florisil no funciona cuando la muestra tiene una gran cantidad de grasa.

Tratamiento con KOH alcohólica para la eliminación de las interferencias de DDT's y DDD's:

Se han obtenido mejores resultados si el tratamiento con KOH se realiza sobre el residuo de organoclorados, exento de lípidos, después de evaporar totalmente el disolvente. En la actualidad estamos haciendo pruebas, que parecen prometedoras, para separar PCB's de DDT's mediante una cromatografía con Florisil adecuada para los niveles de contaminantes.

Primeras experiencias con muestras reales: Para los primeros análisis, sobre muestras reales, se partió de los materiales suministrados por el Instituto Español de Oceanografía. Las muestras venían trituradas en forma de papilla y contenidas en frascos de vidrio. Estas fueron las siguientes:

Mytilus galloprovincialis (mejillón) de Valencia

Mullus barbatus (salmonete) de Vinaròs, de Castelló, de València, y de Alacant.

La tipificación de estas muestras fue bastante defectuosa y su tratamiento inicial no pudo hacerse de acuerdo con las normas establecidas.

Intercalibración:

Se analizaron las muestras de intercalibración "oyster homogenate" (MA-M-1) y "copepod" (MA-A-1) enviadas por el International Laboratory of Marine Radioactivity (IAEA) de Mónaco.

## RESULTADOS

Los primeros resultados obtenidos sobre los Mytilus galloprovincialis y Mullus barbatus fueron suministrados en los LOG FORM-S.

## DISCUSION DE LOS RESULTADOS

Son los primeros análisis que hemos realizado y no tenemos base de comparación. Posiblemente nuestros resultados sean demasiado elevados, debido a contaminaciones originadas en la manipulación previa de la muestra, o bien en la etapa de extracción.

Centre de Recherche : Institut national scientifique et  
technique d'Océanographie et de  
Pêche  
SALAMMBO  
Tunisie

Chercheur principal : Salem HADJ ALI

Ne pouvant faire un rapport scientifique tel que demandé, l'INSTOP a transmis à la FAO (CGPM) quelques remarques sur l'exécution du projet pilote MED POL III.

1. La collecte des échantillons dans les zones retenues (Golfe de Tunis et de Hammamett) a été réalisée avec les fréquences voulues et ceux-ci ont été lyophilisés et gardés en vue de leur analyse.
2. Le PNUE et la FAO (CGPM) n'ayant pu fournir le chromatographe en phase gazeuse, celui-ci a été acquis par INSTOP moyennant un retard. De plus l'acquisition de gaz (l'azote pur et l'hydrogène) non disponible sur le marché local, n'ont été acquis que dernièrement.
3. La FAO (CGPM) a facilité la visite d'un consultant (janvier 1980), organisé une bourse pour un technicien à l'INSTOP (février 1980) et fourni des accessoires et produits chimiques (juin 1980).
4. Les analyses ne pourront démarrer avant la fin de 1980 quand toutes les dispositions pratiques seront prises.

Research Centre:           Hydrobiological Research Institute  
                              University of Istanbul  
                              ISTANBUL  
                              Turkey

Principal Investigator:    I. ARTUZ

Period of reporting:       December 1976 to March 1979

Due to unexpected difficulties with the infrastructure and financial difficulties, the Institute was not in a position to complete the programmed work. However, the results obtained up to March 1979 were published in Summary Reports on the Scientific Results MED POL (UNEP/IG.18/INF.3, 6 February 1980, pp. 175-176).

Research Centre: Marine Science Department  
Middle East Technical University  
Erdemli, ICEL  
Turkey

Principal Investigator: I. SALIHOGLU

Reporting Period: September 1976 - March 1980

## INTRODUCTION

The Marine Science Department started monitoring chlorinated hydrocarbons in living organisms with the signature of the MED POL III pilot project.

## METHODOLOGICAL CONSIDERATIONS

The selection of the species was made according to the MED POL III pilot project documents (FAO, 1975). Among the selected species, the obligatory ones were Mullus barbatus, Mullus surmuletus, Parapenaeus longirostris and Carcinus mediterraneus. The alternative species studied were Mugil auratus, Mugil saliens, Penaeus kerathurus and Lithophaga lithophaga (FAO, 1977). Mytilus sp. and Xiphias gladius, were not sampled since they were not available in the area studied. Boops salpa, Callinectes sapidus, Upeneus moluccensis and Patella caerulea were also studied since they have high commercial value in this particular area.

### Pollutants analyzed:

The organochlorine residues searched for were aldrin, dieldrin, endrin, DDT, DDD (TDE), DDE, isomers of BHC, lindane, PCBs, methoxychlor and heptachlor epoxide.

### Area studied:

Figure 1 shows the area studied, which is located in the North Levantine part of the Mediterranean. Geologically, the area is on the Cilician Basin, where the boundaries of the basin are the Toros Mts. in the North and the Kyrenia (Cyprus) range in the south. The sea-water temperature varies seasonally between 16.5° and 31°C and the salinity is relatively high (min. 37.8 and max. 39.2‰). Thermal stratification generally begins in March and water starts to become well mixed in October, where the thermocline, during stratification, is at 60 m on the average.

The wind system, and thus the current system, of the area is rather complicated; the currents mainly have two components, one of which is a high-frequency 24 h component, which is due to land-breeze/sea-breeze. The second is a low-frequency component which varies between 3 and 10 days, and is possibly related to cyclonic disturbances. The productivity of the area is relatively low. Some of the benthic and pelagic organisms are of Indo-Pacific origin. There is not much available information about the chemistry and biology of the area.

## METHODOLOGY

Sampling, preservation of the species and sample preparation were carried out according to FAO Fisheries Technical Paper 158, pp. 41, 44 and 45 (FAO, 1976).

In order to extract organochlorine residues, about 5 g of the sample were mixed with an equal weight of anhydrous Na<sub>2</sub>SO<sub>4</sub>, and soxhlet extracted with 50 ml of hexane. Half the hexane extract was used for % EOM determination, and the volume of the other half reduced to about 1 ml. The 1 ml extract was eluted from 1 g alumina column with 20 ml of hexane. The final volume was adjusted to exactly 2 ml under a nitrogen stream and 5 ul of the aliquots injected to GC.

#### Intercalibration exercise:

The laboratory participated in the intercalibration exercise for chlorinated hydrocarbons. The samples analysed to-date are: Fish (MA-M-2), oyster (MA-M-1), copepod (MA-A-1) and sediment sample (SMM/DC).

#### RESULTS

The results obtained from the analysis of species mentioned in terms of µg/kg F.W. are plotted as a function of the length of the species (Fig.2). Table I includes the minimum, maximum, mean and standard deviation values of total DDT and PCBs for each species analysed. In addition to fillet, in some Mullus barbatus collected during the spawning period, eggs and liver were also analysed. Table II includes the t-DDT concentrations obtained from the analyses of fillet, liver and eggs. The observed t-DDT concentrations are plotted as a function of % EOM in Fig.3.

#### DISCUSSION OF RESULTS

From the results given in Table I it is obvious that there is no appreciable amount of PCBs in any of the species analysed, except in one Mullus barbatus and five Mugil saliens. Patella coerulea also showed appreciable amounts of PCBs, up to 138 µg/kg F.W. The absence of PCBs in most of the species is consistent with the results reports by Elder and Villeneuve (1974). They observed a decreasing trend in PCB concentration from the western to the eastern Mediterranean. Harvey, et al., (1974) and Bidelman and Olney (1974) explained low dissolved PCB values in the Sargasso Sea by a co-distillation process. In the eastern Mediterranean, evaporation also exceeds precipitation, and co-distillation of PCBs is possible in this area too. The lack of local sources is possibly the main factor for low PCB concentrations.

Satsmadjis and Gabrielides (1977, 1979), reported total DDT concentrations between 9 and 390 µg/kg in Mullus barbatus caught from Saronikos Bay, Greece. On the other hand, Reimold (1975) analysed Mullus barbatus from the coast of Puerto Rico and the U.S. Virgin Islands and reported only PCBs but no DDT. The total DDT concentrations from Saronikos Bay are fairly close to the results obtained in this work.

The total DDT concentrations obtained in Mugil saliens and Mugil auratus in the eastern Mediterranean are comparable with those reported from the northern Adriatic. Picer, et al., (1978) and Revelante and Gilmartin (1975) reported total DDT values between 28 and 409 µg/kg F.W.

Harvey, et al., (1974) observed lower DDT concentrations in shrimps from the Georges Bank (Atlantic Ocean) than we observed in Parapenaeus longirostris and Penaeus kerathurus from the eastern Mediterranean, while Giam, et al., reported total DDT values about 10 times higher still in the Caribbean Sea.

The only available data about Patella coerulea were reported by Robinson, et al., (1976) from the Northumberland (U.K.) coast, who showed them to contain about one third of the total DDT found in the area studied by us. As can be seen from Figure 2, the total DDT in Mugil auratus and Callinectes sapidus, within the experimental error limits, increases linearly with the increasing length, while in the other species studied the total DDT values are scattered. The spawning period of Mullus barbatus in the Eastern Mediterranean begins in early April and ends in June. Table II includes the results of t-DDT concentrations obtained from the analysis of different organs of M. barbatus during the spawning period. As can be seen from this table, the t-DDTs in liver and eggs are much higher than in the fillet. This might be explained with the % EOM content, since % EOM of liver and eggs are higher than that of fillet. Basturk, et al., (1980) found that the organochlorine residue concentrations of living organisms increase with the increased % EOM.

The plotted t-DDT concentrations (functions of % EOM) are scattered but the general trend is that with the increased % EOM the t-DDT also increase.

More samples have been collected and are being analysed at present.

#### PUBLICATIONS

BALKAS, T.I., et al., (1978) Trace metals and organochlorine residue content of Mullidae family fishes and sediments in the vicinity of Erdemli (Içel), Turkey. XXVI' Congress and Plenary Assembly, CIESM, Antalya, 1978.

BASTURK, O., et al., (1980), DDT, DDE and PCB residues in fish, crustaceans and sediments from Eastern Mediterranean coast of Turkey. Mar. Pollut. Bull. 11(7), pp. 191-195, 1980.

SUNAY, M., et al., (1978) Determination and distribution of organochlorine residues and heavy metals in tar balls. XXVI' Congress and Plenary Assembly, CIESM, Antalya, 1978

#### REFERENCES

BIDELMAN, T.F. and OLNEY, C.E., (1974). Chlorinated hydrocarbons in the Sargasso Sea, atmosphere and surface waters. Science, 183:516-8

ELDER, D.L. and VILLENEUVE, J.P., (1974). Polychlorinated biphenyls in the Mediterranean Sea. Mar. Pollut. Bull., 8:19-22

GIAM, C.S., et al., (1972). DDT, DDE and polychlorinated biphenyls in biota from the Gulf of Mexico and Caribbean Sea, Pestic. Monit. J., 6(3):139-43

FAO. Report of the FAO(GFCM)/UNEP Expert Consultation on the Joint Coordinated Project on Pollution in the Mediterranean, Rome, 23 June - 4 July 1975, 25 p.

FAO (1976). Manual of methods in aquatic environment research. Part 3. Sampling and analysis of biological material. FAO Fish. Tech. Pap., (158):124 p.

HARVEY, G.R., STEINHAEUER, W.G. and MIKLAS, H.P. Decline of polychlorinated biphenyl concentrations in North Atlantic surface waters. Nature, 252:387-8

HARVEY, G.R., et al., (1974). Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms, *Marine Res.*, 32:103-18

PICER, M., PICER, N. and AHEL, M., (1978). Chlorinated insecticide and PCB residues in fish and mussels of east coastal waters of the Middle North Adriatic Sea, 1974-1975, *Pestic. Monit. J.*, 12(3):102-12

REIMOLD, R.J., (1975). Chlorinated hydrocarbon pesticides and mercury in coastal biota, Puerto Rico and the U.S. Virgin Islands, 1972-1974. *Pestic. Monit. J.*, 9(1):39-43

REVELANTE, N. and GILMARTIN, M., (1975). DDT, related compounds and PCB in tissues of 19 species of North Adriatic commercial fishes. *Invest. Pesq.*, 39(2):491-507

ROBINSON, J., et al., (1967). Organochlorine residues in marine organisms. *Nature*, 214:1307-11

SATSMADJIS, J. and GABRIELIDES, G.P., (1977). Chlorinated hydrocarbons in striped mullet (Mullus barbatus) of Saronikos Bay. *Thalassographica*, 1(2):151-4

SATSMADJIS, J. and GABRIELIDES, G.P. (1979). Observations on the concentration levels of chlorinated hydrocarbons in a Mediterranean fish. *Mar. Pollut. Bull.*, 10:109-11



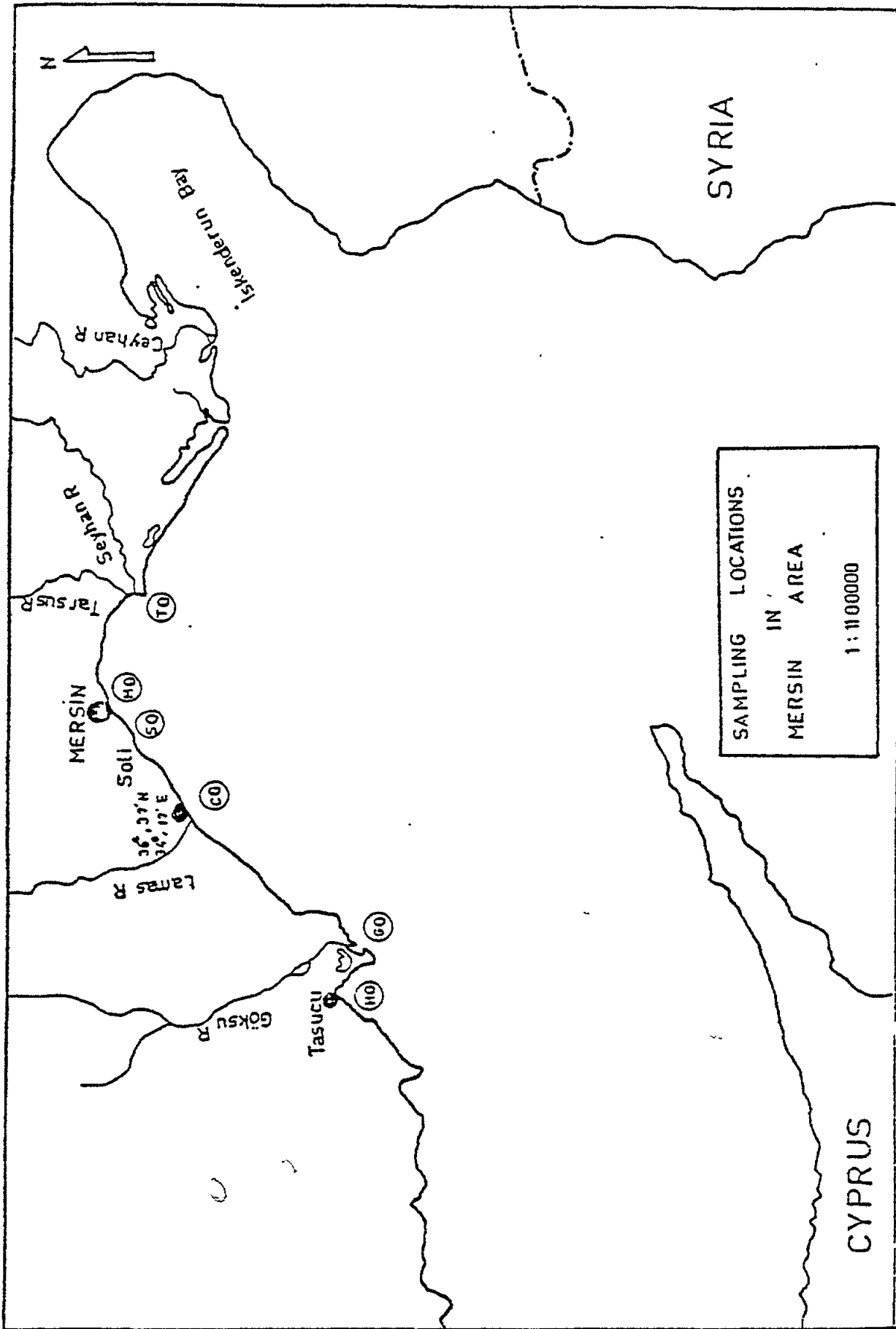


Fig. 1. Area studied

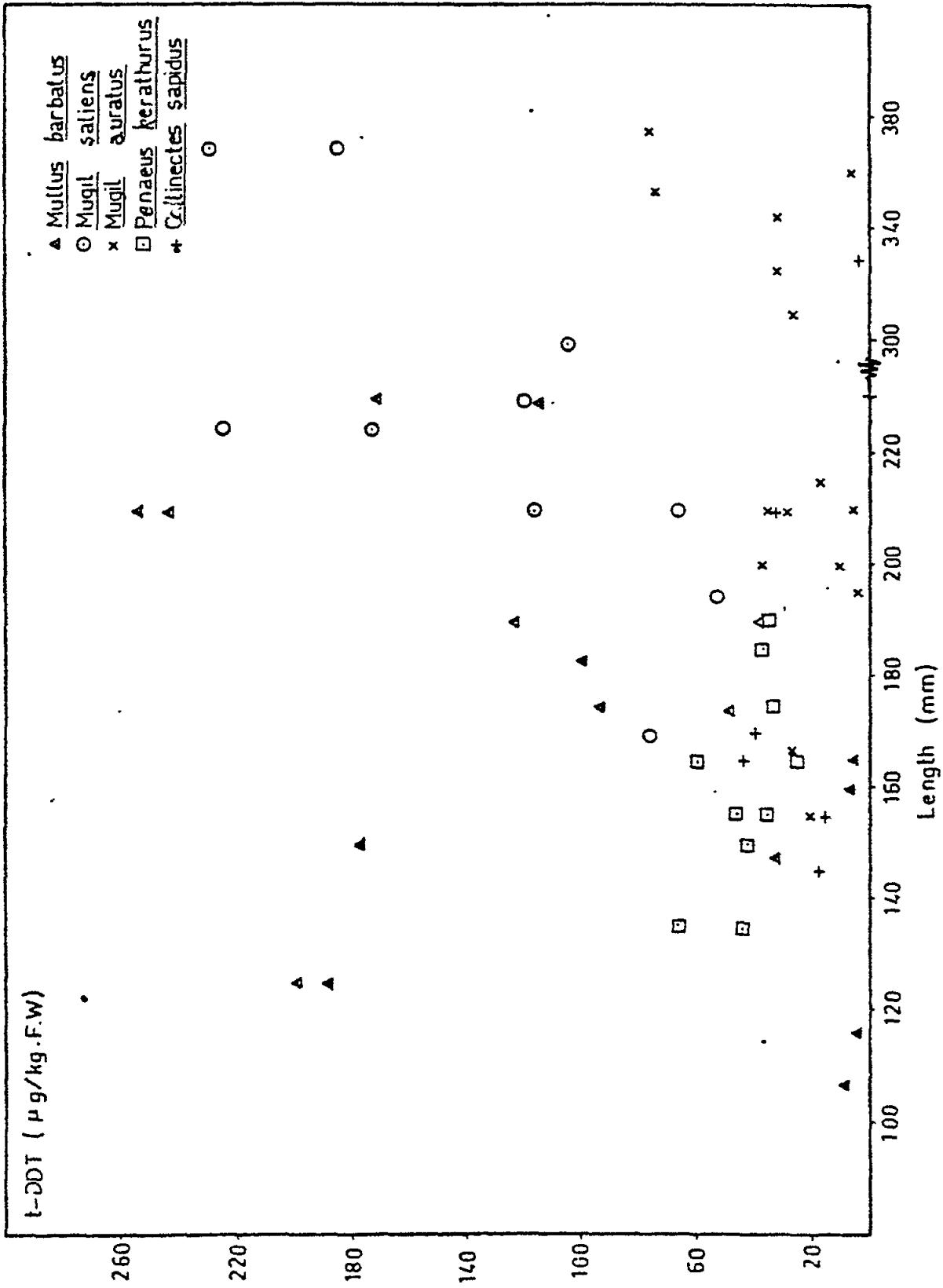


Figure 2: Total DDT concentrations as a function of organism length

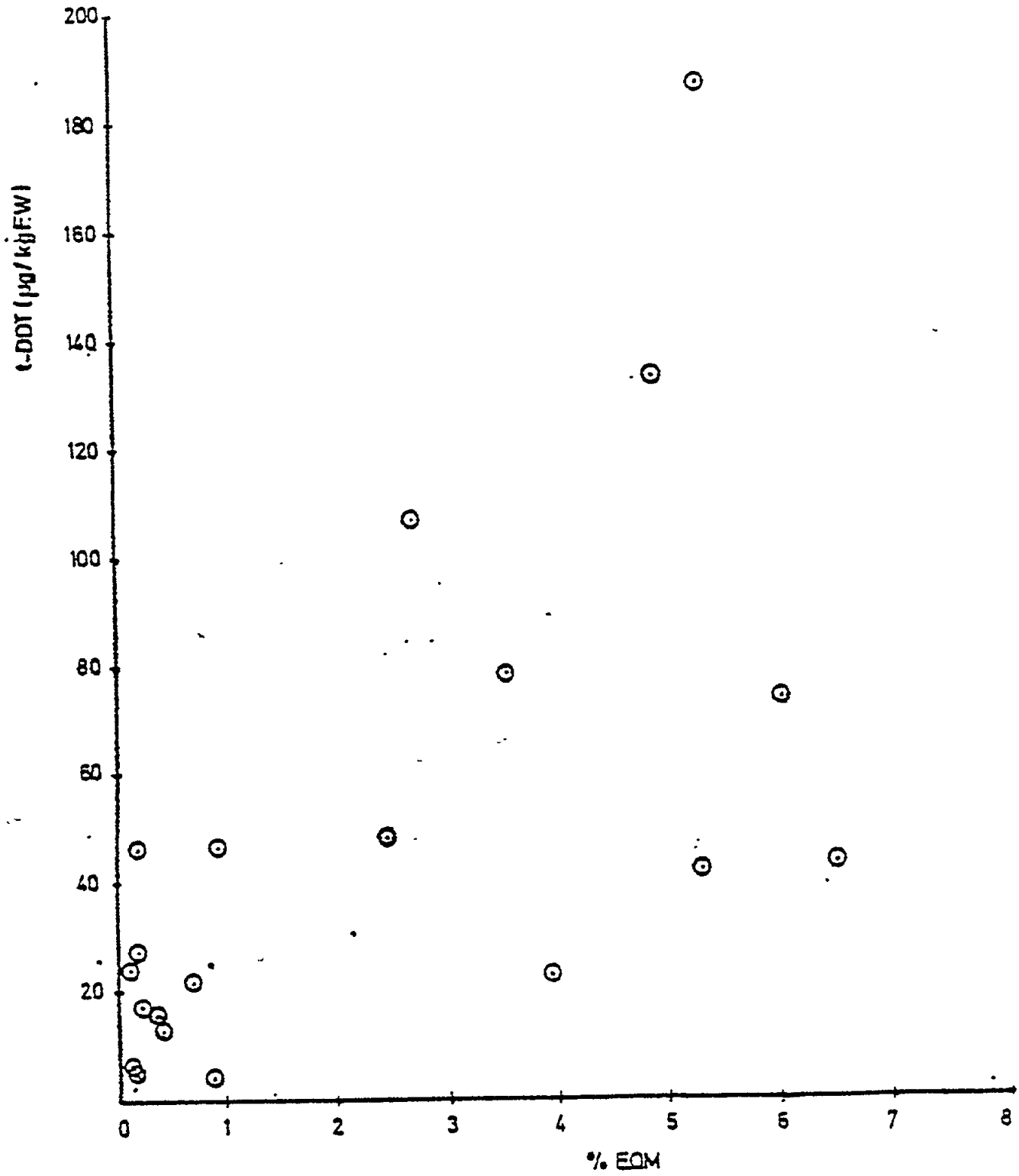


Fig. 3. t-DDT concentrations as a function of % EOM in Mullus barbatus

Table I. Minimum, Maximum, Mean and Standard Deviation  
 Values of t-DDT and t-PCB in Different Species Analysed from September 1976  
 to March 1981 ( $\pm \sigma$  values are the standard deviation)

Name of Species	No. of species analysed	Average length of species (mm)	Min.	t-DDT			t-PCB		
				Max.	Mean. $\pm \sigma$	Min.	Max.	Mean. $\pm \sigma$	
Mullus barbatus	28	170	2	251	71 79	N	N	N	(-)
Mullus surmuletus	3	190	21	42	27 11	N	N	N	(-)
Upeneus moluccensis	2	132	44	86	67 (-)	N	N	N	(-)
Mugil saliens	12	258	2	237	130 64	N	77	17	22
Mugil auratus	34	257	2	75	27 20	N	N	N	(-)
Carcinus mediterraneus	10	191	2	58	30 19	N	N	N	(-)
Callinectes sapidus	3	N.D.	5	22	11 10	N	N	N	(-)
Penaeus kerathurus	12	161	25	65	40 15	N	N	N	(-)
Parapenaeus longirostris	5	162	3	17	10 65	2	3	2	(-)

N : Below the detection limit

(-) : Calculation has not been done since there is not sufficient data

N.D. : Not determined.

Table II. The Organochlorine Concentrations ( $\mu\text{g}/\text{kg}$  F.W.) in Different Organs of *Mullus Barbatus* caught in May 1980..

Sample No.	Sex	Age group	Tissue Analyzed	% E.O.M.	DDE	$\gamma$ -DDT	% DDE
1	Female	4	Fillet	0.33	7	16	44
			Liver	5.28	25	42	60
2	Female	4	Fillet	0.11	4	6	67
			Liver	0.93	16	47	34
			Eggs	3.55	50	78	64
3	Female	4	Fillet	0.14	2	5	40
			Liver	2.47	17	48	35
			Eggs	3.96	19	22	86
4	Male	-	Fillet	0.23	6	17	35
			Liver	5.37	27	187	14
5	Male	-	Fillet	0.90	4	4	100
			Liver	6.50	14	43	33
6	Male	-	Liver	12.40	20	42	48
7	Female	1 or 2	Fillet	0.42	8	14	57
			Liver	0.50	54	72	75
8	Female	3	Fillet	0.1	6	24	25
			Liver	2.72	59	108	55
			Eggs	4.90	95	134	71
9	Male	1	Fillet	0.20	28	46	61
			Liver	1.13	91	157	58
10	Male	1	Fillet	0.22	18	27	67
			Liver	1.31	10	21	48
11	Female	1	Fillet	0.69	16	21	76
			Eggs	6.22	57	74	77

Research Centre: Marine Biological Station  
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Reporting period: 1976 to March 1980

#### INTRODUCTION

The Marine Biological Station has been monitoring the distribution of chlorinated hydrocarbons, particularly in sediments, plankton and selected larger biota (fish mussels) from 1973 on; however, the analyses were performed by the collaborating laboratory of the Agronomical Institute in Ljubljana. Samples were collected in open waters of the whole Adriatic and particularly, in the framework of "mussel watch", along the shores of the northern Adriatic. Results were partly published (Stirn, et al., 1974).

#### METHODOLOGICAL CONSIDERATIONS

##### Selection of the species:

Obligatory species: Due to local conditions, only the mussel Mytilus galloprovincialis was available regularly and at all sampling stations. The red mullet Mullus barbatus was sampled only occasionally. Carcinus mediterraneus (crab) was available only in atypical lagoony environments while it was absent in polluted areas. According to some preliminary analysis, this species turned out to be unsuitable for the Station's monitoring purposes. Penaeid shrimps are totally absent from the area; therefore, another benthic shrimp, Upogebia littoralis, which inhabits both clean and polluted areas, was sampled. However, analyses are not yet completed. No tuna or similar, alternative fish have been caught in the area for many years.

The following facultative species were also sampled and analysed in order to obtain an overview of concentrations of a number of chlorinated hydrocarbons in commercial fish species: grey mullet (Mugil auratus), a sparid (Pagellus erythrinus) and pilchard (Sardina pilchardus). Biota from experimentally-polluted natural ecosystems (ecological investigations are carried out within MED V) was also monitored in order to assess types and concentrations of sewage-borne pesticides and PCBs which are accumulated at various trophic levels (for the list of species see relevant chapter of results).

Pollutants analysed:  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ -HCH(BHC), DDT and its metabolites, aldrin, dieldrin, heptachlor, heptachlor/epoxide, hexachlorobenze and PCBs.

##### Areas studied:

Coastal waters along S.R. Slovenia: Sampling sites were located in the Bay of Strunjan, which served as a reference area free of local pollution sources and in the Bay of Koper, which is heavily polluted by sewage discharges, partly by some industrial wastes and influenced by the River Rizana. In addition, the

sampling of fish was performed in open waters off the Bay of Piran and off Grado, i.e. at trawling grounds of the North Adriatic. In figure 1 the geographical co-ordinates are given for sampling stations; the localities are also indicated on the map. The experimental area was located in the Lagoon of Strunjan, where the samples were obtained from two basins with natural communities. One of them was receiving 300 l of sewage daily (experimentally discharged), while the other was kept clean for comparative purposes.

#### METHODOLOGY

Methods used for extraction and cleaning of samples to be analysed by GCH were, in principle, those outlines in FAO Fish. Tech. Pap. No. 158 with, however, some specific modifications. In order to obtain the most adequate extraction as related to the size of the samples, fat content and specific goals of analyses for invertebrate samples, the following two methods were used:

**Hot extraction:** Samples with the anhydrous  $\text{Na}_2\text{SO}_4$  (1:4) were homogenized and extracted hot according to FDA (U.S.A.) standards, Rotavapor dried and hexane redissolved. Extracts were cleaned up by florisil and eluted with 6 per cent and 15 per cent diethyl ether in petrol ether. The final extract was evaporated up to 5 or 10 ml and 10  $\mu\text{l}$  were GCH injected. For the confirmation of aldrin, total DDT and dieldrin, and for elimination of PCB-interfering esters, ethanolic KOH hydrolysis was carried out. For determination of PCBs, Trotter's acidic oxidation after hydrolysis was performed.

**Cold extraction (for long analytical series on mussels):** Fresh wet samples in hexane-acetone mixture were homogenized and extracted in the Ultra-turrax. Extracts with added ether were primary purified in separatory funnels against an NaCl water solution. Primary cleaned extracts with an addition of absolute ethanol were dried and redissolved in hexane. Small portions of final extracts were prepared for GCH without florisil only by the simple clean-up with concentrated  $\text{H}_2\text{SO}_4$ . For identifications of PCBs, ethanolic KOH hydrolysis was used. For GCH injections, volumes of 1-4  $\mu\text{l}$  of extracts were used.

Identification was accomplished on a Varian 2700 GC unit coupled with electron capture detector (ECD) with  $\text{NI}^{63}$  source. The separation was on 10 foot 2 mm dia coiled glass column filled with 1.5 per cent OV 17, and 1.95 per cent OV 210 on Varaport 30 (80-100 mesh size).  $T_i$ ,  $T_c$  and  $T_d$  were usually 250°C, 230°C and 280°C. Nitrogen flow rate was usually 20 ml/min. Confirmation of GCHM was done by comparison with standards; for PCBs they were Aroclor 1254, 1260, 1211, 1242 and their mixtures. Quantification was performed by planimetry of peak areas. Recovery at all steps of the methods used was studied by contamination of known samples by standard substances. For DDT 95 per cent and for PCBs 90 per cent recovery was found.

**Analytical procedure for fish samples:** Hot extraction in 2:1 hexane-acetone mixture followed by concentrated  $\text{H}_2\text{SO}_4$  and florisil clean-up. For PCBs identification, alkaline hydrolysis in KOH ethanol and oxidation in  $\text{H}_2\text{O}_2$ -acetic acid were used. Identification was made on Varian 1700 GC with ECD with separation on 183 cm/1 mm glass column filled with 1.5 per cent OV 17 + 1.95 per cent QF-1 on Varaport 30, 100-120 mesh.  $T_i$ ,  $T_c$  and  $T_d$  were 210°C (225°C for PCB), 190°C (210°C for PCB) and 270°C. Nitrogen flow rate was 50 ml/min (70 ml/min for PCB).

Intercalibration exercise:

The research centre participated in three intercalibration exercises, analysing the following samples: oyster (MA-M-1), copepod (MA-A-1) and fish (MA-M-2).

RESULTS

All data are reported as range, mean and standard deviation in µg/kg F.W. Total DDT is calculated as DDT + 1 114 DDE + 1 108 DDD. Total PCB is obtained against standard 1:1 mixture of Aroclor 1254 + 1260.

Chlorinated hydrocarbons in Mytilus galloprovincialis

Polluted environment:

	Range	Mean	Standard deviation
op DDT	0.0 - 308.4	102.8	178.0
pp DDT	0.0 - 705.2	258.4	388.5
op DDD	0.0 - 139.1	46.4	80.3
pp DDD	0.1 - 401.2	147.4	220.7
pp DDE	23.0 - 118.4	73.8	48.0
<u>Total DDT</u>	<u>25.7 - 1 744.1</u>	<u>658.1</u>	<u>944.7</u>
Lindane	0.0 - 0.1	0.0	0.06
<u>Total PCB</u>	<u>29.0 - 2 622.0</u>	<u>1.052.0</u>	<u>1 380.3</u>

Clean coastal zone:

	Range	Mean	Standard deviation
op DDT	0.0 - 12.2	3.1	6.1
pp DDT	0.1 - 28.0	11.3	11.9
op DDD	0.0 - 0.1	0.0	0.0
pp DDD	0.1 - 8.6	7.2	9.4
pp DDE	0.1 - 17.0	6.7	7.2
<u>Total DDT</u>	<u>0.3 - 56.5</u>	<u>29.9</u>	<u>28.1</u>
Lindane	0.0 - 0.1	0.0	0.0
<u>Total PCB</u>	<u>11.0 - 84.0</u>	<u>39.7</u>	<u>31.6</u>



Offshore clean reference area:  
(Single composite sample)

pp DDE	11
pp DDD	TR
op DDT	10
<u>Total DDT</u>	<u>12</u>
<u>Total PCB</u>	<u>88</u>

Chlorinated hydrocarbons in Carcinus mediterraneus:  
(Single sample)

	Polluted environment	Clean environment
$\alpha$ -HC	7	5
$\beta$ -HCH	7	2
$\gamma$ -HCH-Lindane	<u>34</u>	<u>21</u>
Aldrin	35	16
pp DDE	39	42
pp DDD	57	40
pp DDT	32	20
<u>Total DDT</u>	<u>138</u>	<u>110</u>
<u>Total PCB</u>	<u>23</u>	<u>17</u>

Chlorinated hydrocarbons in Mullus barbatus:

North Adriatic inshore

	Range	Mean	Standard deviation
$\alpha$ -HCH	1.9 - 2.8	2.3	0.6
$\beta$ -HCH	1.0 - 2.2	1.6	0.8
$\gamma$ -HCH-Lindane	2.2 - 2.2	2.2	0.0
$\delta$ -HCH	0.8 - 1.6	1.2	0.6
pp DDE	24.4 - 37.3	30.8	9.1
pp DDD	8.5 - 14.5	11.5	4.2
op DDT	3.7 - 20.8	12.2	12.1
pp DDT	22.8 - 66.4	44.6	30.8
<u>Total DDT</u>	<u>63.1 - 144.8</u>	<u>103.9</u>	<u>57.8</u>
Heptachlor	0.1 - 0.2	0.1	0.1
Heptachlor epoxide	0.1 - 0.7	0.4	0.4
Hexachlorobenzene	1.0 - 3.3	2.1	1.6
<u>Total PCB</u>	<u>58.5 - 201.4</u>	<u>129.9</u>	<u>101.0</u>

Chlorinated hydrocarbons in Pagellus erythrinus:

North Adriatic offshore

	Range	Mean	Standard deviation
$\alpha$ -HCH	0.4 - 0.6	0.5	0.1
$\beta$ -HCH	1.3 - 1.4	1.3	0.1
$\gamma$ -HCH (lindane)	0.2 - 0.7	0.4	0.3
$\delta$ -HCH	0.5 - 0.8	0.6	0.2
pp DDE	6.4 - 9.2	7.8	2.0
pp DDD	0.4 - 1.5	0.9	0.8
op DDT	2.2 - 5.0	3.6	2.0
pp DDT	2.2 - 12.8	7.5	7.5
<u>Total DDT</u>	<u>12.0 - 29.7</u>	<u>20.8</u>	<u>12.5</u>
Hexachlorobenzene	0.7 - 0.7	0.7	0.0
<u>Total PCB</u>	<u>51.6 - 96.1</u>	<u>73.8</u>	<u>31.5</u>

Mid-Adriatic offshore reference area:  
(Single composite sample)

$\alpha$ -HCH	0.5
$\beta$ -HCH	1.1
$\gamma$ -HCH (lindane)	0.7
$\delta$ -HCH	0.7
pp DDE	12.6
pp DDD	1.4
op DDT	1.8
pp DDT	5.5
<u>Total DDT</u>	<u>22.9</u>
Hexachlorobenzene	1.6
<u>Total PCB</u>	<u>25.8</u>

Chlorinated hydrocarbons in Mugil auratus:

Slightly polluted lagoony environment

	Range	Mean	Standard deviation
$\alpha$ -HCH	0.2 - 0.6	0.4	0.3
$\beta$ -HCH	0.5 - 2.3	1.4	1.3
$\gamma$ -HCH	0.3 - 0.6	0.4	0.2
$\delta$ -HCH	0.8 - 1.1	0.9	0.2
pp DDE	13.6 - 22.2	17.9	6.1
pp DDD	3.4 - 8.7	6.0	3.7
op DDT	3.9 - 4.9	4.4	0.7
pp DDT	18.3 - 22.1	20.2	2.7
<u>Total DDT</u>	<u>42.1 - 60.4</u>	<u>51.2</u>	<u>12.9</u>
Hexachlorobenzene	0.1 - 0.1	0.1	-
<u>Total PCB</u>	<u>64.3 - 73.9</u>	<u>69.1</u>	<u>6.8</u>

Preliminary results from experimentally-polluted ecosystems:

Daily introduction of 300 l of municipal sewage into an artificially-limited but natural lagoony community induced quite evident accumulation of DDTs, PCBs and aldrin in selected biota of a polluted ecosystem as compared with the same but non-polluted environment, as is shown in the table below (in  $\mu\text{g}/\text{kg}$  F.W.).

Chlorinated hydrocarbons	<u>Carcinus mediterraneus</u>		<u>Mytilus galloprovincialis</u>		<u>Holothuria tubulosa</u>	
	Blank lagoon	Polluted lagoon	Blank lagoon	Polluted lagoon	Blank lagoon	Polluted lagoon
$\alpha$ -HCH	5	7	15	10	11	14
$\beta$ -HCH	2	7	3	30	-	8
$\gamma$ -HCH	21	34	-	-	-	63
Aldrin	16	35	-	25	12	60
pp DDE	42	39	17	80	-	28
pp DDD	40	57	20	41	3	28
pp DDT	20	32	10	70	-	25
PCB 1211+1242 (1)	8	50	21	28	4	31
PCB 1254+1260 (2)	17	23	11	29	18	20
Total DDT						
	4	2	1	6.5	0.1	1.4
Total PCB						

- (1) Against 1:1 mixture of Arochlor 1211 + 1242 standards  
 (2) Against 1:1 mixture of Arochlor 1254 + 1260 standards

Similar and even more significant accumulations were found in muddy sediments of experimental lagoons (in ug/kg dry weight).

	Polluted lagoons	Clean lagoons
Lindane	37	28
Aldrin	83	5
Total DDT	228	24
Total PCB	50	44
DDT )	4.6	0.6
PCB )		

There is stronger affiliation of PCBs to biota than to sediments, while the distribution of DDTs and aldrin is about equal in biota and sediments.

REFERENCES

SALIHOGU, J., FAGNELI, J. and STIRN, J. Organochlorine residues in some living organisms and sediments in the region of Piran (North Adriatic). Rev. intern. Oceanogr. Medic. (In press).

STIRN, J., et al. (1974). Pollution problems of the Adriatic Sea - an interdisciplinary approach. Rev. Intern. Oceanogr. Medic., 35-36: 21-7.

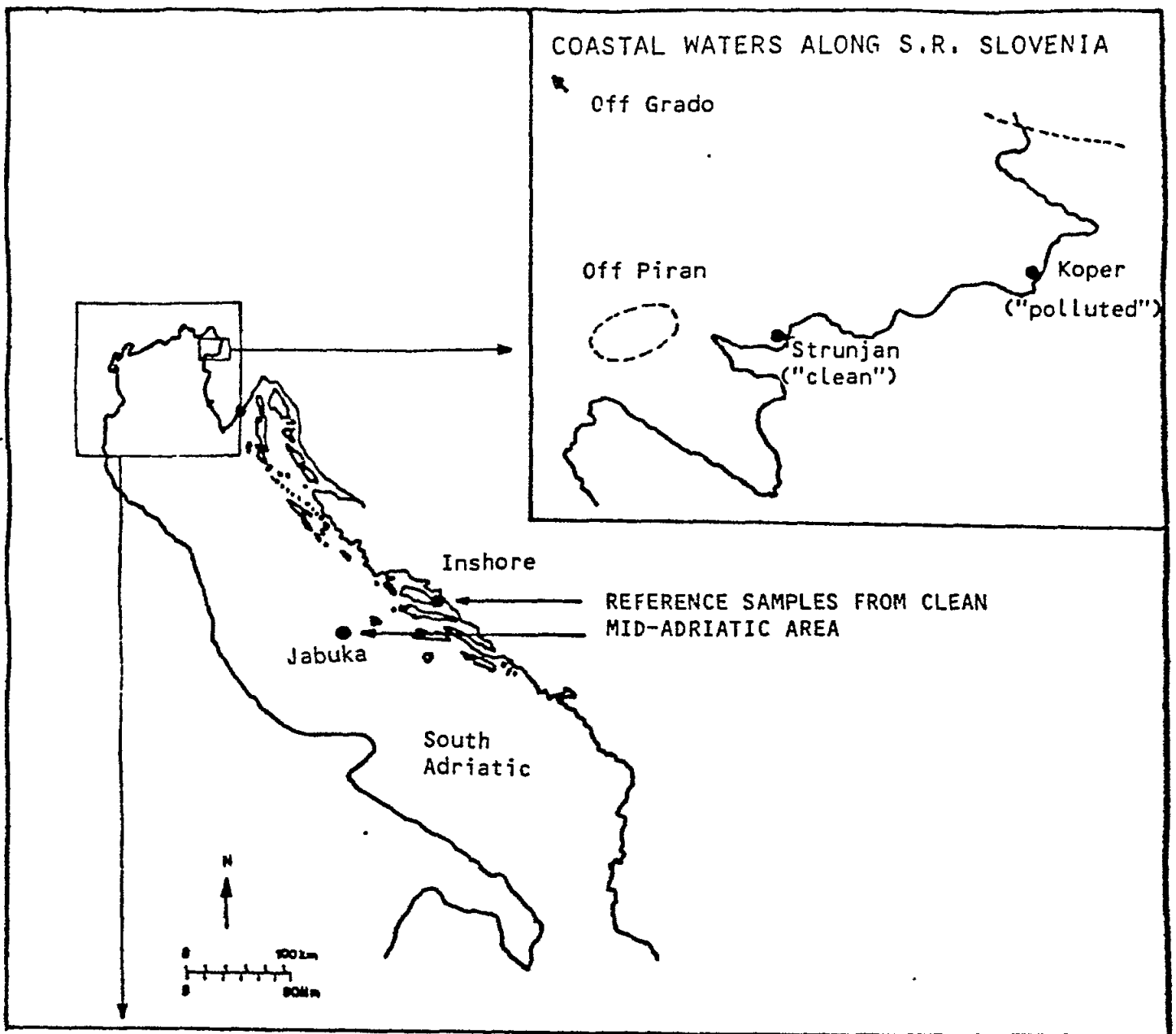


Figure 1. Geographical positions of sampling localities

Locality:		Latitude °'N:	Longitude °'E:
Off Piran	open NE Adriatic)	45 ° 33'	13 ° 33'
Off Grado	(open NW Adriatic)	45 ° 41'	13 ° 23'
Strunjan	(coastal "clean")	45 ° 32'	13 ° 36'
Koper	(coastal "polluted")	45 ° 33'	13 ° 44'
Savudrija	(coastal "clean")	45 ° 30'	13 ° 30'
Mid Adriatic	(inshore)	43 ° 12'	17 ° 02'
Mid Adriatic	(offshore - I. Jabuka)	43 ° 07'	15 ° 28'
South Adriatic	(offshore)	41 ° 32'	18 ° 08'

Research centre: Centre for Marine Research  
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Reporting period: June 1976 to March 1980

## INTRODUCTION

Several years ago (1974) the Centre for Marine Research started with analyses of chlorinated hydrocarbons in biota, sediments and sea-water in the Zagreb laboratories. The Rovinj laboratories started with some preliminary analyses of chlorinated hydrocarbons in sea-water in 1973 and those of zooplankton were performed two years later. With the beginning of the MED III pilot project, the Rovinj and Zagreb laboratories worked together on the analyses of chlorinated hydrocarbons in biota and the Zagreb laboratories in sediments and sea-water.

## METHODOLOGICAL CONSIDERATIONS

### Selection of the species:

The species analysed were: Mytilus galloprovincialis, Ostrea edulis, Patella coerulea, Monodonta turbinata, Trisopterus minutus capellanus, Merluccius merluccius, Boops boops, Boops salpa, Mullus barbatus, Mullus surmuletus, Mugil auratus, Mugil capito, Pagellus erythrinus, Oblada melanura, Maena maena, Gadus merlangus, Belone belone, Loligo vulgaris, Trachurus trachurus, Engraulis encrasicolus, Sardina pilchardus, Sardinella aurita, Venerupis aurea and zooplankton. Carcinus mediterraneus was not analysed because of technical difficulties in sampling and sample preparation.

The areas studied with sampling locations are shown in the figures.

The West Istrian coast (figure 1) is under the influence of the coastal sea-water. Chemical and biological characteristics are typical of oligotrophic areas. Depending on the meteorological situation, it could be under the influence of the northern Adriatic rivers (Po and others) so that sometimes eutrophic conditions could appear. Physical characteristics are typical for shallow coastal areas (up to 40 m) with well-defined stratification during summer and complete mixing during winter.

Rijeka Bay (figure 2) is somewhat deeper (up to 70 m) with the same characteristics as the West Istrian coast, but with the influence of a large industrial city.

### Pollutants analysed:

- DDT metabolites, dieldrin and PCBs.

## METHODOLOGY

Mussels were collected manually or by dredging in intertidal or very shallow water at various localities. Plankton was collected with a plankton net



(1m<sup>2</sup>; 250 µm) at several stations located in Rijeka Bay. Most of the fish samples were purchased on local markets, i.e. obtained from commercial catches. All samples were stored in a deep freezer (-25°). The analytical procedure included homogenization and extraction with petrolether, filtration through a column of anhydrous N<sub>2</sub>SO<sub>4</sub>, cleaning on an aluminium column, separation of PCBs from organochlorine insecticides on a miniature silica gel column and EC gas chromatographic analysis. Mirex was used as an internal standard.

All sample analyses, carried out by Mr. Devescovi and Miss Ivancic, were as follows: the sample was homogenized and extracted with an hexane/acetone mixture (Jensen, et al., Ambio Special Report No. 1. 1972, pp. 71-85). After dilution with a 0.1 M H<sub>3</sub>PO<sub>4</sub>/NaCl mixture, the hexane layer was dried on an N<sub>2</sub>SO<sub>4</sub> anhydrous column and volume-reduced to approximately 2 ml to analyse on GC. DDT metabolites were confirmed with KOH and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

A water sample of 35 l was extracted twice with 300 ml of n-pentane. The extract was dried by passing it through an Na<sub>2</sub>SO<sub>4</sub> anhydrous column, evaporated to 1 ml and cleaned up on the alumina column. PCBs were separated from organochlorine insecticides on a miniature silica gel column. Eluates, after concentration to 0.1 ml, were analysed by gas chromatography.

Water Analysis (XAD-2 resin adsorption): Water samples of 50 l were passed through the column with Amberlite XAD-2 resin. The column was eluted with methanol and acetonitrile. Eluates were re-extracted with n-pentane and the extract evaporated to a small volume and treated as described earlier.

Sediment analysis: Sediments were collected by means of a standard grab sampler. Representative aliquots of 10 g were extracted in the soxhlet extractor during a 4-hour period with 1:1 volume mixture of acetone and n-hexane. Extracts were evaporated to 1 ml and cleaned up by passing through the column of activated alumina and by means of KCN solution in acetone. Separation and further treatment were performed as described earlier.

#### Intercalibration exercise:

The intercalibration exercise was performed in the International Laboratory of Marine Radioactivity, Monaco, on fish (MA-M-2), oyster (MA-M-1) and copepod (MA-A-1) samples.

#### RESULTS

Analyses of the results of DDT metabolites, dieldrin and PCBs in Mytilus galloprovincialis are shown in Table I. Mean values for DDT and PCBs (such as Aroclor 1254) from the West Istrian coast (Pula, Porec, Umag area) are somewhat higher compared with the Rijeka Bay samples. The reason could be higher local pollution, as well as the influence, although seasonal, of the Po river. There is no significant difference in seasonal distribution of chlorinated hydrocarbons in Mytilus galloprovincialis.

Only a few samples of Mullus barbatus were analysed, one from the Rijeka Bay area and three from the Rovinj area. One sample was determined as Mullus surmuletus. Results are as follows: the sample from Rijeka Bay contained 16.5 µg/kg F.W. of DDT, most of which was DDT itself. An equal amount (15 µg/kg F.W.) was determined as Aroclor 1254. Three samples from the Rovinj

area contained between 28 and 87 µg/kg F.W. of DDT, most of which was DDE. In the sample which contained the highest value of DDT, and equal amount of DDT and DDE was observed. PCBs, as Clophen A-60, were in the 161-714 µg/kg F.W. range.

Mullus surmuletus contained 387 µg/kg F.W. of DDT (DDE-75, DDD-107, DDT-205) and 1,160 µg/kg F.W. of PCBs as Clophen A-60. Differences in DDT metabolite content are probably due to a different feeding habit.

Chlorinated hydrocarbons in other marine organisms: As it was difficult to obtain obligatory species, some analyses were performed on other marine organisms. Results are shown in Tables II and III, according to the sampling area. From the Umag area Venerupis aurea was analysed. The species contained low quantities of DDT (range 0.3 - 5.3 µg/kg F.W.) as well as PCBs (1.0-30.5 µg/kg F.W. as Aroclor 1254). From the Rijeka Bay area the highest DDT content was observed in Mugil auratus (228 µg/kg F.W) and the lowest in Pagellus erythrinus. The same was true of PCB content.

From the Rovinj area the highest DDT content was obtained in Sardina pilchardus (293 µg/kg F.W.) and the lowest in Boops salpa (1.8 µg/kg F.W.). The highest value of PCBs (as clophen A-60) was observed in Trachurus trachurus (287 µg/kg F.W.), while the lowest was in Boops boops (6 µg/kg F.W.). Nine individual specimens of Sardina pilchardus were also analysed and results obtained for DDT were in the 80-280 µg/kg F.W. range (mean value 155, standard deviation 74). Results for PCBs, as Clophen A-60, were: range 78-618 µg/kg F.W., mean 189, and standard deviation 168 µg/kg F.W.

Analysing all results for various organisms, any significant differences between the areas or seasons could not be established. Differences between species are probably due to feeding habits.

Analyses of chlorinated hydrocarbons in sea-water, waste-water, surface film, sediments and zooplankton were also performed. All the results were sent to UNEP as part of the non-obligatory results.

#### DISCUSSION OF RESULTS

Differences in the amount of chlorinated hydrocarbons in certain organisms are, in most cases, by an order of magnitude. The variation is probably due to the physiological state of the organisms in question, analysed out of a batch of individuals of similar weight and length. By the analysis of several specimens and by comparing the mean for a single area, the difference in distribution of chlorinated hydrocarbons between the areas can be appreciated, as is the case with Mytilus galloprovincialis. All other organisms show no significant differences in chlorinated hydrocarbon content. The results obtained are satisfactory and are comparable with others obtained in similar areas.

#### PUBLICATIONS

KRSINIC, B.F., et al (1978). Noxious effects of diesel oil D-2 and the synergistic effect of polychlorinated biphenyls (Aroclor 1242) on zooplankton species Euridica truncata. IV<sup>es</sup> Journées Etud. Pollution, Antalya. CIESM, 307-

- NAZANSKY, B., et al (1978). Monitoring of chlorinated hydrocarbons in biota of the north and middle Adriatic coastal waters. IV<sup>es</sup> Journées Etud. Pollution, Antalya, CIESM, 133.
- PICER, M., PICER, N. and AHEL, M. (1976). Discussion of international intercalibration results of organochlorine compound measurement in marine environment samples. II Yugoslav Symposium "Standardization '76" G2:1-
- PICER, M. and AHEL, M. (1978). Separation of polychlorinated biphenyls from DDT and its analogues on a miniature silica gel column. J. Chromatogr., 150:119-
- PICER, M., PICER N. and STROHAL, P. (1977). Evidence on behaviour of low concentration DDT in laboratory sorption experiments. Sci. Total. Environ., 8:159-
- PICER, M. PICER, N. and AHEL, M. (1978). Chlorinated insecticide and PCB residues in fish and mussels of east coastal waters of the middle and north Adriatic Sea, 1974-1975. Pest. Monit. J., 12:102-
- PICER, M., et al (1978). Investigation of the fate of some chlorinated hydrocarbons in laboratory grown phytoplankton culture. IV<sup>es</sup> Journées Etud. Pollution, Antalya, CIESM, 453-
- PICER, M., et al (1979). Investigation on the distribution of DDT and Aroclor 1254 in laboratory-grown marine phytoplankton. Bull. Environ. Contam. Toxicol., 21:743-
- PICER, M., PICER, N. and NAZANSKY, B. Persistent chlorinated hydrocarbons in Rijeka Bay. Thalassia Jugoslavica. (In press).
- PICER, M., et al. Investigation on the distribution of some chlorinated hydrocarbons in laboratory-grown phytoplankton culture. Sci. Total. Environ. (In press).
- PICER, N. (1978). Disadvantages of DDT and similar compounds in the environment. Pomorski zbornik, 16:485-
- PICER, N., PICER, M. and STROHAL, P. (1975). Determination of <sup>14</sup>C-DDT radioactivity in sea-water and marine suspended matter by liquid scintillation. Bull. Environ. Contam. Toxicol., 14:565-
- PICER, N., PICER, M. and STROHAL, P. (1977). The interaction of DDT with suspended particles in sea-water. Water, Air, Soil Pollut., 8:429-
- PICER, N. and PICER, M. (1978). Monitoring of chlorinated hydrocarbons in water and sediments of north Adriatic coastal waters. IV<sup>es</sup> Journées Etud. Pollution, Antalya, CIESM, 133-
- PICER, N., PICER, M. and NAZANSKY, B. (1979). Chlorinated hydrocarbons in the Adriatic. Proceedings of 2nd Conference on Protection of the Adriatic Sea. Hvar, 1979. 11:367-
- PICER, N. and PICER, M. Evaluation of macroreticula resins for low concentration determination of chlorinated hydrocarbons in sea-water and tap water. J. Chromatogr. (In press).
- SMODLAKA, N., DEVESCOVI, M. and IVANCIC, I. (1981). Comparison of two methods for analyses of chlorinated hydrocarbons in marine organisms. V<sup>es</sup> Journées Etud. Pollution, Cagliari, 1980. 43.

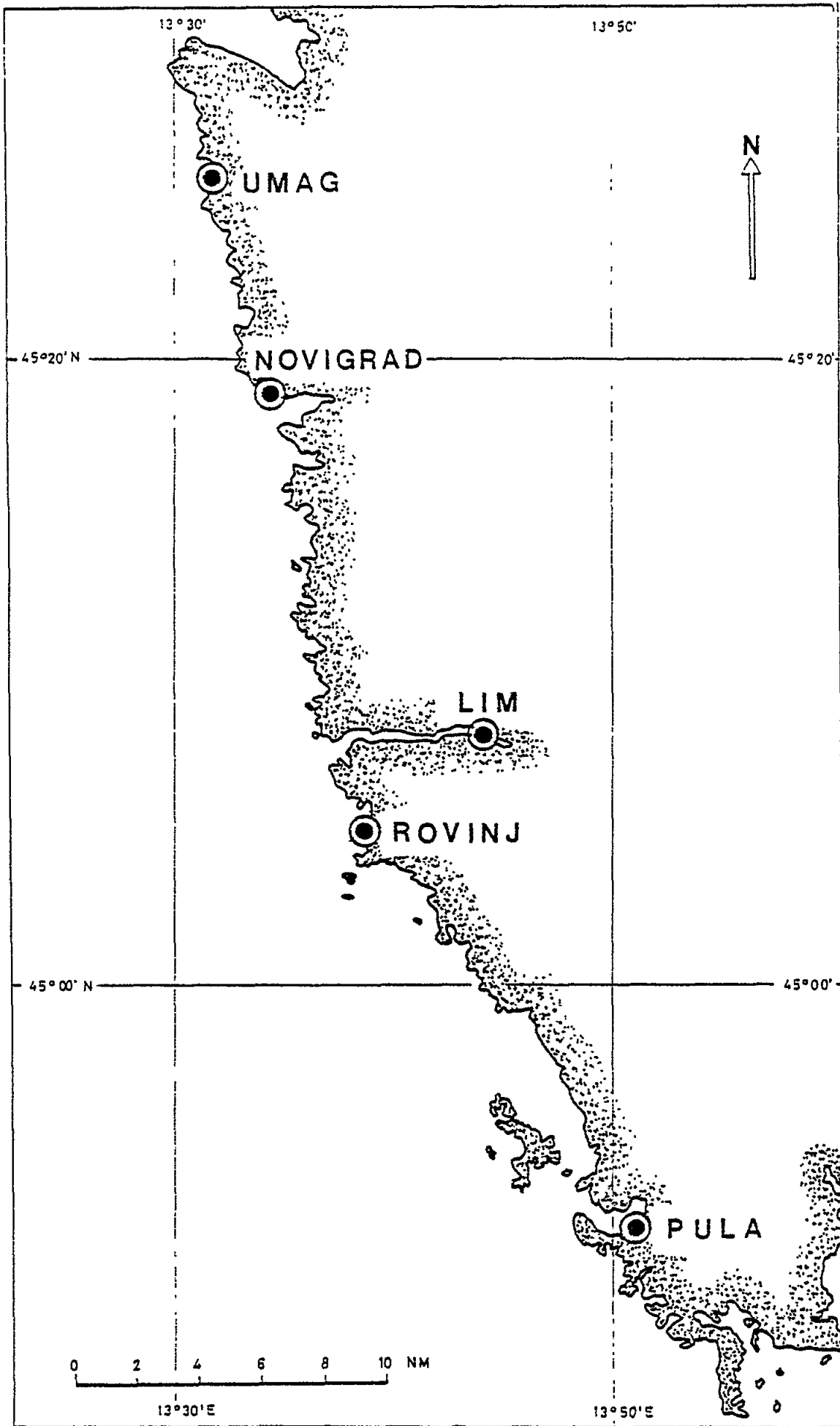


Fig. 1. West Iстриan coast

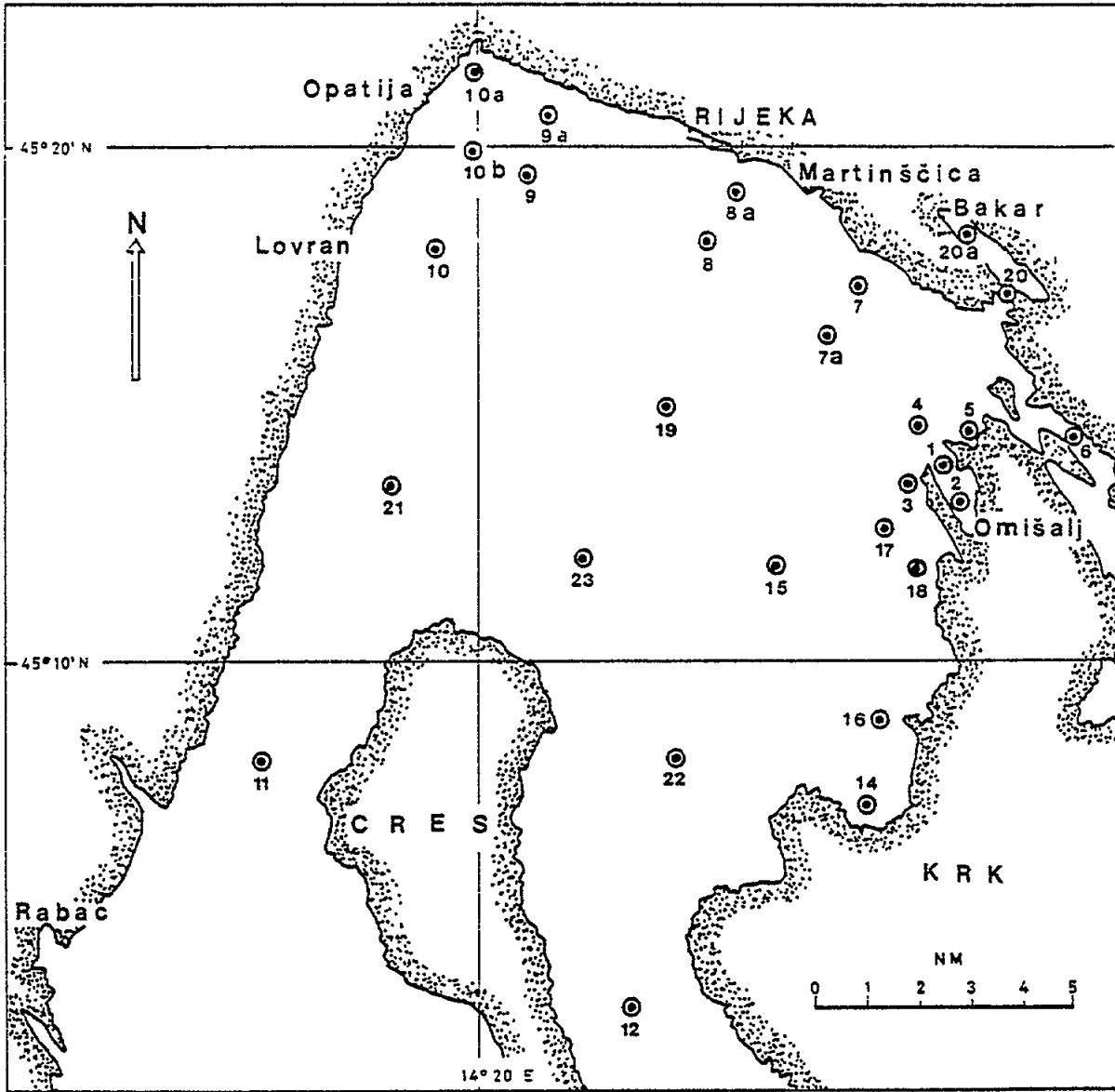


Fig. 2. Rijeka Bay area

Table 1. Mytilus galloprovincialis ( $\mu\text{g}/\text{kg}$  fw)

Pollutant	DDT	DDD	DDE	$\Sigma$ DDT	DIE	PCB
Pula	range	0,1 - 21,7	0,1 - 13,2	0,7 - 91,7	0,1 - 2,0	5,0 - 157,0
area	$\bar{x} \pm \sqrt{n-1}$	5,7 $\pm$ 6,3	4,9 $\pm$ 4,0	24,7 $\pm$ 26,1	0,2 $\pm$ 0,6	67,0 $\pm$ 62,3
	n	12	12	12	12	12
Rovinj	range	0,4 - 65,5	0,1 - 29,1	2,8 - 217,6	0,1 - 56,0	5,0 - 343,3
area	$\bar{x} \pm \sqrt{n-1}$	30,3 $\pm$ 19,6	4,7 $\pm$ 8,5	36,2 $\pm$ 69,7	3,8 $\pm$ 14,4	66,1 $\pm$ 107,3
	n	15	15	15	15	15
Poreč	range	0,3 - 26,8	0,6 - 15,0	0,9 - 109,7	0,1 - 0,6	5,0 - 145,5
area	$\bar{x} \pm \sqrt{n-1}$	25,5 $\pm$ 8,3	6,2 $\pm$ 4,5	37,9 $\pm$ 31,0	0,1 $\pm$ 0,2	56,9 $\pm$ 51,4
	n	14	14	14	14	14
Umag	range	0,1 - 0,9	2,0 - 4,8	2,0 - 5,2	0,1 - 1,3	34,0 - 51,4
area	$\bar{x} \pm \sqrt{n-1}$	0,3 $\pm$ 0,5	2,7 $\pm$ 1,9	4,0 $\pm$ 1,7	0,6 $\pm$ 0,7	41,8 $\pm$ 8,8
	n	3	3	3	3	3
Rijeka	range	0,1 - 4,0	0,1 - 41,2	0,7 - 121,9	0,1 - 0,6	0,0 - 121,0
area	$\bar{x} \pm \sqrt{n-1}$	1,1 $\pm$ 1,2	2,3 $\pm$ 7,7	2,3 $\pm$ 7,7	0,1 $\pm$ 0,2	24,7 $\pm$ 35,5
	n	28	28	28	28	28

Table II Distribution of  $\Sigma$  DDT and PCB in different species from the Rovinj area.

Species	No of analyses	$\Sigma$ DDT range ( $\mu\text{g}/\text{kg}$ fw)	PCB range ( $\mu\text{g}/\text{kg}$ fw)
<u>Engraulis engrasicolus</u>	4	25 - 81	21 - 59
<u>Sardina pilchardus</u>	3	176 - 293	129 - 258
<u>Sardinella aurita</u>	1	126	455
<u>Trachurus trachurus</u>	4	19 - 156	34 - 287
<u>Loligo vulgaris</u>	4	19 - 114	30 - 235
<u>Boops boops</u>	2	10 - 28	46 - 64
<u>Boops salpa</u>	1	1.8	6
<u>Mugil capito</u>	1	112	164
<u>Belone belone</u>	1	63	84
<u>Sadus merlangus</u>	1	6.3	31
<u>Trisopterus minutus capelanus</u>	1	5	17
<u>Macoma matua</u>	1	91	112

Table III. Distribution of  $\Sigma$  DDT and PCB in different species from the Rijeka Bay area.

Species	No of analyses	$\Sigma$ DDT range ( $\mu\text{g}/\text{kg}$ fw)	PCB range ( $\mu\text{g}/\text{kg}$ fw)
<u>Patella</u> <u>coerula</u>	1	8.6	5.0
<u>Monodonta</u> <u>turbinata</u>	1	8.0	5.0
<u>Trisopterus</u> <u>minutus</u> <u>capellanus</u>	2	1.7 - 3.9	5.0
<u>Merluccius</u> <u>merluccius</u>	2	20.7 - 37.6	10.0 - 48.0
<u>Boops</u> <u>boops</u>	1	4.2	30.0
<u>Mugil</u> <u>auratus</u>	2	44.0 - 228.0	120.0 - 1060.0
<u>Pagellus</u> <u>erythrinus</u>	1	2.9	5.0
<u>Oblada</u> <u>melanura</u>	1	24.8	25.0
<u>Ostrea</u> <u>edulis</u>	1	4.8	17.3
Zooplankton	13	0.7 - 2.8	5.0 - 135



Research Centre: Biological Institute  
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Principal Investigator: D. VILICIC

Period of reporting: September 1976 - March 1980

#### INTRODUCTION

The monitoring of chlorinated hydrocarbons in biota samples relevant to the MED POL programme in Southern Adriatic coastal waters started in September 1976 and lasted until March 1980.

#### METHODOLOGICAL CONSIDERATIONS

##### Selection of the species:

The following species were taken for samples: Mullus surmuletus, Merluccius merluccius, Mytilus galloprovincialis, Ostrea edulis and Xantho hydrophilus. Zooplankton was collected using a 250 µm net with copper bucket.

##### Pollutants analyzed:

The following chlorinated hydrocarbons were analysed: DDT, TDE, DDE, DIE and PCBs.

##### Areas studied:

The samples were taken from three areas i.e. at the mouth of the Neretva river (highly productive lowland covered by orchards, vegetables and flowers), in the Mali Ston Bay (the end of the Neretva channel with oyster and mussel beds, and near the town of Dubrovnik (affected by different kinds of pollution).

A total of 6 sampling stations (Fig.1) coincide with the co-ordinate reported in LOG FORM-s.

#### METHODOLOGY

Biota samples were collected and prepared for the analyses using procedures recommended by FAO Fisheries Technical Paper, 1976. The method used for the analysis of biota included homogenization and extraction with petrolether, filtration through a column of anhydrous Na<sub>2</sub>SO<sub>4</sub>, clean up on alumina column (Holden and Marsden 1969), separation of PCBs from organochlorine insecticides on a miniature silica gel (Picer and Ahel 1978), and EC chromatographic analysis. Mirex was used as an internal standard.

##### Intercalibration exercise:

The intercalibration exercise has been performed by the collaborating research centre which carried out the analyses.

## RESULTS

Table I shows the maximum, minimum and mean concentrations of DDT, PCBs and dieldrin for the species analysed. The DDT, PCBs and dieldrin mean values are presented as geometrical means on a fresh weight basis ( $\mu\text{g}/\text{kg}$  FW).

### Discussion of results:

Figure 2 shows the distribution of the pollutant concentrations in the various organisms in a histogram form on fresh weight basis. Concentrations of DDT are very low, sometimes (e.g. in Mali Ston Bay, Station 2) even lower than those found in W. Mediterranean (UNEP 1978). PCB concentrations are relatively high in the vicinity of Dubrovnik (Stations 4, 5 and 6) probably due to ship-repairing and paint-work carried on there.

### PUBLICATIONS

FAO, 1976: Fisheries Technical Paper No. 158.

HOLDEN, A.V. and MARSDEN, K. (1969): Single stage clean-up of animal tissue extracts for organochlorine residue analysis. *J. Chromatogr.* 40(1), 481-492.

PICER, M. and AHEL, M. (1978): Separation of polychlorinated biphenyls from DDT and its analogues on a miniature silica gel column. *J. Chromatogr.* 150, 119-127.

UNEP, 1978: Preliminary report on the state of pollution of the Mediterranean sea., 3.2 Concentration of chlorinated hydrocarbons in the marine environment, 20 p.

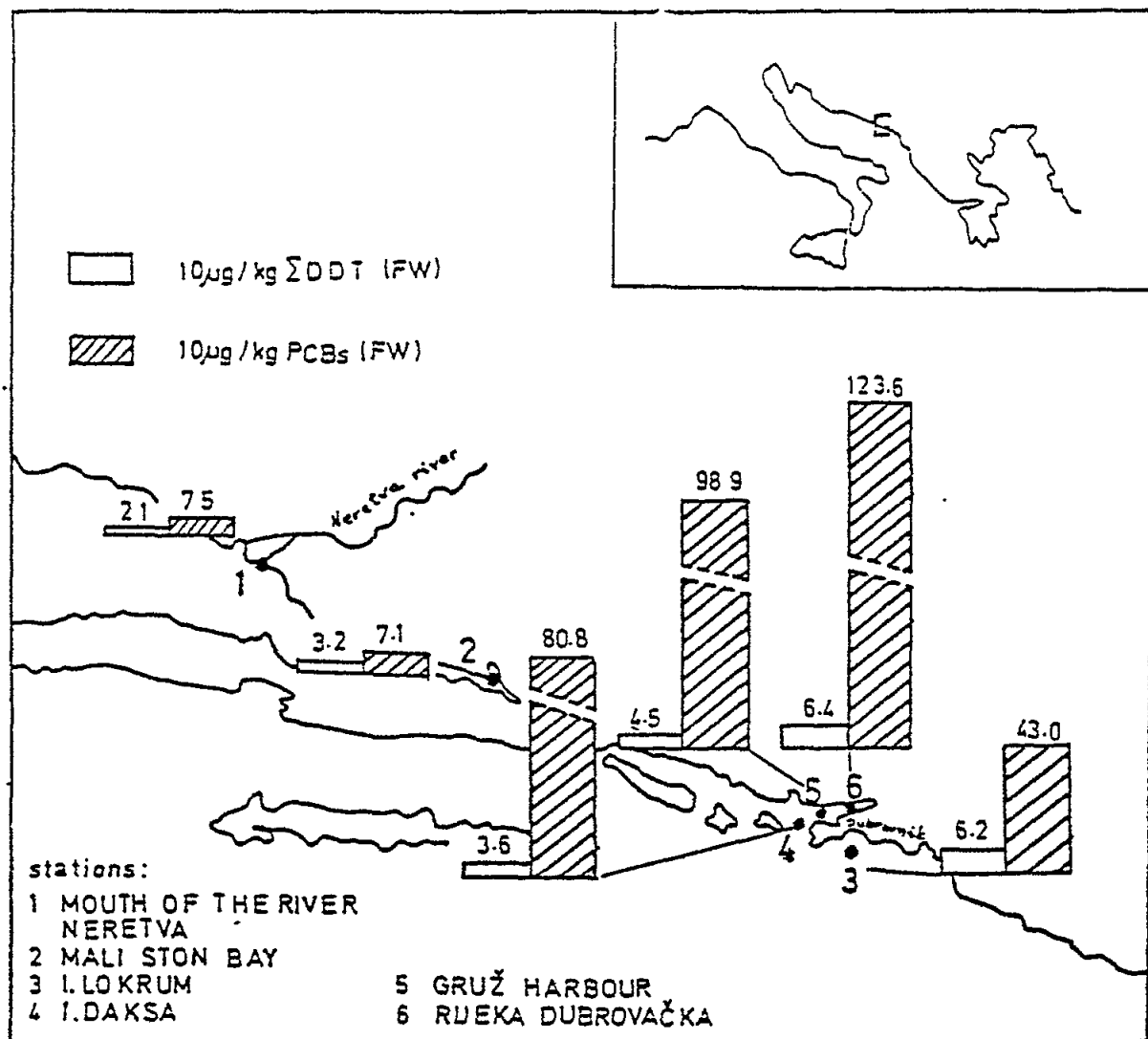


Fig. 1. Sampling stations and concentrations (µg/kg FW) of total DDT and PCBs in Mytilus galloprovincialis expressed graphically as geometrical means

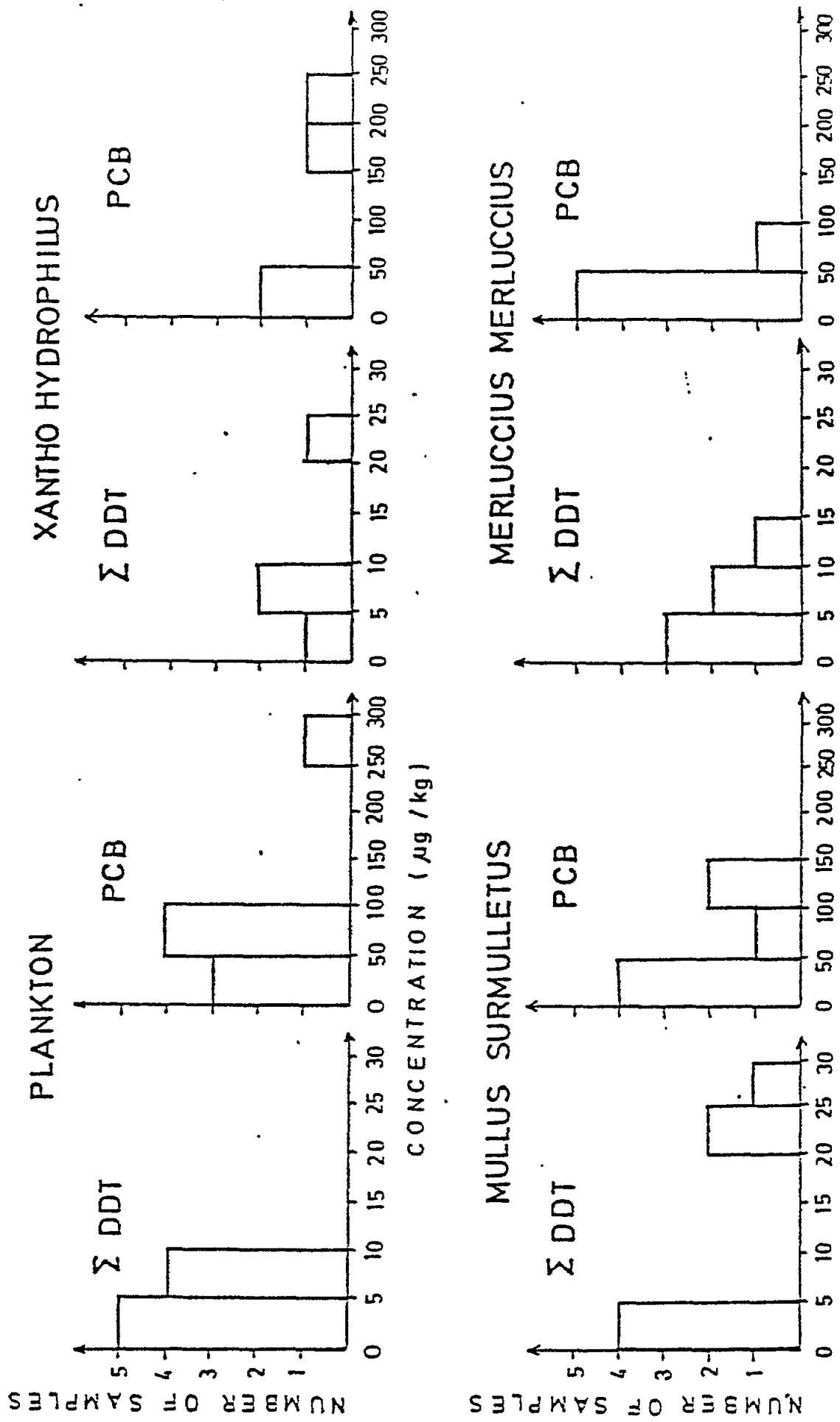


Fig.2 -- Distribution of total DDT and PCBs concentrations (µg/kg FW) in tested organisms

Table I. Concentrations ( $\mu\text{g}/\text{kg}$  F.W.) of  $\Sigma\text{DDT}$ , PCB-s and dieldrin in various species and plankton at 6 different stations (1-6; Fig. 1) shown as range, mean and (number of samples).

Species	1	2	3	4	5	6
<u>Mytilus galloprovincialis</u>	$\Sigma\text{DDT}$	1.1 - 10.6	1.5 - 16.7	1.9 - 8.3	1.2 - 9.6	2.6 - 65.3
	PCB	3.2 (7)	6.2 (7)	3.6 (5)	4.5 (5)	6.4 (5)
	DIE	7.1 (7)	43.0 (7)	80.8 (5)	98.9 (5)	123.6 (5)
<u>Mullus surmuletus</u>	$\Sigma\text{DDT}$	0.1 - 0.7	0.1 - 1.9	0.1 - 1.0	0.3 - 0.6	0.1 - 11.7
	PCB	0.2 (7)	0.2 (7)	0.3 (5)	0.4 (5)	0.64 (5)
	DIE		0.7 - 25.0			
<u>Ostrea edulis</u>	$\Sigma\text{DDT}$		6.0 (7)			
	PCB		5.0 - 145.0			
	DIE		33.0 (7)			
<u>Merluccius merluccius</u>	$\Sigma\text{DDT}$	2.1 - 4.5	2.3 - 11.7	0.1 - 0.6	0.4 (7)	
	PCB	3.1 (2)	3.6 (6)			
	DIE	5.0 - 30.0	5.0 - 20.0			
<u>Xantho hydrophilus</u>	$\Sigma\text{DDT}$	12.2 (2)	12.8 (6)			
	PCB	0.1 - 2.0	0.1 - 0.6			
	DIE	0.4 (2)	0.2 (6)			
<u>Zooplankton</u>	$\Sigma\text{DDT}$	0.4 - 12.5	0.4 - 12.5	0.4 - 24.6		4.6 - 7.0
	PCB	3.2 (6)	3.2 (6)	4.5 (4)		5.8
	DIE	5.0 - 52.0	12.9 (6)	14.6 - 242.4		68.6 - 266.0
<u>Zooplankton</u>	$\Sigma\text{DDT}$	0.1 - 0.7	0.1 - 0.7	64.9 (4)		110.3
	PCB	0.3 (6)	0.3 (6)	0.1 - 8.5		0.1 - 0.4
	DIE	4.7 - 17.3	3.0 - 14.8	1.2 (4)		0.2
<u>Zooplankton</u>	$\Sigma\text{DDT}$	7.3 (4)	7.4 (4)	2.1 - 9.5		
	PCB	7.5 - 100.0	19.0 - 134.3	17.5 - 63.1		
	DIE	47.0 (4)	44.0 (4)	38.1		
<u>Zooplankton</u>	$\Sigma\text{DDT}$	0.1 - 4.3	0.5 - 4.4	0.1 - 1.5		
	PCB	0.8 (4)	1.7 (4)	0.1 - 0.2		
	DIE					

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Reporting period: September 1978 - January 1980

## INTRODUCTION

The analysis of chlorinated hydrocarbons in biota started in March 1977 with the aim of contributing to a better understanding of the level of these pollutants in the area of the Central Adriatic.

## MATERIAL AND METHODS

The selection of the species was made according to the agreement. The species were: Mullus barbatus, Mytilus galloprovincialis, zooplankton and Carcinus maenas, but Carcinus were not always available.

Pollutants analyzed: DDT, TDE (DDD), DDE, DIE and PCBs.

### Areas studied:

The sampling of marine organisms took place on the east coast of the Central Adriatic. The area covered three important industrial and agricultural regions (Zadar, Split, Ploce).

Physical, chemical and biological characteristics of the investigated area are incorporated in other MED POL reports.

## METHODOLOGY

Fish samples were obtained from experimental catches with the research trawler m/b "BIOS". Shellfish were collected manually and zooplankton was collected with a plankton net (1 m<sup>2</sup> - 300 microns). Samples were kept in the deep-freeze and speedily analysed. Methods used are described in FAO Fisheries Technical Paper No. 158, and Picer, M. and M. Ahel, 1978:

"Separation of polychlorinated biphenyls from DDT and its analogues on a miniature silica gel column", J. Chrom. 150, pp. 119-127. Analytical procedure includes homogenization and extraction with hexane filtration through a column of anhydrous Na<sub>2</sub>SO<sub>4</sub>, cleaning on an aluminium column, separation of PCBs from organochlorine insecticides on a miniature silica gel column and EC Gas-chromatographic analysis. Mirex was used as an internal standard.

### Intercalibration exercise:

Intercalibration exercises were carried out with the international laboratory for Marine Radioactivity (IAEA) in Monaco on the following samples: oyster (MA-M-1), copepod (MA-A-1) and fish (MA-M-2).

RESULTS AND THEIR INTERPRETATION

Minimum and maximum values for all samples from March 1977 to March 1980 are shown below ( in  $\mu\text{g}/\text{Kg}$  fresh weight):

	t-DDT		PCBs	
	Min.	Max.	Min.	Max.
<u>Mullus barbatus</u>	0,3	50,0	1,0	497,9
<u>Mytilus galloprovincialis</u>	1,0	31,0	3,0	179,4
Zooplankton	0,3	2,3	6,4	25,8

Average values of all data from the Central Adriatic (east coast) seem to be among the lowest in the Mediterranean sea.

PUBLICATIONS

DUJMOV, J., VUCETIC, T., PICER, M. and PICER, N., 1978. Some results of the monitoring of chlorinated hydrocarbons in organisms from the Central Adriatic, IV<sup>es</sup> Journées Etud. Pollutions, pp. 137-141, Antalya, CIESM.

PUBLICATIONS IN THE MAP TECHNICAL REPORTS SERIES

- No. 1 UNEP/IOC/WMO: Baseline studies and monitoring of oil and petroleum hydrocarbons in marine waters (MED POL I). MAP Technical Reports Series No. 1. UNEP, Athens 1986.
- No. 2 UNEP/FAO: Baseline Studies and Monitoring of Metals, particularly Mercury and Cadmium, in Marine Organisms (MED POL II). MAP Technical Reports Series No. 2. UNEP, Athens 1986.

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