



MEDITERRANEAN ACTION PLAN

MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME



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

BASELINE STUDIES AND MONITORING OF METALS, PARTICULARLY
MERCURY AND CADMIUM, IN MARINE ORGANISMS (MED POL II)

ETUDES DE BASE ET SURVEILLANCE CONTINUE DES METAUX, NOTAMMENT
DU MERCURE ET DU CADMIUM, DANS LES ORGANISMES MARINS (MED POL II)

FINAL REPORTS OF PRINCIPAL INVESTIGATORS
RAPPORTS FINAUX DES CHERCHEURS PRINCIPAUX

MAP Technical Reports Series No. 2

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PNUE/FAO: Etudes de base et surveillance continue des métaux, notamment du mercure et du cadmium, dans les organismes marins (MED POL II). MAP Technical Reports Series No. 2. UNEP, Athens 1986.

This volume is the second 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 second 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 Metals, particularly Mercury and Cadmium, in Marine Organisms (MED POL II)".

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 des métaux, notamment du mercure et du cadmium, dans les organismes marins (MED POL II)".

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Centre de Recherche : Centre de recherches océanographiques et
des pêches
ALGER
Algérie

Chercheur principal : A. AISSI

Période couverte par le rapport : Décembre 1976 - mars 1980 (Ce rapport
a été préparé sur la base des données
présentées dans les formulaires
d'enregistrement)

INTRODUCTION

La participation au projet pilote MED POL concernant la surveillance continue des métaux, principalement le mercure et le cadmium, dans les organismes marins a permis au centre de recherche de nouvelles et intéressantes expériences dans ce domaine.

CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces :

Les espèces sélectionnées recueillies régulièrement 5 fois par année, ont été:
Mytilus perna et *Mullus surmuletus*.

Polluants analysés :

Dans tous les échantillons prélevés on a déterminé les teneurs en mercure total et en cadmium.

Zone étudiée :

La baie d'Alger a été choisie comme la zone de travail avec deux stations d'échantillonnage (Fig. 1). La station 1 se trouve dans la rade du port derrière la Jetée Nord, où il y a une certaine pollution due soit à la localisation du port, soit, et surtout, aux émissaires urbains provenant de la Casbah et de Bab El Oued. La station 2 est située hors de l'extrémité Est de la baie d'Alger, où, même s'il y a encore l'influence de certains collecteurs urbains, la pollution devrait être plus faible.

METHODOLOGIE

L'échantillonnage des rougets a été effectué par des trémails; les moules ont été prélevées par grattage des parois rocheuses des îlots Sandja et de la Jetée Nord du port. Chaque échantillonnage a été réalisé en utilisant 6 spécimens de moule et 6 spécimens de rouget. La conservation des échantillons et le prélèvement des parties molles des moules et des filets des rougets ont été effectués suivant la méthode de référence FAO, Document technique sur les pêches n°. 158.

Des sous-échantillons du matériel à analyser étaient utilisés pour déterminer le rapport poids humide/poids sec (24 h à 105-110°C). La minéralisation était par voie humide sous pression (bombe en teflon) et les métaux dosés par spectrophotométrie d'absorption atomique sans flamme (mercure: génération de vapeurs froides; cadmium : four en graphite).

Programme d'intercalibration :

Le laboratoire a participé aux quatre exercices d'intercalibrations sur le matériel envoyé, par le Laboratoire de Monaco (IAEA).

RESULTATS

Métaux lourds dans Mytilus perna :

Mercure : Les teneurs moyennes (Tableau I) sont très faibles, avec un maximum de 122 µg/kg de poids frais (P.F.) dans la station 1.

Cadmium : Les valeurs sont de l'ordre de 100 µg/kg P.F. avec une tendance à augmenter dans les deux dernières années (Tableau I).

Métaux lourds dans Mullus surmuletus :

Mercure : Les teneurs moyennes varient de 38 à 159 µg/kg P.F., sans aucune différence parmi les deux stations (Tableau II), les teneurs augmentent avec le temps et nous le remarquons pour les années 1979 et 1980.

Cadmium : Les résultats sont très semblables à ceux de M. perna.

DISCUSSION DES RESULTATS

Les résultats obtenus montrent que les teneurs en mercure et en cadmium dans les deux espèces analysées sont encore très faibles, mais les teneurs semblent augmenter avec le temps, et une surveillance continue de la baie d'Alger est souhaitable.

TABLEAU I

Baie d'Alger : Les concentrations de mercure et de cadmium dans Mytilus perna. Moyennes et gammes (min-max), en µg/kg P.F.

Station	Année	n	Hg	Cd
1	1976	6	57 (40-80)	37 (30-40)
	1977	30	76 (30-113)	91 (30-264)
	1978	30	69 (20-100)	162 (80-310)
	1979	30	122 (30-330)	190 (90-310)
2	1976	6	80 (80-80)	70 (70-70)
	1977	30	65 (28-110)	93 (50-361)
	1978	30	80 (50-110)	100 (70-160)
	1979	18	49 (23-100)	163 (103-210)
	1980	12	51 (26-65)	133 (105-177)

TABLEAU II

Baie d'Alger : Les concentrations de mercure et de cadmium dans
Mullus surmuletus. Moyennes et gammes (min-max), en µg/kg P.F.

Station	Année	n	Hg	Cd
1	1976	6	38 (30-50)	42 (30-50)
	1977	30	55 (30-80)	96 (20-180)
	1978	30	79 (60-100)	128 (50-250)
	1979	30	135 (70-230)	209 (100-310)
	1980	6	159 (150-170)	263 (250-280)
2	1976	6	38 (30-50)	38 (30-50)
	1977	30	73 (50-156)	109 (50-260)
	1978	30	69 (35-95)	127 (55-250)
	1979	24	118 (70-170)	230 (200-306)
	1980	12	153 (140-170)	241 (200-260)

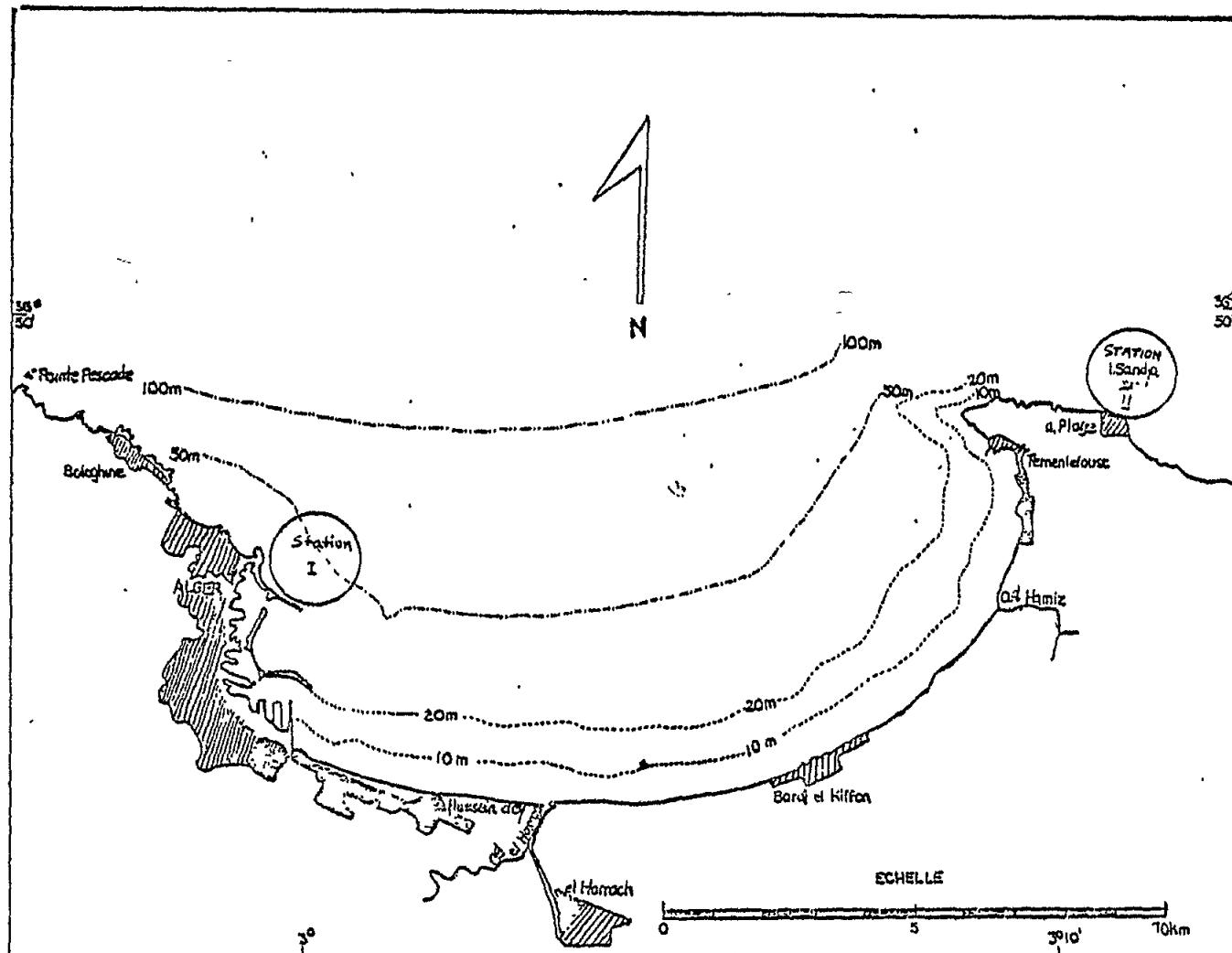


Fig. 1 Carte de la Baie d'Algier avec les stations de prélèvements d'échantillons

Research Centre:

Department of Fisheries
Ministry of Agriculture and Natural
Resources
NICOSIA
Cyprus

Principal Investigators:

A. DEMETROPOULOS - L. ATHANASSIADOU

Period of Reporting:

September 1976 to March 1980

INTRODUCTION

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

The work is important as the levels of these metals will have a bearing on national legislation and other actions and may have repercussions on the marketing of seafood.

METHODOLOGICAL CONSIDERATIONS

Selection of species:

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

Sometimes it was difficult to find the samples required.

Pollutants analysed: Cu, Zn.

Areas studied:

(a) Akrotiri Bay (Fig. 1).

Akrotiri Bay is on the south coast of Cyprus and is bounded on the west by the Akrotiri peninsula and on the north by the mainland. On the bay is situated Limassol, a town of about 65,000 inhabitants; it has two commercial ports. Limassol has light industries which include soft drink factories, wine and spirit factories, a flour mill and a slaughter house. Further away towards the east, there is an electrical power station, a cement factory and an ore concentrate plant (iron and copper pyrites). These factories, being situated near the coast, allow their effluents to reach the sea untreated. The total amount of waste-water entering Akrotiri Bay is about 1,377,000 tonnes for the year 1977 from industries up to (and including) the Moni area. Pollution from rivers is comparatively insignificant as there are no permanent rivers, only streams which flow during the rainy period. The increasing construction of water dams also limits the quantity of water reaching the sea.

Surface sea-water temperatures reach a maximum of approximately 27.0°C and a minimum of around 14.5°C.

During the summer months the thermocline is formed at about 25-30 meters depth. Salinity varies from about 38.6‰ to 39.5‰. The content in dissolved oxygen during winter is approximately 5.5 ml/l, reaching a

maximum of about 5.9 ml/l at a depth of 50-75 meters. During summer the content in dissolved oxygen is approximately 5 ml/l reaching the same maximum at the same depths. Analyses for suspended solids show values from 0-400 ppm. Summaries of physical and chemical parameters are shown in separate tables (not included in this report).

The sea-bed in Akrotiri Bay is as follows: sand with some shingle (beach), Posidonia meadows/sand (5m); Posidonia meadows/muddy sand (10 m); muddy sand with Caulerpa (20 m); mud with Caulerpa (30 m); mud with Caulerpa (40 m); mud with Caulerpa (60 m); mud aphyal.

(b) Larnaca Bay (Fig. 2).

Larnaca Bay is situated on the south-east side of the island. The main town is Larnaca with a population of about 35,000 inhabitants. Major industries situated near the coast are the electrical power station near Dhekelia, the refinery and a soap detergent factory.

The total amount of waste-water from industries entering Larnaca Bay was about 10,261,800 tonnes for the year 1977.

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 from the biological point of view, but it appears to be similar to Akrotiri Bay.

(c) Paphos area (Fig. 3).

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. There is no real industrial development except a wine factory situated near the coast.

The total amount of waste-water from industries flowing into the area was about 124,539 tonnes for the year 1977.

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 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 plastic bags and are then placed in thermoisolated boxes which are cooled with ice and are transferred to the laboratory where they are kept deep-frozen.

Sample preparation:

The fork and total lengths are determined, in the case of Mullus barbatus, and the fresh weight is recorded. The fish is then rinsed with dilute H₂SO₄ and distilled water.

The fillet of the fish (Mullus barbatus) is separated and the skin is pulled away from the flesh with plastic tweezers.

The fillet is then removed with a plastic knife from the vertebral column. The fillet is weighed. The same procedure is followed to remove the second fillet. The fillets are then placed in plastic bags and are kept deep-frozen. For a composite sample all the fillets are kept together. A piece of Xiphias gladius is taken and the skin is taken off using plastic tweezers. Then it is rinsed with dilute H₂SO₄ and distilled water. All samples are homogenized, dried in an oven at 100°C, and are pulverized using an agate pestle and mortar.

Digestion of samples:

The samples are weighed and transferred into Uniseal decomposition vessels; 8 ml of conc. HNO₃ are then added. The vessels are heated in an oven for 90 minutes at 140°C.

When cool they are transferred into volumetric flasks and diluted with double distilled water.

Measurement procedure:

A Varian Techtron 1250 Atomic Absorption Spectrophotometer is used. Standard solutions of different concentrations are analysed and the absorbances are recorded.

Analysis of samples follows with periodic checks of the zero and of some standards.

Intercalibration exercise:

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

RESULTS

Heavy metals in Xiphias gladius:

Cu x 15370 (ug/kg fresh weight)	±	343 (standard deviation of replicate analyses)
Zn x 15508 (ug/kg fresh weight)	±	254 (standard deviation of replicate analyses)

DISCUSSION OF RESULTS

The results obtained are the first and cannot be commented upon. In the available literature no data on heavy metals concentration in Xiphias gladius have been found.

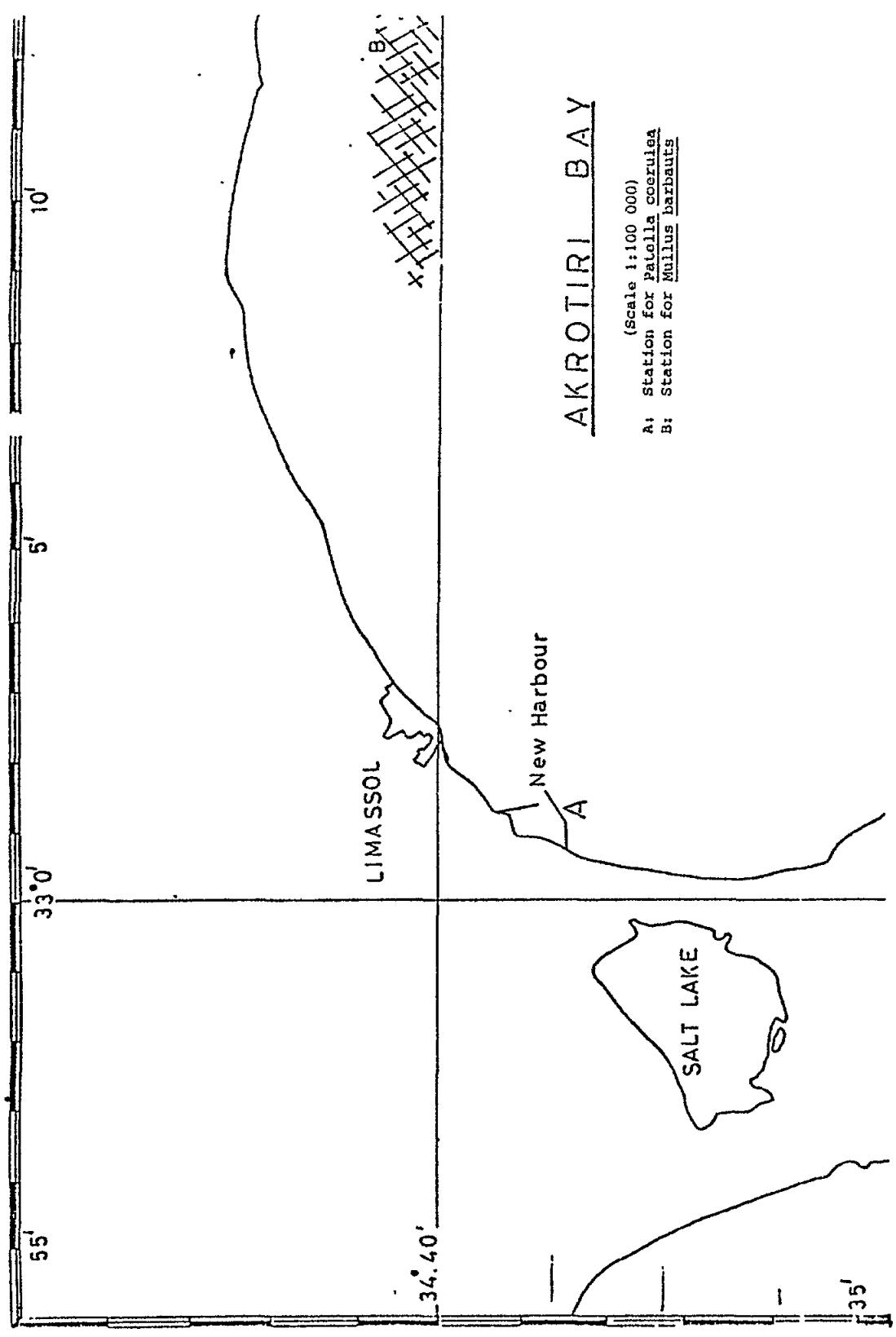


Figure 1. Sampling stations in Akrotiri Bay

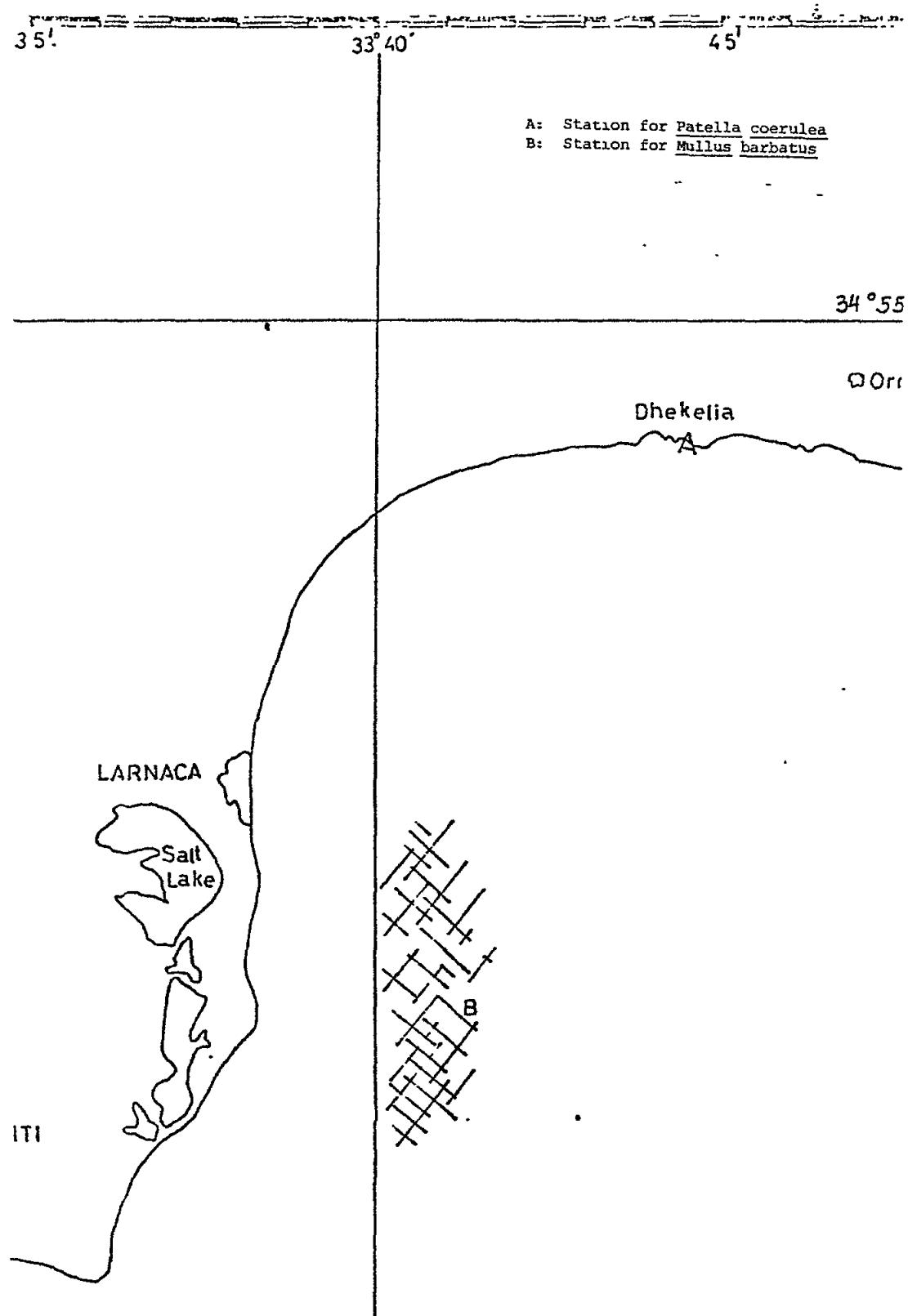
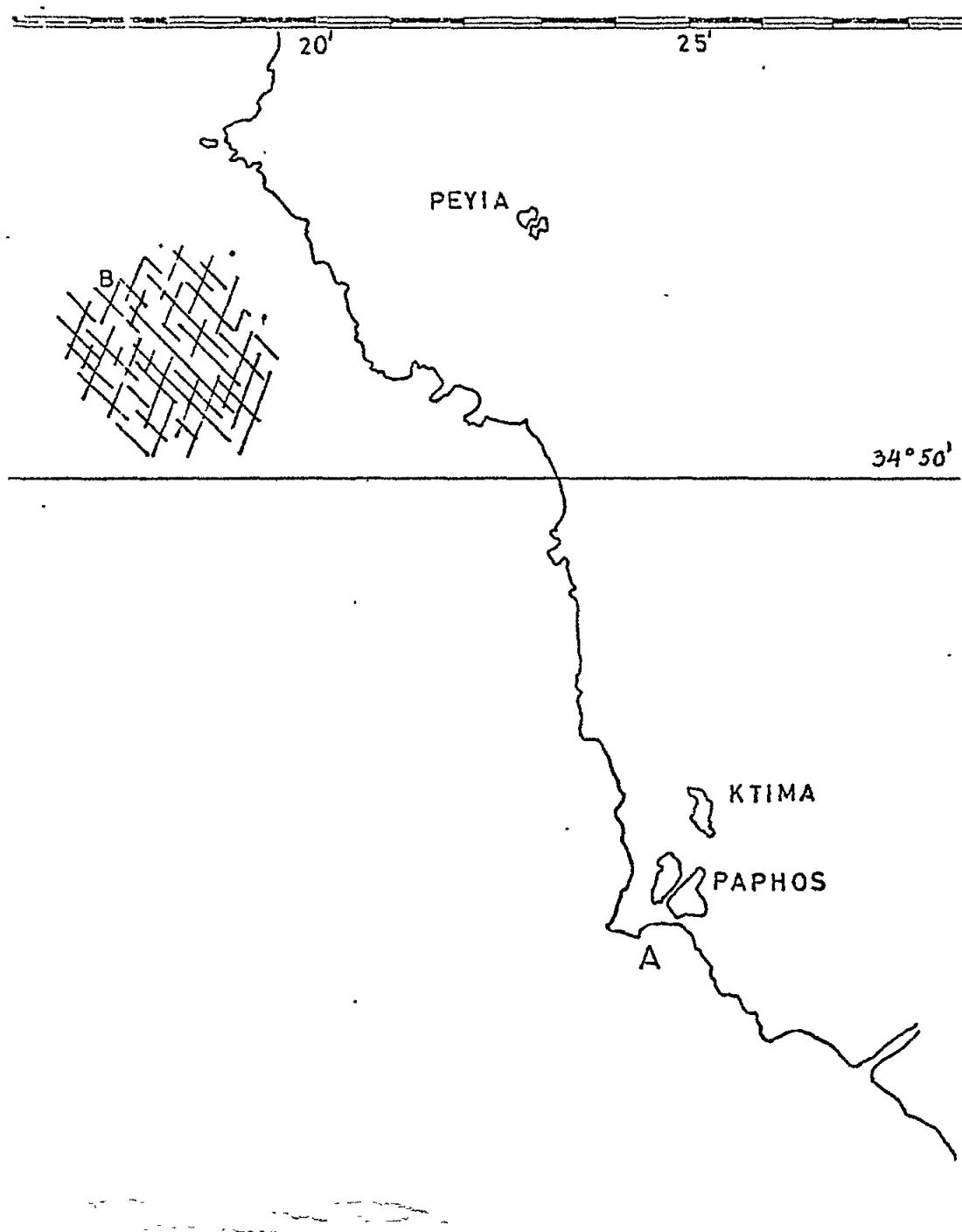


Figure 2. Sampling stations in Larnaca Bay



A: Station for Patella coerulea
B: Station for Mullus barbatus

Figure 3. Sampling stations in Paphos area

Research centre: Centre for Post-Graduate Studies and
 Research (UNARC)
 Alexandria University
 ALEXANDRIA
 Egypt

Principal Investigator: I.H. EL-SOKKARY

Period of reporting: February - October 1980

INTRODUCTION

The coast of Alexandria receive various sources of Hg-pollutants from the surrounding area. This occurs extensively at both the east (Abo Qir) and the west (El Mex) borders of the city.

It is obvious that Hg introduced into the sea water from Hg-pollutants is highly concentrated in marine organisms. Since this area is an important fishing ground, evaluation of Hg concentration in fish is of vital importance to public health.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

Mullus barbatus, Mullus surmuletus and Scorpaena porcus were selected for the analyses.

Pollutants analysed:

Total mercury concentration was determined in fish tissue.

Area studied:

The fish were sampled from the western area of Alexandria. Mullus barbatus and Mullus surmuletus were collected from a site located at 31°16' Lat. and 29°54' Long. Scorpaena porcus was collected from a site at 31°10' Lat. and 29°50' Long. (Fig. 1).

METHODOLOGY

The fish samples were placed in plastic bags after collection and were transported immediately to the laboratory where they were prepared for analysis as outlined in FAO Fisheries Technical Paper No. 158, pages 39-44. Total mercury in the tissue was determined according to the method given in the same publication (pages 65-78).

Intercalibration exercises:

The intercalibration exercise has been performed on samples MA-A-1 and MA-A-2.

RESULTS

It is clear from the data in Table I that Hg concentration varied according to species although they were collected from the same water and at the same date. Scorpaena porcus contained the highest level (2625 µg Hg/kg FW) while Mullus surmuletus and Mullus barbatus contained the lowest (47 and 60 µg Hg/kg FW respectively). However, Mullus barbatus showed greater capacity for accumulating Hg than Mullus surmuletus, particularly in samples collected in summer (122 and 83 µg/kg FW, respectively). Friberg and Vostal (1972), Brondum and Bernhard (1980) and Uysal (1978) found that various fish species accumulate Hg in their tissues with different levels.

Table I. Hg concentration in fillet of various fishes species

Fish species	Sampling location and month (1980)	No. of fishes	Average		
			Length mm	Weight g.	Total Hg µg/kg FW
<u>Scorpaena porcus</u>	El Mex, February	1	105	83	2625
<u>Mullus barbatus</u>	Anfoushi, February	1	120	31	60
<u>Mullus surmuletus</u>	Anfoushi, February	1	125	34	47
<u>Mullus barbatus</u>	Anfoushi, August	7	72	6	122
<u>Mullus surmuletus</u>	Anfoushi, August	8	73	7	83

Also as shown in Table II, Hg concentration varied according to the fishing season. Fish collected in winter contained lower Hg than those collected in summer. Seasonal variations were also noticed by Uysal, 1978.

Table II. Hg concentration in fillet of fishes collected from Anfoushi at two seasons

Fish species	Season (1980)	No. of fishes	Average		
			Length mm	Weight g.	Total Hg µg/kg FW
<u>Mullus surmuletus</u>	Winter	1	125	34	47
<u>Mullus surmuletus</u>	Summer	4	130	42	123
<u>Mullus barbatus</u>	Winter	1	120	31	60
<u>Mullus barbatus</u>	Summer	4	116	40	300

The data in Table III show a positive relationship between Hg concentration and weight of fish. The variations in Hg concentrations are found even with fish collected from the same water and having different weights and ages (Friberg and Vostal, 1972).

Table III. Hg concentration in fillet of fishes collected from Anfoushi in August 1980 in relation to fish size

Fish species	No. of fishes	Average		
		Length mm	Weight g	Total Hg μg/kg FW
<u>Mullus surmuletus</u>	3	168	89	194
	8	73	7	83
<u>Mullus barbatus</u>	3	137	51	402
	7	72	7	122

As shown in Table IV, the levels of Hg in the same fish species varied with fishing area. Mullus surmuletus collected from El-Mex contained higher Hg concentration than those collected from Anfoushi. However, this was not clear with Mullus barbatus.

Table IV. Hg concentration in fillet of fishes collected in summer 1980 from three fishing sites

Fish species	Location	No. of fishes	Average		
			Length mm	Weight g	Total Hg μg/kg FW
<u>Mullus surmuletus</u>	El-Mex	4	148	87	1295
	Anfoushi	3	168	89	194
<u>Mullus barbatus</u>	Abo Qir	4	133	49	397
	Anfoushi	3	137	51	402

It is obvious that Hg content in fish correlates positively with Hg concentration in the water recipient (Friberg and Vostal, 1972). This indicates that the degree of exposure of fish to pollution is an influential factor. Therefore, it could be predicted that the El-Mex area is more highly polluted with Hg than Anfoushi and Abu Qir.

In order to elevate the level of Hg in the local Mullus species, a comparison with others collected from various locations (Brondi and Bernhard, 1980) is represented in Table V.

Table V. Comparison of Hg concentration (ppb) in fishes of the present work with those of Brondi and Bernhard; 1980

Fish species	The present work	Mediterranean	Atlantic Ocean
<u>Mullus barbatus</u>	60 - 402 (252)	21 - 766 (159)	50 - 615 (260)
<u>Mullus surmuletus</u>	42 - 2200 (1032)	58 - 319 (119)	187 - 393 (281)

It is clear from Table V that Mullus surmuletus collected from El-Mex contained greater Hg concentration than the maximum permissible level in fish as reported by WHO (500 µg Hg/kg FW). Therefore, possibilities of health risks from the consumption of this fish is expected. In Egypt, the average per capita consumption is low. However, fishermen usually consume amounts as high as about 200 g/day or 1400 g/week. Consequently the weekly intake of Hg by consuming fish from Abu Qir will reach 353 µg Hg/person/week, and fish from El-Mex will be 1445 µg Hg/person/week.

Since, in 1976, WHO recommended 300 µg Hg/week/70kg person as the maximum tolerable weekly intake, this indicates possibilities of Hg poisoning.

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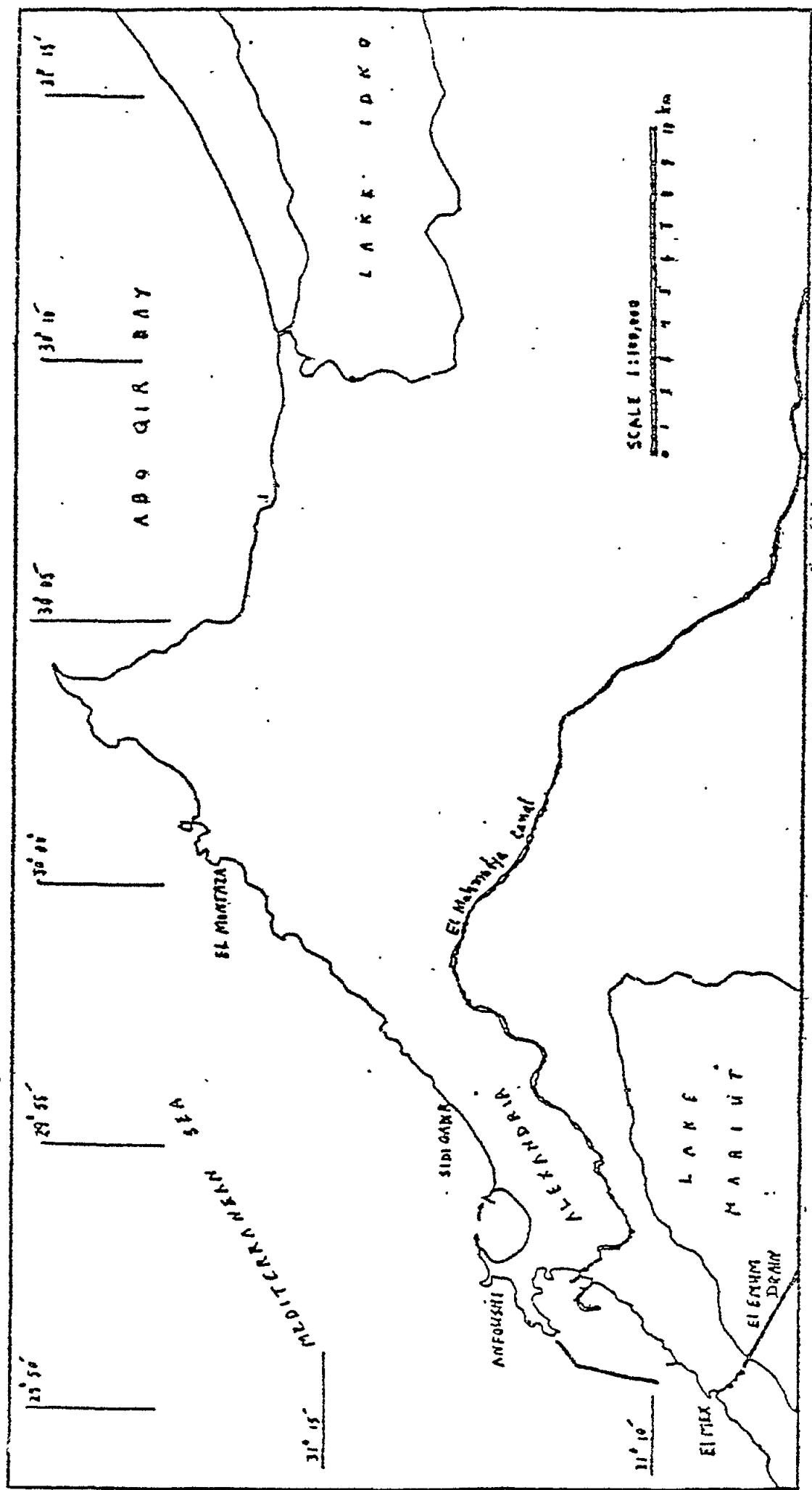


Fig. 1 -- Alexandria Coastal Area.

Research centre: Institute of Oceanography and Fisheries
ALEXANDRIA
Egypt

Principal investigator: H. EMARA

Period of reporting: March - December 1980

INTRODUCTION

In the past the Department had not carried out monitoring work such as programmed under this pilot project. The activities related to MED POL II started with the signature of the agreement.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

From the mandatory species: Mullus barbatus.

As exceptions to the mandatory species: Sardina pilchardus, Solea vulgaris, Sparus auratus, Sciaena aquilla, Penaeus semisulcatus.

Pollutants analysed:

Total mercury, cadmium and copper.

Areas studied:

Sampling was performed in Abu Kir Bay (Fig. 1), Lat. 31°23', Long. 30°08'. This Bay is located at the eastern side of Alexandria and is polluted with industrial wastes from textile mills and paper pulp plants in addition to the drains from Lake Edku thus adding pesticides to the industrial wastes.

METHODOLOGY

Samples were collected by trawling net, placed in plastic bags and put in a deep freezer.

Predigestion was carried out by placing about 1g FW of the pooled sample (2-5 specimens) in each teflon crucible and 2 ml of nitric acid (65%) was added to each crucible. Aliquots of standard solutions containing 500, 1000, 1500 ng of mercury and copper and 5, 10, 15 ng of cadmium were added to the crucibles.

The steel block was allowed to heat at 120°C for about 3 hours, then the block was left to cool overnight. The digested sample was then diluted with bidistilled water to the volume of 15 ml.

Mercury was determined by adding 1/2 ml hydroxylamine hydrochloride (12%) to 1 ml of the digested sample followed by 1 ml of stannous chloride (10%). After that the peak height was measured immediately.

Cadmium and copper were determined using an electrothermal atomization system (VARIAN CRA - 90).

RESULTS

The concentration of heavy metals Hg, Cd and Cu were determined and the following minimum and maximum values in $\mu\text{g}/\text{kg}$ FW have been recorded for the above species (number in brackets represents the number of specimens of the pooled sample).

Concentration of heavy metals in $\mu\text{g}/\text{kg}$ FW

	Hg		Cd		Cu	
	Min.	Max.	Min.	Max.	Min.	Max.
<u>Mullus barbatus</u>	227 (4)	323 (5)	9.0 (4)	12.8 (2)	319 (3)	653 (2)
<u>Penaeus semisulcatus</u>	157 (5)	238 (4)	11 (4)	14 (5)	2144 (5)	2303 (4)
<u>Sardina pilchardus</u>	230 (5)	245 (4)	8.2 (5)	9.8 (4)	1308 (5)	1592 (4)
<u>Solea vulgaris</u>	130 (3)	146 (3)	15 (3)	16.9 (3)	280 (3)	302 (3)
<u>Sparus auratus</u>	289 (3)	346 (4)	6.1 (3)	8.0 (4)	2100 (3)	3016 (4)
<u>Sciaena aquilla</u>	154 (3)	236 (4)	6.4 (3)	9.8 (4)	305 (3)	628 (4)

CONCLUSIONS

- The levels of mercury in the benthic fishes Mullus barbatus and Sparus auratus are somewhat higher than the levels obtained from the other fish.
- Cadmium has been found in low concentrations with the exception of Penaeus semisulcatus and Solea vulgaris, which showed higher concentrations.
- The concentration of copper was very high in Sardina pilchardus, Sparus suratus and Penaeus semisulcatus.
- The level of copper obtained from fresh-water fish Tilapia (987 - 1200 ppb) collected from Lake Edku, which has a direct connection to the Mediterranean, was found to be very high compared with sea water fish from Abu Kir Bay (except Sardina pilchardus and the crustacean Penaeus semisulcatus).

In addition to that, the level of mercury in Tilapia reflected low concentrations, which do not exceed 74.5 ppb from Lake Edku and 69 ppb from Lake Brullos.

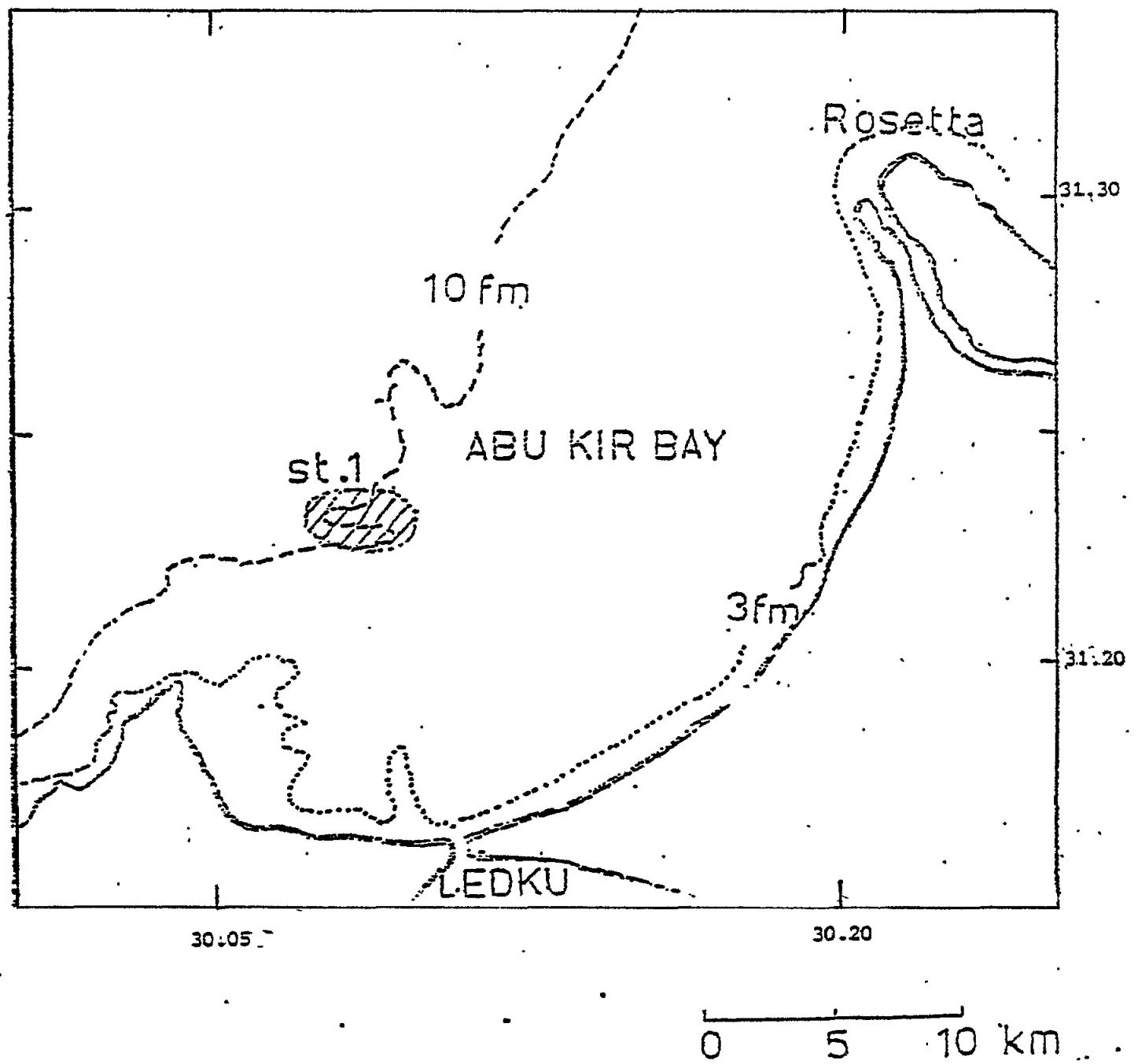


Fig. 1. Sampling stations

Centre de Recherche : Laboratoire de chimie analytique et toxicologie
Université de Montpellier
MONTPELLIER
France

Chercheur principal : S. BRUN

Période couverte par le rapport : Mai 1977 à décembre 1977

INTRODUCTION

Avant l'étude de ce projet notre laboratoire, lors d'une mise au point du dosage du mercure dans les poissons, a été amené à déterminer cet élément dans des échantillons de taupe de mer, de thon, de sardine et de maquereau, travail qui fait l'objet d'une thèse. Le laboratoire de chimie analytique et toxicologie de la Faculté de pharmacie de Montpellier s'est intéressé au dosage des éléments métalliques dans les boissons et les aliments depuis de nombreuses années sous la direction de Monsieur le Professeur Jaulmes et de Madame le Professeur Brun. En 1976 le laboratoire a été sollicité par le Ministère de la Qualité de la vie pour participer à un inventaire national de la qualité alimentaire. Cet inventaire a porté sur la recherche et le dosage du plomb, du cadmium, de l'étain et du mercure.

CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces :

La sélection a été faite par le Laboratoire Arago (M. Soyer, Directeur à Banyuls-sur-Mer) qui a procédé aux prélèvements.

Mullus barbatus :

Les gros exemplaires ont été pêchés sur des fonds de 200-300 m, à environ 30 km de la côte au large de Banyuls, le 27 mai 1977. L'engin de pêche utilisé était un chalut de type pélagique. Le chalutage a été effectué par le "Pr. Lacaze Duthiers" :

- les petits rougets ont été pêchés lors d'un chalutage côtier (distance de la côte : 1 à 2 km, profondeur : 50 m environ) effectué le 27 mai 1977 par la "Nereis";
- le stockage, après détermination des espèces, a été fait au congélateur, dans des feuilles d'aluminium.

Carcinus mediterraneus :

Les individus ont été prélevés le 25 mai 1977 dans l'étang de Sigean (Aude) à l'aide d'une petite drague et conservés vivants.

Mytilus galloprovincialis :

Les individus ont été grattés le 27 mai 1977 à côté du Laboratoire Arago.

Polluants analysés :

Cd, Hg et Mn. Certains éléments n'ont pas été déterminés sur certaines espèces par manque d'échantillons. Le Laboratoire Arago envoyait les échantillons au Laboratoire du Professeur Mestres qui après analyse nous transmettait le reste d'échantillons.

Zone étudiée :

Carte de la zone de prélèvements. (Figure 1).

METHODOLOGIE

Les analyses ont été effectuées dans leur intégralité au laboratoire de chimie analytique et toxicologie. Un temps important a été réservé à l'étude des méthodes analytiques mises en oeuvre. Une description de ces méthodes a été préparée en détail.

Programme d'intercalibration :

Nous avons reçu fin mars les échantillons d'homogénéisation de poisson MA-A-1 et MA-A-2. Nous ne sommes pas en mesure de vous communiquer des résultats.

RESULTATS

Les résultats présentés étaient fournis seulement dans les formulaires d'enregistrement.

Les concentrations de Hg déterminées dans Mytilus galloprovincialis étaient entre 13.4, et 34.3 µg/kg P.F. pendant la période entre le 26 mai 1977 et le 20 décembre 1977. Pour les mêmes échantillons les concentrations de Cd se trouvent entre 64 et 153 µg/kg P.F.

La concentration de Hg dans Mullus barbatus échantillonnes pendant la même période varie de 78,6 à 222,5 µg/kg P.F., tandis que la concentration en Cd était entre 15 et 205 µg/kg P.F. Dans les mêmes échantillons, la concentration déterminée pour Mn était entre 121 et 360 µg/kg P.F.

Dans Carcinus mediterraneus les concentrations déterminées varient pour Hg entre 119 et 844 µg/kg P.F. et pour Cd entre 20 et 740 µg/kg P.F.

DISCUSSION DES RESULTATS

Les teneurs des différents éléments que nous avons trouvées dans les trois espèces analysées nous paraissent des teneurs relativement faibles. Nos résultats sont en concordance avec les résultats publiés par le rapport des IV^{es} Journées d'Etudes sur les Pollutions marines en Méditerranée (Antalya, 24-27 novembre 1978, CIESM/PNUE, 1979).

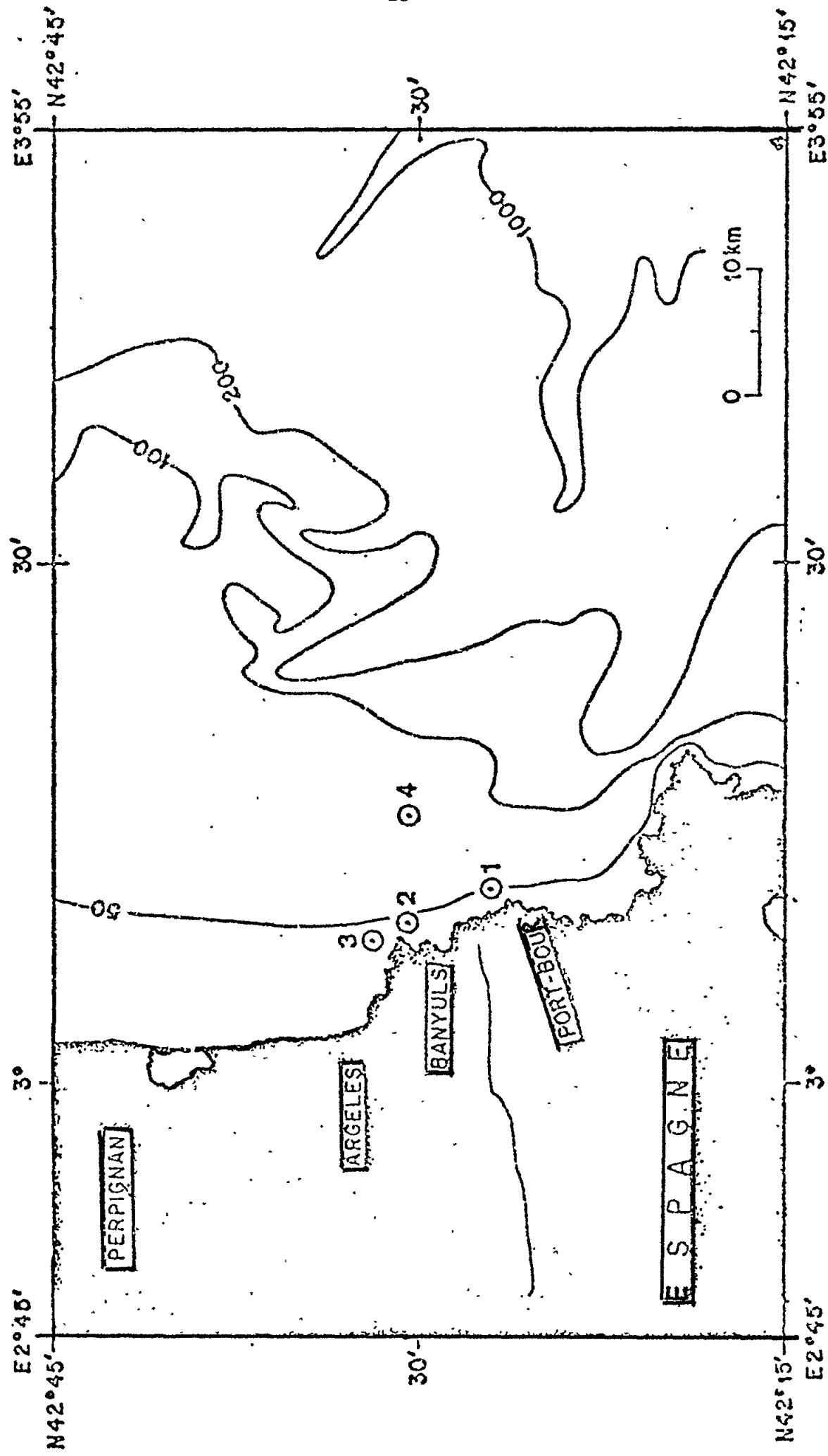


Fig. 1 Zone étudiée

Centre de Recherche :

Laboratoire Central d'Hygiène Alimentaire
Direction des Services Vétérinaires
Ministère de l'Agriculture
PARIS
France

Chercheur principal :

G. CUMONT

Période couverte par le rapport : mars 1977 à décembre 1979

INTRODUCTION

L'aspect pollution par le mercure des produits de la pêche introduits en France a été envisagé au laboratoire dès 1971 et régulièrement suivi depuis cette date. Pour le cadmium ce contrôle date de 1977. L'échantillonnage habituellement réalisé a été intensifié dans le cadre de ce programme, grâce à l'obligance des Services Vétérinaires implantés sur le littoral et principalement des Directions des Services Vétérinaires des Bouches-du-Rhône, des Alpes-Maritimes et de l'Hérault.

CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces :

Thunnus thynnus et Mullus barbatus sont les deux espèces de poissons échantillonnés et analysés. 420 poissons ont été ainsi échantillonnés et analysés, il s'agit de 278 individus Thunnus et, de 242 individus Mullus (pour une vingtaine d'individus les résultats concernent un échantillon moyen réalisé à partir de 2 ou 3 spécimens).

Polluants analysés :

Le mercure a été dosé dans les 420 poissons, le cadmium dans tous les Mullus et une grande partie des Thunnus. Des résultats pour le plomb apparaissent à partir de la seconde moitié de 1978. Les données pour le cuivre et le zinc sont fournies, à titre indicatif, en complément pour 1979; ces valeurs n'ont pas été reportées sur les formulaires d'enregistrement car elles ne concernent qu'un nombre réduit de poissons.

Zones étudiées :

La carte ci-après indique les principales zones de pêche et les ports de rattachement qui ont servi, dans certains cas, de repères pour définir les coordonnées géographiques d'échantillonnage. Ces zones sont les témoins d'une assez grande variabilité des caractéristiques physico-chimiques (salinité 35 à 39‰, pH 7,5 à 8,5) (RNO.1977), et biologiques surtout près du littoral (MES, DCO et DBO peuvent varier d'un facteur 1000).

METHODOLOGIE

L'échantillonnage n'a pu être réalisé suivant les conditions décrites dans les méthodes de référence MED POL. L'expédition des échantillons au laboratoire a été faite sous le régime du grand froid. Les différentes étapes de l'examen :

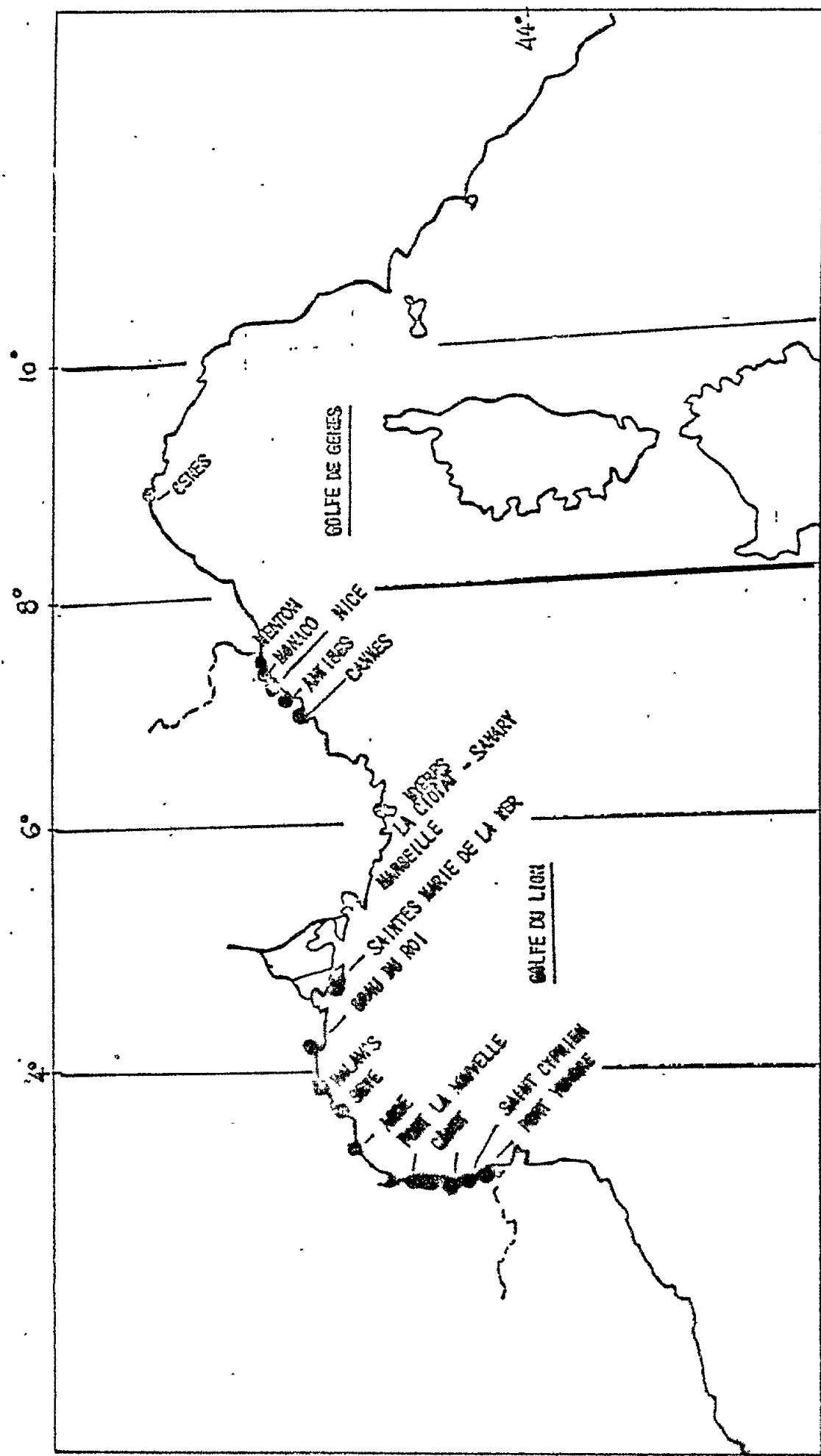


FIG. 1 Les lieux d'échantillonage dans le Golfe du Lion et le Golfe de Gênes

prélèvement du tissus musculaire, homogénéisation, minéralisation, dosage, ont été réalisées avec les précautions habituelles et particulièrement bien soulignées dans le Document technique des Pêches de la FAO n°. 158.

- Le mercure est dosé par spectrophotométrie d'absorption atomique sans flamme suivant une technique automatisée mise au point en 1974 par G. Cumont (1).
- Le cadmium, plomb, cuivre, zinc, sont dosés par spectrophotométrie d'absorption atomique à flamme après minéralisation par voie sèche, suivant une technique décrite par M. Feinberg (2).

Programme d'intercalibration :

- Les échantillons "sea plant" (SP-M-1), "copepod" (MA-A-1) et "fish flesh" (MA-A-2) ont été analysés.

RESULTATS

Métaux lourds dans *Mullus barbatus* : Résultats obtenus suivant les époques d'échantillonnage.

Mercure :

Epoque	n	Teneur mercure (µg/kg)		Poids(g)				Gamme Min. Max.
		Moyenne	Ecart type	Gamme	Min.	Max.	Moyen	
1977 : 2°/2	29	308	390	30	1740	70,7	24,5	41 - 165
1978 : 1°/2	26	140	142	40	670	66,3	27	30 - 122
1978 : 2°/2	19	175	133	40	570	38	12	26 - 71
1979 : 2°/2	68	138	184	10	947	33	15	9 - 107
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	142	178		10	1740	47,4		9 - 165

Cadmium :

Epoque	n	Teneur cadmium (µg/kg)		Poids(g)			Gamme Min. Max.
		Moyenne	Ecart type	Min.	Max.	Moyen (rappel)	
1977 : 2°/2	27	130	176	trace	590	70,7	
1978 : 1°/2	25	43	61	2	220	66,3	
1978 : 2°/2	19	23	14	2	44	38	
1979 : 2°/2	68	27	27	4	126	33	
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	142	48		2	590	47,4	

Plomb :

Epoque	n	Teneur plomb ($\mu\text{g}/\text{kg}$)		Gamme		Poids(g) Moyen (rappel)
		Moyenne	Ecart type	Min.	Max.	
1978 : 2 ^e /2	19	75	28	23	109	38
1979 : 2 ^e /2	42	98	55	9	244	33
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	61	91		9	244	34,6

Commentaires

- Mercure : La comparaison d'une année sur l'autre des résultats ainsi obtenus n'a pas grand intérêt, étant donné que la taille des individus échantillonnés et analysés peut varier du simple au double pour les moyennes et de 1 à 10 pour les individus. La teneur, la plus élevée, de 1740 $\mu\text{g}/\text{kg}$ a été mesurée sur un individu de 100 g pêché au large de Marseille, des concentrations voisines ou supérieures à 500 $\mu\text{g}/\text{kg}$ ont été relevées sur quelques individus de taille voisine pêchés au large d'Adge, de Sète, du Grau du Roi et de Sainte Marie de la Mer. Ces résultats sont cependant trop exceptionnels pour traduire un certain niveau de pollution mercurielle de ces zones de pêche puisqu'ils sont accompagnés d'une majorité de résultats beaucoup plus faibles, ainsi qu'en témoigne la moyenne de 178 $\mu\text{g}/\text{kg}$.

La relation entre la teneur en mercure et le poids des rougets n'est pas vérifiée sur les spécimens analysés, cependant dans le Golfe du Lion nous constatons sur deux petites populations échantillonnées pour des poids moyens inférieurs à 25 g et supérieurs à 70 g une différence notable dans la teneur en mercure, soit respectivement 39 $\mu\text{g}/\text{kg}$ et 493 $\mu\text{g}/\text{kg}$.

- Cadmium : Le niveau de contamination du Mullus barbatus par le cadmium est faible : 48 $\mu\text{g}/\text{kg}$; 4 valeurs sur 142 sont supérieures à 500 $\mu\text{g}/\text{kg}$ et 10 supérieures à 200 $\mu\text{g}/\text{kg}$.

Ces valeurs ne sont pas reliables à la taille ni à la zone de pêche; il s'agit certainement de pollution très localisée. Cependant, toujours pour le Golfe du Lion, les deux populations <25g et>70g présentent aussi une différence importante dans la teneur en cadmium, soit respectivement 9 $\mu\text{g}/\text{kg}$ et 148 $\mu\text{g}/\text{kg}$.

- Plomb : Les résultats en plomb dans Mullus barbatus sont moins nombreux ils ne concernent que le 2^e semestre 1978 et 1979. La contamination moyenne en plomb est faible : 91 $\mu\text{g}/\text{kg}$, identique, comme nous le verrons, à celle des thons. Aucune comparaison ne peut être faite entre ces 2 espèces, le poids moyen des Mullus est, ici, de 34.6 g, celui du thon est de 154 kg. Pour le Golfe du Lion nous constatons une inversion entre concentrations en plomb et cadmium en fonction du poids.

- Cuivre et zinc : Le cuivre et le zinc ont été dosés en complément sur

les échantillons de M. barbatus prélevés en 1979. Nous ne donnons que les teneurs moyennes calculées en indiquant la grande distribution des résultats dans la gamme obtenue :

	Effectif	Moyenne µg/kg	Ecart type	Gamme	Poids moyen
				Min. Max.	(g)
Cuivre	68	541	2162	316 8803	33
Zinc	69	4676	1524	2500 10553	33

Métaux lourds dans Thunnus thynnus thynnus :

L'échantillonnage a été effectué suivant les indications portées au paragraphe 'Méthodologie'. Un certain nombre de résultats, ne concernant d'ailleurs que le mercure obtenus sur des thons introduits en France suivant une autre procédure, ont été ajoutés aux données recueillies sur l'échantillonnage. Les nombreux résultats présentés à Dubrovnik (3) n'ont pas été compilés avec ceux-ci, il y aurait lieu éventuellement de les regrouper pour en faire une exploitation globale; c'est ce que nous nous proposons de faire en 1981.

Résultats obtenus suivant les époques d'échantillonnage :

Mercure :

Epoque	n	Moyenne µg/kg	Poids (kg)					
			Ecart type	Gamme	Ecart			
					Min.	Max.	Moyen	type
1977 : 2°/2	28	770	410	370 2390	38	59	220	
1978 : 1°/2	33	741	253	480 1680	28	34	160	
1978 : 2°/2	76	1309	1280	130 6290	93	85	218	
1979 : 1°/2	99	1188	341	336 2579	82	108	296	
1979 : 2°/2	42	1256	430	383 2179	154	73	382	
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	278	1136		130 6290	85			

Cadmium :

Epoque	n	Moyenne µg/kg	Ecart type	Gamme Min. Max.	Poids (kg) Moyen (rappel)
1977 : 2°/2	27	88	115	20 590	38
1978 : 1°/2	33	68	101	12 425	28
1978 : 2°/2	5	19	22	4 59	-
1979 : 2°/2	42	17	13	5 70	154
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	107	50,7		4 590	82

Plomb :

Epoque	n	Moyenne µg/kg	Ecart type	Gamme Min. Max.	Poids (kg) Moyen (rappel)
1978 : 2°/2	5	45	6	37 51	-
1979 : 2°/2	42	90	156	23 1041	154
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	47	85		23 1041	154

Commentaires

Notre surveillance de la contamination par le mercure des thons rouges (*Thunnus thynnus*) de la Méditerranée remonte maintenant à 8 ans et porte sur un échantillonnage de plus de 1000 individus. La provenance de ces thonidés n'est pas toujours précisément connue étant donné le mode de vie pélagique de ces poissons qui parcouruent plusieurs milles par jour, et leurs habitudes migratrices; l'absence des coordonnées des lieux de pêche n'est pas un obstacle à l'appréciation des résultats et à leurs commentaires.

Les résultats présentés dans ce rapport concernent 278 thons comprenant des individus échantillonés dans le cadre du programme FAO ou introduits en France et dont l'origine méditerranéenne est certaine.

- Mercure : La teneur moyenne relevée sur 278 thons sur l'échantillonnage de 3 années du programme est de 1136 µg/kg et les résultats sont distribués dans la gamme de 130 à 6290 µg/kg. Les 76% environ de ces résultats dépassent la valeur retenue par la réglementation italienne et française comme seuil de tolérance pour la consommation humaine (0,7 mg/kg). Des observations identiques ont été faites antérieurement (4-5). Aucune relation n'apparaît entre ces données et les sites d'échantillonnage, par contre si dans nos rapports précédents nous ne trouvions pas de liaison entre teneur en mercure et taille des thons, nous avons mis en évidence sur l'échantillonnage de 1978, 2° semestre,

un groupe de 19 individus présentant une concentration moyenne de 3100 µg/kg (1450 à 6290 µg/kg) pour des poids assez groupés de 152 à 218 kg, qu'il est possible d'opposer à un groupe de 50 individus de poids inférieur à 30 kg présentant des concentrations 6 fois moins élevées. Il est certain que suivant la population échantillonnée de telles relations peuvent être constatées alors que pour d'autres on ne mettra en évidence qu'une grande hétérogénéité des données. Cela tient certainement à la manière dont se regroupent les bancs de thons à la suite de leur migration dans l'océan ou de leur déplacement au sein même de la Méditerranée.

- Cadmium : La teneur moyenne du muscle mis en évidence sur 107 Thunnus thynnus est faible (50 µg/kg) pour une gamme étendue mais dont le maximum n'atteint pas la valeur habituellement observée dans les émonctoires des mammifères terrestres.

Aucune relation n'a été mise en évidence entre la teneur et le poids, ni avec l'origine. Cette concentration moyenne doit être rattachée à une contamination naturelle du tissu musculaire. La pollution de l'environnement par le cadmium, si elle existe en Méditerranée, n'a donc, semble-t-il, pas de répercussion sur sa concentration dans le thon.

- Plomb : La teneur moyenne calculée sur les résultats de l'examen de 47 Thunnus thynnus est de 85 µg/kg, située entre les valeurs extrêmes de 23 et 225 µg/kg; une donnée unique de 1041 µg/kg semble aberrante. Huit valeurs sur les trente-cinq dépassent 100 µg/kg, donnée qui peut être considérée comme naturelle. Aucune relation n'existe entre ces teneurs et le poids des thons.
- Cuivre et zinc : Le cuivre et le zinc ont été dosés en complément sur un certain nombre de thons échantillonnés en 1979; les données moyennes obtenues sont les suivantes :

Effectif	Moyenne µg/kg	Ecart type	Teneur Max.	Poids moyen (kg)
Cuivre	35	460	246	1358
Zinc	35	8712	4687	22288

DISCUSSION DES RESULTATS

Dans le cadre de cette étude de base et de surveillance continue des métaux lourds dans les deux espèces Mullus barbatus et Thunnus thynnus thynnus, il apparaît que seule la contamination par le mercure atteint des niveaux préoccupants, préoccupants au regard de certaines données toxicologiques, des normes et réglementations peut-être arbitraires, établies pour assurer la protection des consommateurs et le commerce des produits de la mer. Certaines précisions peuvent être apportées pour essayer d'expliquer cette contamination anormale. On doit admettre que le métabolisme du méthylmercure varie d'un individu thon à l'autre suivant son état physiologique, sa flore microbienne, son alimentation, les carences liées à son parasitisme, il s'ensuit que

l'accumulation du mercure peut varier elle aussi dans de grandes proportions parmi les individus des diverses populations de thonidés. Ceci n'explique pas cependant le fait que la teneur moyenne du thon rouge méditerranéen est trois fois supérieure à celle de son parent d'Atlantique. Il faut donc convenir que la Méditerranée est un milieu favorable à l'accumulation du mercure dans les produits de la pêche en général et dans le thon en particulier, et éventuellement montrer que cette accumulation est aussi en relation avec une pollution mercurielle de l'environnement méditerranéen; la plus forte concentration de gisements, exploités ou non, de minerais de mercure est en effet localisée dans cette région de notre planète.

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Centre de Recherche :

Institut Scientifique et Technique
des Pêches Maritimes
NANTES
France

Chercheur principal :

Y. THIBAUD

Période couverte par le rapport : 1978 et 1979

INTRODUCTION

Parallèlement aux travaux effectués dans le cadre de MED POL, l'I.S.T.P.M. 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 :

- a) Les crevettes et crabes verts sont difficiles à prélever en quantité suffisante pour satisfaire aux besoins de toutes les analyses.
- b) Les prélèvements faits spécialement pour le C.G.P.M. 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 II sont :

- moule : Mytilus galloprovincialis
- crevette : Crangon crangon
- crabe vert : Carcinus maenas
- poissons : Boops boops, Maena smaris, Trisopterus minutus capelanus,
Solea solea.

Polluants analysés :

Tous les polluants obligatoires ont été recherchés : mercure, cadmium et plomb.

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'I.S.T.P.M. a effectué les intercalibrations prévues par le programme.

RESULTATS

Les résultats des analyses correspondant aux échantillons d'organismes marins collectés en 1978 et en 1979 sont donnés sur le formulaire d'enregistrement. Les teneurs en mercure, plomb et cadmium concernent principalement la moule Mytilus galloprovincialis. Les déterminations des 3 métaux ont aussi été effectuées sur des échantillons de poissons appartenant aux espèces suivantes : Gadus capelanus, Solea solea, Boops boops, Maena maena.

DISCUSSION DES RESULTATS

Les teneurs sont dans leur ensemble assez proches de celles que l'on rencontre habituellement dans les mêmes espèces originaires des côtes françaises tant pour l'Atlantique que pour la Méditerranée. Cela est notamment vrai pour les teneurs en mercure dans la moule, l'espèce la plus échantillonnée. Dans ce cas en effet les teneurs sont assez voisines de la moyenne de 60 µg/kg de poids frais qui a été antérieurement trouvée par nous-mêmes en 1972 (1) et en 1976 (2). Les teneurs en plomb et en cadmium toujours pour la moule, sont aussi assez comparables à celles que l'on rencontre dans les échantillons appartenant à la même espèce, collectés dans d'autres régions de la Méditerranée et de l'Atlantique. Seulement quelques valeurs relativement élevées de ces deux métaux ont été trouvées dans le golfe de Marseille; elles s'expliquent par la proximité de la ville et peut-être aussi une certaine activité industrielle.

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Research Centre: Radioanalytical Laboratory
Department of Chemistry
Nuclear Research Center "Demokritos"
ATHENS
Greece

Principal Investigators: A. P. GRIMANIS and C. PAPADPOULOU

Period of Reporting: October 1975 to March 1980

INTRODUCTION

The Laboratory has been carrying out research on trace elements in the marine environment since 1963 and has published about 20 papers on this subject. Some of these publications have dealt with the study of trace element concentrations in species of molluscs and edible fish caught from polluted and unpolluted areas of the Aegean Sea.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

Species monitored seasonally were Mytilus galloprovincialis, Mullus barbatus, and Parapenaeus longirostris. Monitoring of Xiphias gladius was not possible due to extreme difficulties in acquiring samples.

In an attempt to include more species of edible fish and thus have a more representative monitoring of trace element concentrations, the following species have been monitored since 1979:

Merlangius merlanus, Mullus surmuletus, Boops boops, Pagellus acarne, Epinephelus guaza, Trachurus mediterraneus, Serranus cabrilla, Scorpaena scrofa and Conger conger.

These fish are all edible and constitute typical catches with bottom gill nets and long lines.

Pollutants analysed:

Mercury analyses were performed routinely for all samples. Determination of Cd was not continued because the NAA method, used in the Laboratory, is not sensitive enough for routine analysis (sensitivity 0.01 µg of Cd). The following trace elements were also determined: Ag, As, Cr, Cs, Co, Cu, Fe, Rb, Sb, Se, and Zn. These trace elements were included for two reasons: (i) they can be determined simultaneously with instrumental Neutron Activation Analysis (with the exception of As and Cu where fast radiochemical separations were used); and (ii) some of them are considered as potential pollutants. Selenium in particular seems to be of extreme importance since it has been reported to decrease Hg toxicity in fish.

Areas studied:

(a) Saronikos Gulf

Keratsini and Elefsis Bays at the northern end of Saronikos Gulf receive both industrial and domestic sewage from the greater Athens Metropolitan Area. The northern part of Saronikos Gulf is highly eutrophicated.

Close to the main sewage outfall and in Elefsis Bay the sediments have accumulated high concentrations of trace elements. Increased concentrations of trace elements have also been reported in the water close to the outfall. Samples of marine organisms were collected from four stations AA, A, B and C (Fig. 1). Specimens of Mytilus galloprovincialis were collected from only one station. All stations except AA are away from the immediate effects of the central sewage outfall in Keratsini Bay. Station C is the Aegean Sea.

(b) Antikyra and Kissamos Bays (Fig. 2)

During 1979 it was decided to extend the trace element monitoring programme, to include more areas. Antikyra bay in Korinthiakos Gulf, where an aluminium industry is situated, and Kissamos Bay in Crete, an agricultural area, were chosen. During March 1980 monitoring was extended to cover several areas of the Aegean Sea. Apart from marine organisms, sediments, sea-water and plankton were collected. Results will be presented at a later stage.

METHODOLOGY

Mullus barbatus, Parapenaeus longirostris and Merlangius merlangus were sampled by bottom trawls. Mytilus galloprovincialis specimens were obtained from a mussel farm in Elefsis Bay. All other species were sampled by gill nets and/or long lines.

Sample identifications and preparation were carried out according to the FAO Fisheries Technical Paper No.158 "Manual of Methods in Aquatic Environment Research, Part 3, Sampling and Analyses of Biological Material". Samples were stored in deep-freeze for 4-10 weeks and lyophilized prior to analysis. For the determination of Hg, As, Cu, fast radiochemical separations based on solvent extraction techniques combined with NAA methods were used.

For the determination of Ag, Co, Cr, Cs, Fe, Rb, Sb, and Se, Instrumental Neutron Activation Analysis has been applied.

Intercalibration exercise:

The Laboratory has participated in all four intercalibration exercises organized by the International Laboratory of Marine Radioactivity in Monaco. Values found and mean values reported were in good agreement.

RESULTS

Trace elements in Mytilus galloprovincialis:

Mercury values range from 10 to 214 µg/kg FW with a mean of 45 µg/kg. All values are lower than the 500 µg/kg considered as maximum permissible concentration. Specimens were collected from only one station in Saronikos

Gulf and the number of samples is too small to permit discussion of geographical or seasonal variations.

Mean concentrations of the other elements analysed are shown in Table I. The correlation between Hg and Se concentrations is significant on the 95% confidence level, and Hg to Se ratio is 0.24.

Trace elements in Mullus barbatus:

Mercury values range from 39 to 1400 µg/kg FW with a mean of 290 µg/kg. Only one value (1400 µg/kg) was higher than the 500 µg/kg maximum permissible concentration. Mean concentrations of other trace elements analysed are shown in Table I. Geographical and seasonal variations of trace elements concentrations in Mullus barbatus are shown in Table II and Table III respectively. Concentrations of Cs, Fe, Rb and Zn vary very little from station to station. The lowest concentration of Cr and Co appears in samples from station AA. Samples from station A have the lowest concentrations of Ag and Sb, whereas station C samples have the highest concentrations of Hg, Se and As.

These small variations do not correlate with pollution inputs. The relatively high trace element concentrations in the sediments in the vicinity of the Athens sewage outfall are not reflected in Mullus barbatus. Concentrations of Cr, Cs, Co, Cu, Rb, Sb, Se and Zn do not vary significantly with season. The lowest concentrations of Ag appear in summer samples and the highest concentrations of Fe, Hg and As in spring samples. These variations of Fe, Hg and As might be a consequence of spawning activity during spring.

The correlation between Hg and Se concentrations is significant at 99% level and the Hg to Se ratio is 0.6. This is very interesting since Se has been reported to decrease Hg toxicity in fish.

There is no significant correlation between Hg concentrations and weight, length or age of Mullus barbatus.

Trace elements in other marine organisms. Mean concentrations of trace elements in other marine organisms are shown in Table I. All Hg concentrations are lower than the 500 µg/kg FW level.

Small geographical variations of trace element concentrations in Parapenaeus longirostris were observed. Station C shows the highest concentrations of Hg and Se.

DISCUSSION OF RESULTS

The concentrations of toxic elements found in the marine organisms that were monitored are not high enough to endanger public health.

All Hg values, except one, are lower than the 500 µg/kg FW limit. With the highest mean concentrations reported in Table I, and using the provisional tolerable weekly intake limits of the Joint FAO/WHO Codex Alimentarius Commission, one can conclude that about 1 kg of marine organisms may be consumed weekly per person without exceeding the intake limit for Hg. Arsenic values found in Mullus barbatus are relatively high (19,000 µg/kg). It is, however, doubtful whether these As concentrations are dangerous since As is found in fish mainly in the relatively non-toxic methylated forms.

In general all our results are within the limits reported by other investigators. A more systematic comparison is not possible since information on the statistics of reported results would be needed.

The correlation found between Hg and Se in Mullus barbatus and Mytilus galloprovincialis suggests that these elements have a similar biochemical behaviour and that Se may act antagonistically, counteracting the toxic effects of high mercury levels.

The correlation between all other trace element concentrations in Mullus barbatus has also been investigated.

At the 95% level there is significant correlation between 13 pairs of trace elements (Hg-Zn, Rb-Zn, Cr-Se, Hg-Se, Rb-Se, Cr-Zn, Ag-Se, Cs-Se, Fe-Se, Sb-Se, Fe-Sb, Co-Fe, Ag-Cs).

These correlations again suggest a similar biochemical behaviour of these trace elements in Mullus barbatus, and possible antagonistic or synergistic roles. It is, therefore, very important that as many trace elements as possible should be determined in a monitoring programme.

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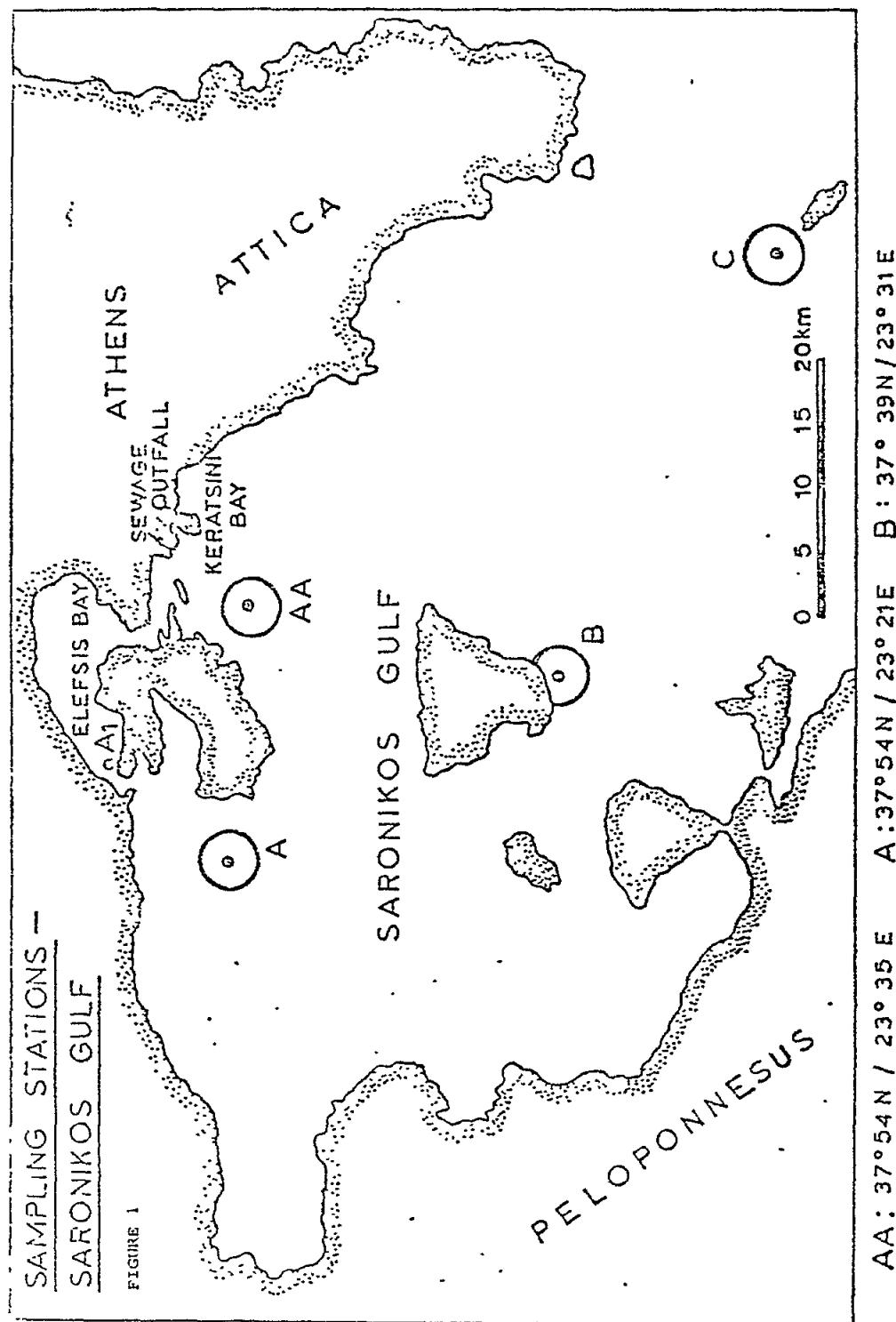


Figure 1. Sampling stations in Saronikos Gulf

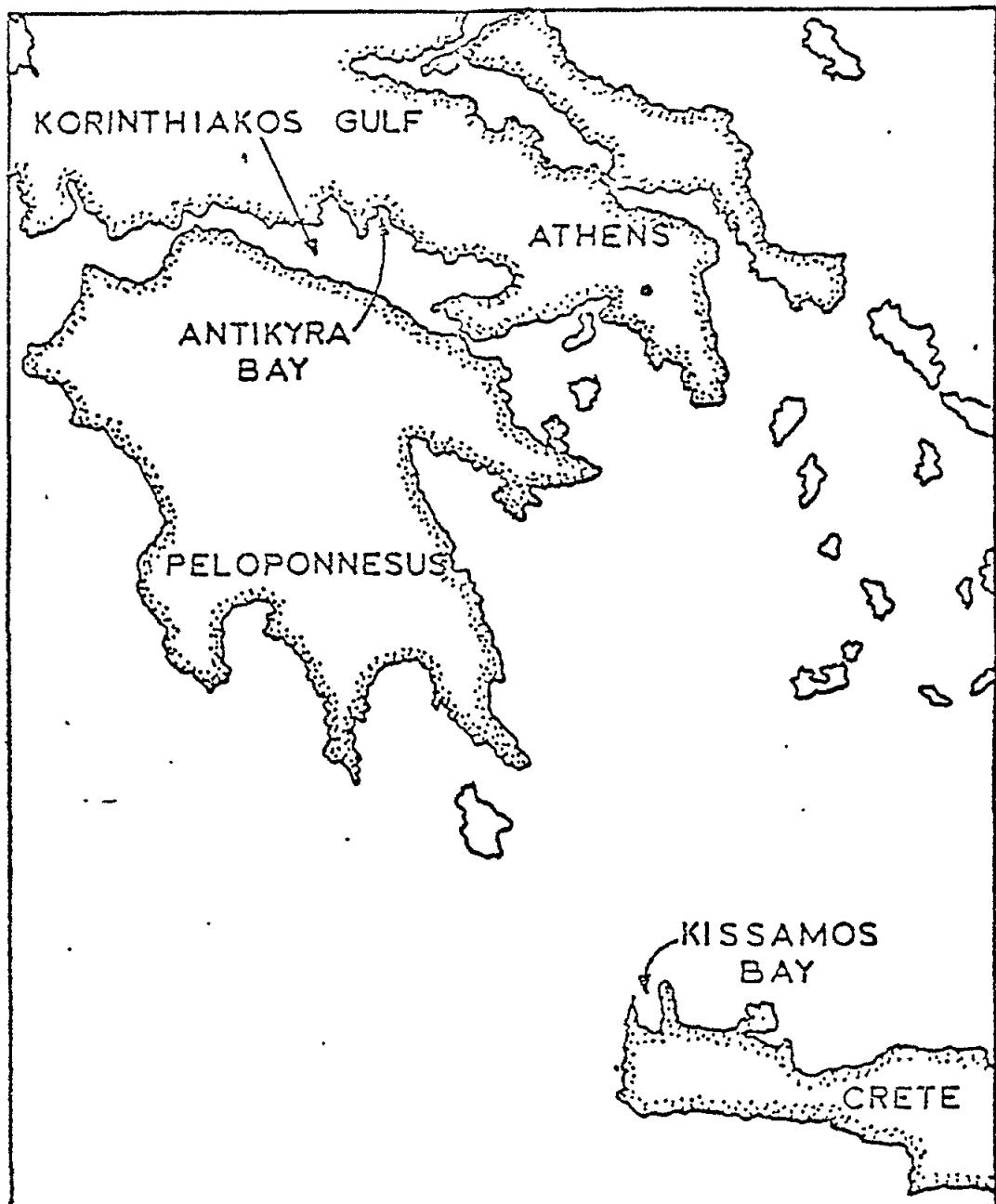


Figure 2. Sampling stations in Antikyra and Kissamos Bays

TABLE I

Means (\pm standard deviations) of trace elements in marine organisms ($\mu\text{g}/\text{kg}$ wet weight)

	No. of composite samples	No. of specimens	Hg	As	Cu	Zn	Co	Se	Cr	Rb	Cs	Fe
SARONIKOS GULF												
<u><i>Mullus barbatus</i></u>	42	288	290	19000	510	3600	30	470	73	850	12	6900
<u><i>Parapenaeus longirostris</i></u>	22	226	290	17800	5200	11000	27	1200	94	790	10	2700
<u><i>Uutilus fallax</i></u> <u><i>provincialis</i></u>	6	98	45	-	-	20500	100	185	170	640	3.7	14000
<u><i>Merlangius merlangus</i></u>	4	7	-	-	-	2600	-	260	90	720	9.4	2200
KISSANIOS GULF												
<u><i>Mullus barbatus</i></u>	1	50	9300	300	6900	25	185	-	990	14	2600	
<u><i>Mullus surmuletus</i></u>	1	5	80	6200	-	3200	19	176	130	940	15	5400
<u><i>Boops boops</i></u>	1	10	20	370	430	6000	23	430	61	1130	17	8300
<u><i>Pagellus acarne</i></u>	1	6	30	3000	270	-	13	450	113	850	-	6880
<u><i>Epinephelus guaza</i></u>	1	270	2700	330	2900	5	620	37	720	15	2800	
<u><i>Trachurus mediterraneus</i></u>	1	70	2600	380	4300	14	370	56	650	20	9200	
KORINTIACOS GULF												
<u><i>Pagellus acarne</i></u>	1	270	-	-	8800	26	1160	-	860	14	5600	
<u><i>Boops loops</i></u>	1	1	170	-	8900	25	1650	56	1250	23	8000	
<u><i>Serranus cabrilla</i></u>	2	10	210	-	-	9300	17	1050	80	1290	48	9800
<u><i>Cosmocampus acrofa</i></u>	1	1	-	-	-	3100	15	1200	120	770	21	4200
<u><i>Conger conger</i></u>	2	6	440	-	8200	24	1600	100	960	23	8100	

TABLE II
GEOGRAPHICAL VARIATION OF
TRACE ELEMENT CONCENTRATIONS in *Mullus barbatus*

STATION	Ag	As	Cr	Cs	Co	Cu	Fe	Hg	Rb	Sb	Se	Zn
AA	7±5	15200 ± 7000	43±13	12±4	12±4	340 ± 85	8100 ±2800	120±90	780 ±130	3.8±1.6	470 ±100	3200 ± 460
A	2.4±0.6 ± 7700	14000	68±26	11±2	22±17	750 ±360	5500 ± 800	93±60	670 ±190	1.9±1	370 ± 70	3500 ± 600
B	7±4	13000 ± 7000	70±40	11±2.5	16±9	530 ±320	5900 ±3000	90±30	930 ±140	3.5±1.6	460 ± 80	3600 ± 700
C	7±3	34000 ±13000	70±55	14±7	23±12	420 ±100	6500 ±1400	280±60	860 ±180	4±3	.580 ± 75	3300 ± 600

Means of 6 to 12 sampling seasons ($\mu\text{g}/\text{kg}$ wet weight) \pm standard deviation

TABLE III
SEASONAL VARIATION
OF TRACE ELEMENT CONCENTRATIONS in *Mullus barbatus* (μg/kg wet weight)

SEASON	Ag	As	Cr	Cs	Co	Cu	Fe	Hg	Rb	Sb	Se	Zn
SPRING	7±3	29000	56± 12	13±6	19±10	.600	7300	230	860	4.3	460	3300
SUMMER	3.5 ±3	15000	56 ±40	12±2	24±16	540	5400	180	710	2.9	460	3600
FALL	9±6	17000	70 ±50	11±3	17±10	390	5500	130	910	2.8	490	3500
WINTER	8±5	18000	70 ±40	12±5	19±11	510	5700	160	860	3.6	460	3000

Means of 3-4 stations ± standard deviations

Research Centre: Division of Environmental Pollution Control
General Chemical State Laboratory
ATHENS
Greece

Principal Investigator: D.G. MARKETOS

Period of Reporting: Summer 1976 to Autumn 1980

INTRODUCTION

Determination of heavy metals, particularly total mercury, in various species of Greek fish exported to other countries has been performed in the laboratory for the last eight years, using the method of flameless atomic absorption spectrophotometry. Chemical analysis of industrial and of marine water polluted by ship's fuel have also currently been performed.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

Mullus barbatus, Parapenaeus longirostris and Mytilus galloprovincialis were regularly monitored. Merlangius merlangus also to be monitored from spring 1979, because it is of commercial importance and is relatively easily sampled along with the other species. Xiphias gladius was sampled and analysed only in summer 1976; the monitoring of this species is now discontinued, since samples could not be transported to the laboratory under refrigeration.

Pollutants analysed: Total mercury.

Area studied:

The Saronikos Gulf has been selected for study. Four sampling stations (Fig.1), indicated as A, B, C, AA in the attached geographical map were used for the collection of the species, seasonally, when possible. This Gulf has a surface area of about 2,900 km² and is bounded on the north and east by Attika and on the west by the Peloponesos. Stream run-off into the Gulf is insignificant except during short periods of heavy rainfall.

Circulation in the Gulf is predominantly induced by wind-driven and, depending upon the prevailing wind direction, a weak cyclonic or anticyclonic mode of circulation is established. Due to the prevailing north winds and the topography of the inner Gulf, the cyclonic mode of circulation is the more frequent. Complete renewal of water is effected in about one month for the eastern part of the Gulf and in about two months for the western part.

Keratsini Bay, in the northern part of Saronikos Gulf, received untreated domestic sewage and industrial effluents from the greater Athens area, through an outfall situated 100 m offshore and 30 m deep. Sewage flow is about 350,000 m³/day. Elefsis Bay, a semi-enclosed bay at the head of Saronikos Gulf, also receives industrial, shipping and domestic wastes. The northern part of Saronikos Gulf is highly eutrophicated. Concentrations of nutrients are up to 15 times higher than in Aegean Sea waters. Consequently, primary production is greatly enhanced. The high biodegradable organic input from the

Keratsini outfall has also resulted in low oxygen concentrations in the deep waters of several parts of Saronikos Gulf, especially Elefsis Bay. Conditions close to the outfall are toxic for benthic communities, whereas to an extent of about 3 km benthos is highly eutrophicated. The discharge of wastes in Keratsini and Elefsis Bays has resulted in elevated concentrations of toxic and other trace elements in sediments of at least 100 km² of sea-floor.

METHODOLOGY

Sampling, sample treatment and statistical considerations used for evaluating results are those recommended by MED POL reference methods. Materials and methods used for the analysis of the samples are those referred to in "Manual of Methods in Aquatic Environment Research, Part 3 - Sampling and Analysis of Biological Material", FAO Fisheries Technical Paper, No. 158, Rome, 1976, Chapter 6, Analytical Procedures.

Intercalibration exercise:

The research centre participated in three intercalibration exercises. The following four samples were analysed: MA-M-1/1975, SP-M-1/1977 and MA-A-2/1978. According to the information received from the International Laboratory of Marine Radioactivity, Monaco, the results are (a) 22% higher, 20% higher, 9% lower, 17% lower, respectively, than the overall averages of the results reported and (b) 74% higher, 45% higher, 18% higher for the first three samples, respectively, than the Dixon's Test values of the results reported.

RESULTS

Total mercury in Mullus barbatus: (Fig. 2)

- Tissue analyzed: White flesh.
- Total number of analyses effected: 48
- Total number of samples and stations (areas) of sampling: 41 composite samples and 7 individual samples from four sampling stations (areas) in the Saronikos Gulf from September 1976 to September 1980.
- Total number of specimens analyzed: 234
- Total mercury values found in all (except four) samples were always below 500 µg/kg fresh weight in all stations (areas) and seasons. Only in two samples were the values found to be two times higher. Maximum and minimum values were observed in winter 1980 (station C) and in spring 1977 (station A), respectively. Results are presented graphically in Fig. 2.

Total mercury in Parapenaeus longirostris: (Fig. 3)

- Tissue analyzed: soft part.
- Total number of analyses effected: 30

- Total number of samples and stations (areas) of sampling: 30 composite samples from four sampling stations (areas) in the Saronikos Gulf from March 1977 to September 1980.
- Total number of specimens analyzed: 295
- Total mercury values found in 20 samples were below 500 µg/kg fresh weight. In 6 of the remaining samples the values found were slightly higher than the above limit. In the last samples (winter 1978 and spring and autumn 1980, stations B and C) the values found were about two times higher. Maximum and minimum values were observed in winter 1978 (station B) and in summer 1977 (station A), respectively. Results are presented graphically in Fig. 3.

Total mercury in Mytilus galloprovincialis: (Fig. 4)

- Tissue analyzed: Soft part.
- Total number of analyses effected: 9
- Total number of samples and stations (areas) of sampling: 9 composite samples from one sampling station (area) (station A) in Saronikos Gulf from April 1977 to October 1980.
- Total number of specimens analyzed: 104
- Total mercury values found in all samples were always below 500 µg/kg fresh weight. Maximum and minimum values were observed in autumn 1977 and in winter 1978, respectively. Results are presented graphically in Fig. 4.

Total mercury in Merlangius merlangus: (Fig. 4)

- Tissue analyzed: White flesh.
- Total number of analyses effected: 16
- Total number of samples and stations (areas) of sampling: 15 composite samples and 1 individual sample from four sampling stations (areas) in Saronikos Gulf from April 1979 to September 1980.
- Total number of specimens analyzed: 39
- Total mercury values found in all samples were always well below 500 µg/kg fresh weight. Results are presented graphically in Fig. 4.

Total mercury in Xiphias gladius:

- Tissues analyzed: white flesh.
- Total number of analyses effected: 5

- Total number of stations (areas) of sampling: 5 individual samples from five areas of greek sea waters (see attached geographical map, Fig. 5).
- Total number of specimens analyzed: 5
- Total mercury values found in all samples seem to be rather low for the species, possibly due to some loss of mercury during their transportation at ambient temperature from the collection area to the Laboratory. On the other hand this conclusion may be false and these values might be true values. However, since the transportation of the samples could not be effected under refrigeration, the monitoring of mercury in this species was discontinued.

DISCUSSION OF RESULTS

Samples of Xiphias gladius, collected in summer 1976, were analyzed for total mercury. The monitoring of this species was, as stated above, discontinued, since the transportation of the samples from the collection area to the laboratory could not be effected under refrigeration.

The four species Mullus barbatus, Parapenaeus longirostris, Mytilus galloprovincialis and Merlangius merlangus were regularly monitored for total mercury in four sampling stations, in Saronikos Gulf, seasonally when possible, from autumn 1976 to autumn 1980. Statistical information on the species analyzed and on the analytical results are given below.

Total mercury was determined in 95 composite and 8 individual samples (672 specimens) of all species collected from four sampling stations (areas) in Saronikos Gulf, from autumn 1976 to autumn 1980. Table I shows mean mercury concentrations for all samples: all means are below 500 µg/kg fresh weight. Tables II and III show geographical and seasonal variations of mean mercury concentrations in the two species M. barbatus and P. longirostris (this elaboration has not been extended to the other two species M. galloprovincialis and M. merlangus due to the small number of samples examined).

As can be seen from Table I, P. longirostris has the highest and M. galloprovincialis and M. merlangus the lowest, mercury concentration. It can also be noted from Tables II and III, that station C shows increased values for M. barbatus relative to the other three stations and that higher values for this species were observed in autumn and winter; also that stations B and C show increased values for P. longirostris relative to stations A and AA and that high values for this species were observed in autumn and winter.

The 90% of the mercury concentrations found in four marine organisms monitored (all samples except 13) are below the WHO maximum permissible concentration (500 µg/kg fresh weight); therefore, no danger for human consumption is to be expected. Although increased concentrations of mercury have been found in the sediments around Keratsini outfall, these are not reflected in the marine organisms.

A brief comparison with bibliographic non-MED data shows that the results for Mullus barbatus and Mytilus galloprovincialis are comparable with results reported for fish and Mytilus edulis, respectively.

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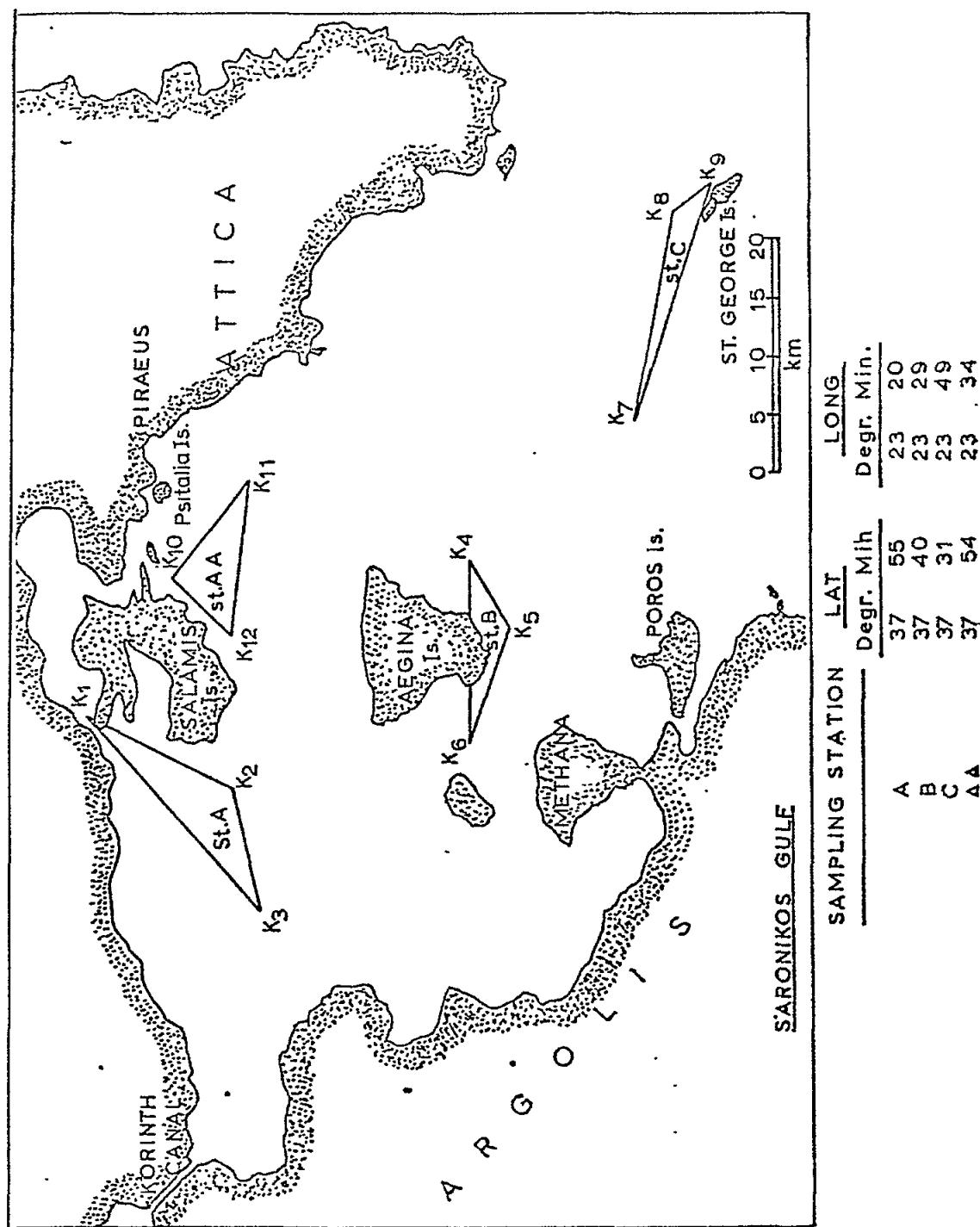


Fig. 1. Sampling stations in Saronikos Gulf

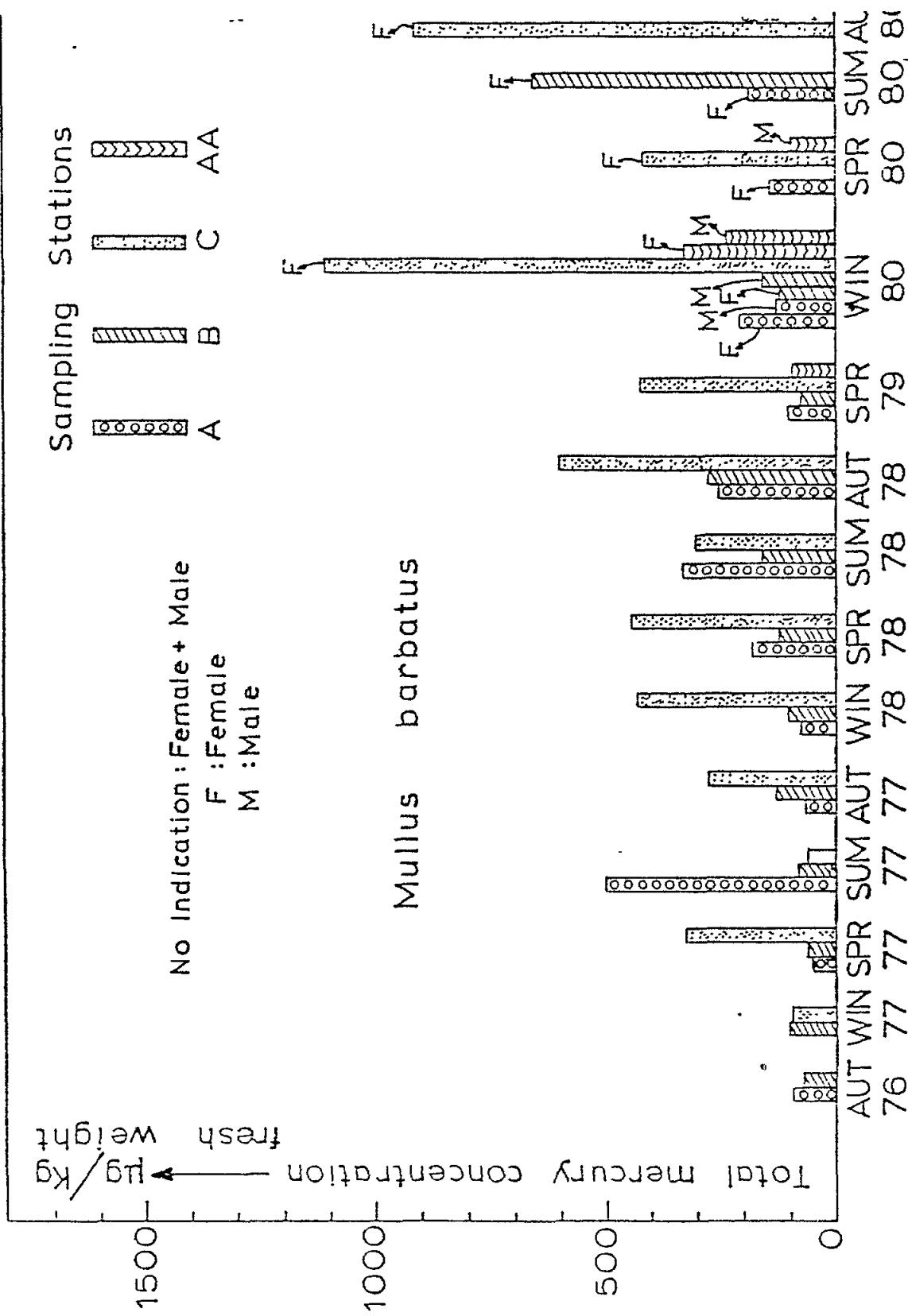


Fig. 2. Results of mercury analysis in *Mullus barbatus*

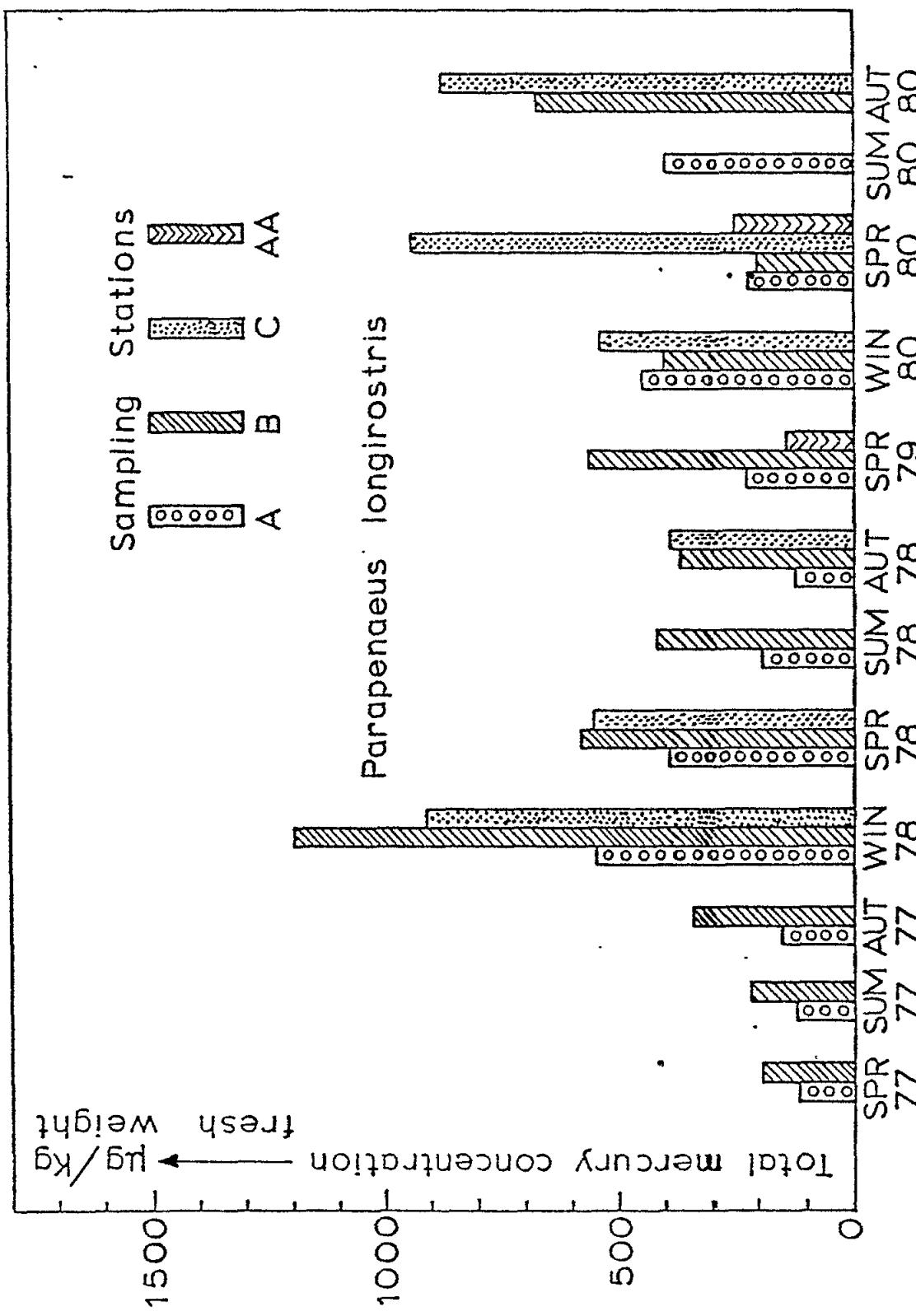


Fig. 3. Results of mercury analysis in Parapenaeus longirostris

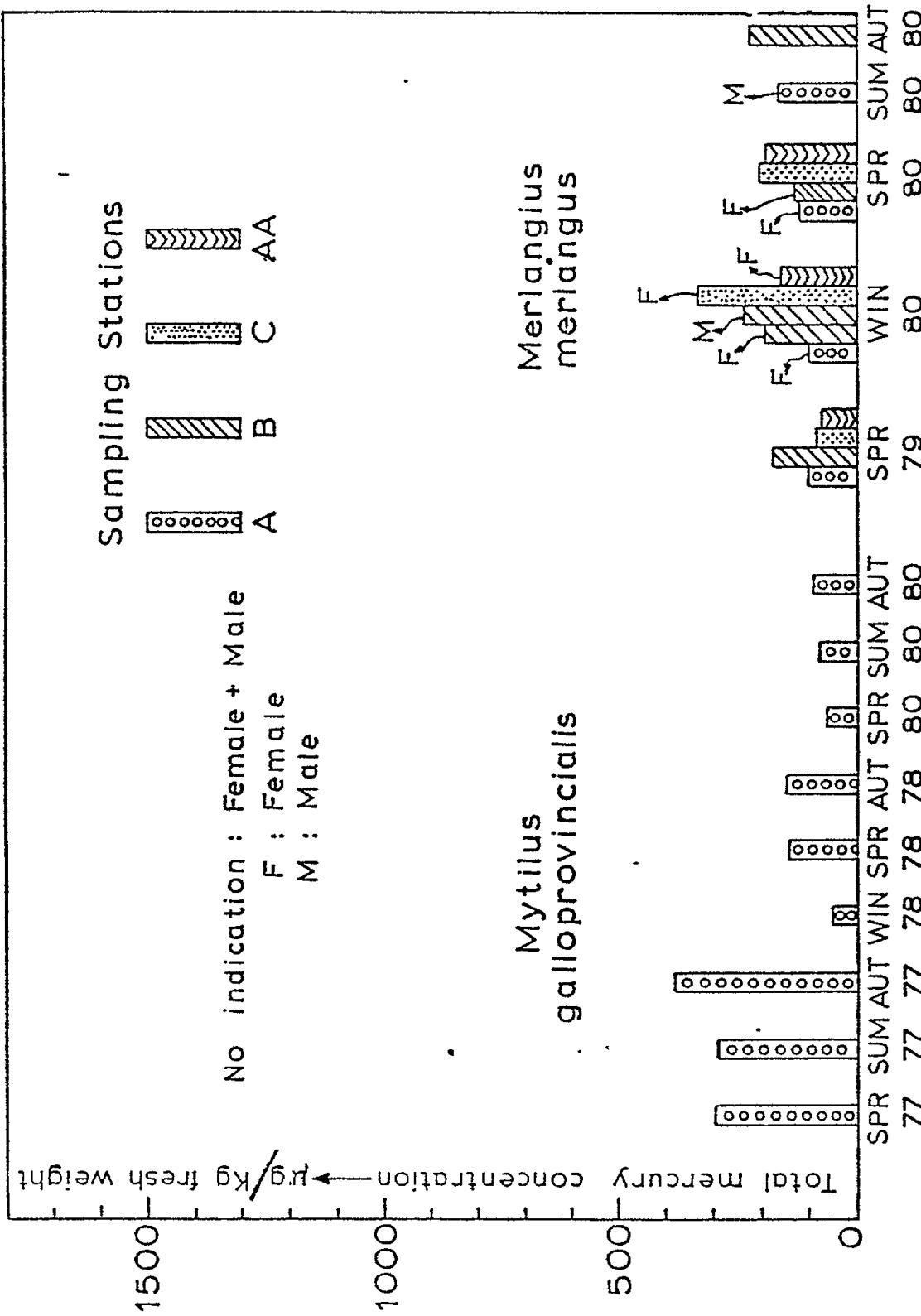


Fig. 4, Results of mercury analysis in *Mytilus galloprovincialis* and *Merlangius merlangus*

MAP OF GREECE



Fig: 5. Sampling areas

- Sample No. 0035: South of Thessaloniki
- Sample No. 0036: Kritikon Pelagos
- Sample No. 0037: Near Kithira Island
- Sample No. 0038: South of Kavala
- Sample No. 0039: South of Kavala

Table I. Mean mercury concentrations of samples collected from autumn 1976 to autumn 1980

Species	Mean mercury concentration ($\mu\text{g}/\text{Kg}$ fresh weight + standard deviation)
<u>Mullus barbatus</u>	229 + 223
<u>Parapenaeus longirostris</u>	422 + 227
<u>Mytilus galloprovincialis</u>	168 + 122
<u>Merlangius merlangus</u>	168 + 66

Table II. Geographical means of mercury concentrations of samples collected from autumn 1976 to autumn 1980

Station	Mean mercury concentrations ($\mu\text{g}/\text{Kg}$ fresh weight)	
	<u>Mullus barbatus</u>	<u>Parapenaeus longirostris</u>
A	174	265
B	140	457
C	480	684
AA	160	192

Table III. Seasonal means of mercury concentrations of samples collected from autumn 1976 to autumn 1980

Season	Mean mercury concentrations ($\mu\text{g}/\text{Kg}$ fresh weight)	
	<u>Mullus barbatus</u>	<u>Parapenaeus longirostris</u>
Spring	182	364
Summer	214	265
Autumn	292	418
Winter	253	673

Research Centre: Laboratory of Analytical Chemistry
Aristotelian University of Thessaloniki
THESSALONIKI
Greece

Principal Investigator: G. VASILIKIOTIS

Period of Reporting: September 1976 to March 1980

INTRODUCTION

Since 1974 the Laboratory of Analytical Chemistry has been carrying out analyses on marine waters and sediments of the Thessaloniki Gulf and on waste-waters discharged into it. Results obtained showed elevated heavy metal concentrations near the sites where industrial waste waters and municipal sewage were discharged. The main subject was the investigation of mercury and lead distribution.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The following species were studied: Mytilus galloprovincialis, Mullus barbatus, Thunnus thynnus thynnus and Xiphias gladius.

Pollutants analysed:

Total mercury, cadmium, and lead were analysed.

Areas studied: The following areas of the Northern Aegean Sea were covered:

(a) Thessaloniki Gulf (part of Thermaikos Gulf, Fig. 1).

Sampling station Th 1 is located in the vicinity of the industrial area, Th 2 in an area used extensively for fishing and recreation; station Th 3 has been included at a later stage. Thessaloniki Gulf consists of two basins communicating together and to the open sea by narrow and shallow straits. It receives waste-water from a great variety of industrial units and from a city of about 800,000 inhabitants.

(b) Kavala region (Fig. 2):

Two stations, St 1 and St 2, are located in the harbour, St. 3 near an industrial complex, while St 4 and St 5 are located at cleaner sites for comparative purposes.

(c) Strymonikos Gulf (Fig. 3).

Two sampling stations, S1 and S2, were selected in this area which, in general, is considered to be rather unpolluted.

METHODOLOGY

Samples were collected by the Laboratory of Zoology (Prof. M. Katoulas) and

stored deep-frozen. When possible, composite samples were prepared (up to 12 specimens) and the destruction was performed by wet ashing with concentrated HNO₃, under reflux or in pressure decomposition vessels. Each determination was carried out twice, the second being done by the standard addition technique, and reported values represent their average.

Intercalibration exercise:

Three of the four intercalibration samples have been analysed.

RESULTS

Table I, based on submitted LOG-Forms, gives results on average, number of analyses and ranges of concentrations of heavy metals of each sampling station. Results achieved show that higher heavy metal concentrations were observed in marine organisms collected from sampling stations near areas heavily populated or industrialized. Mytilus galloprovincialis can be considered as a good indicator for the characterization of the contamination level in an area around a sampling station. Other species are not so abundant; therefore, data on them give only a general picture. There are some indications that these organisms have lower concentrations of heavy metals during spring and summer.

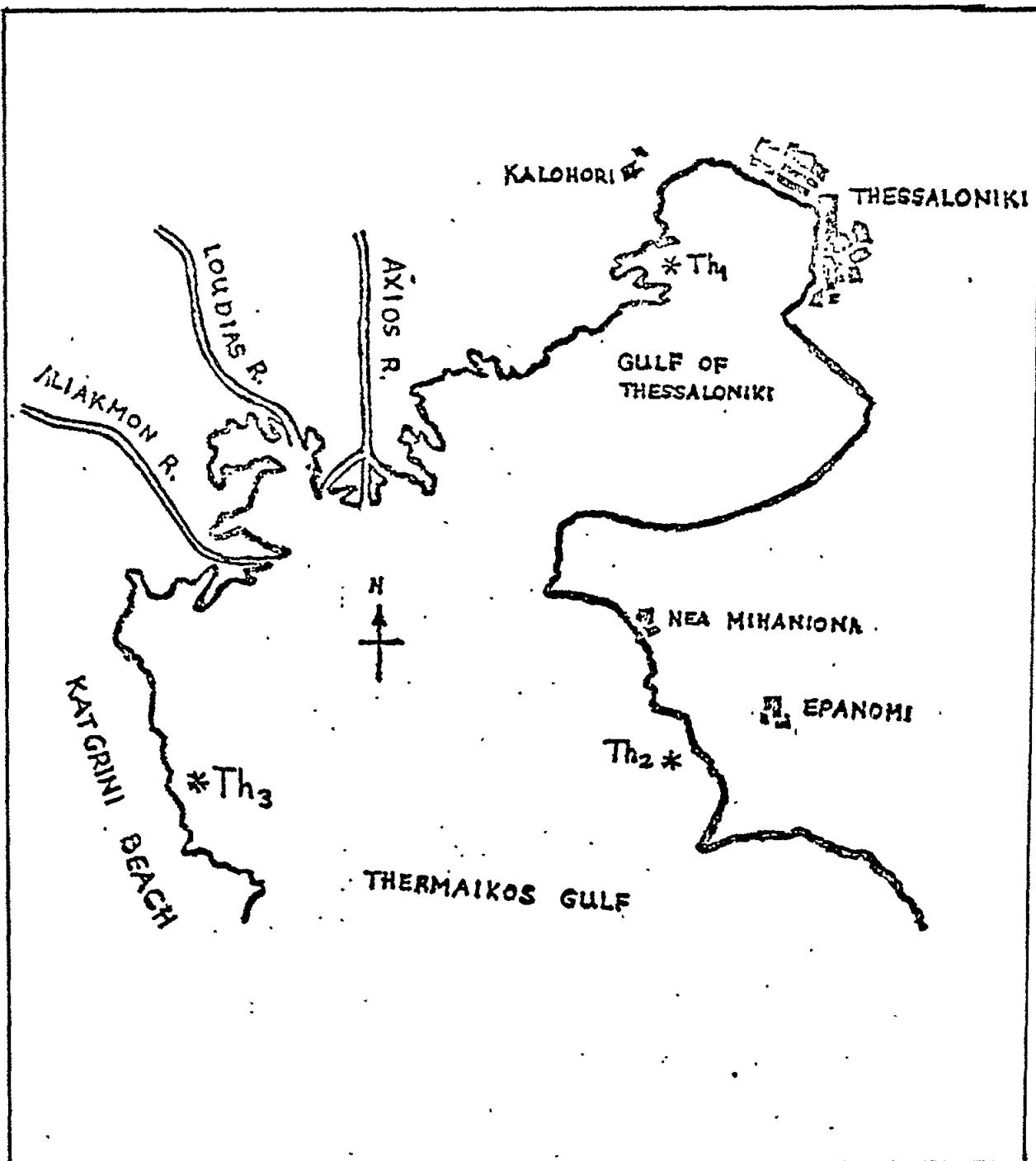


Fig. 1. Sampling sites in Thermaikos and Thessaloniki Gulfs
(Stations Th₁, Th₂ and Th₃)

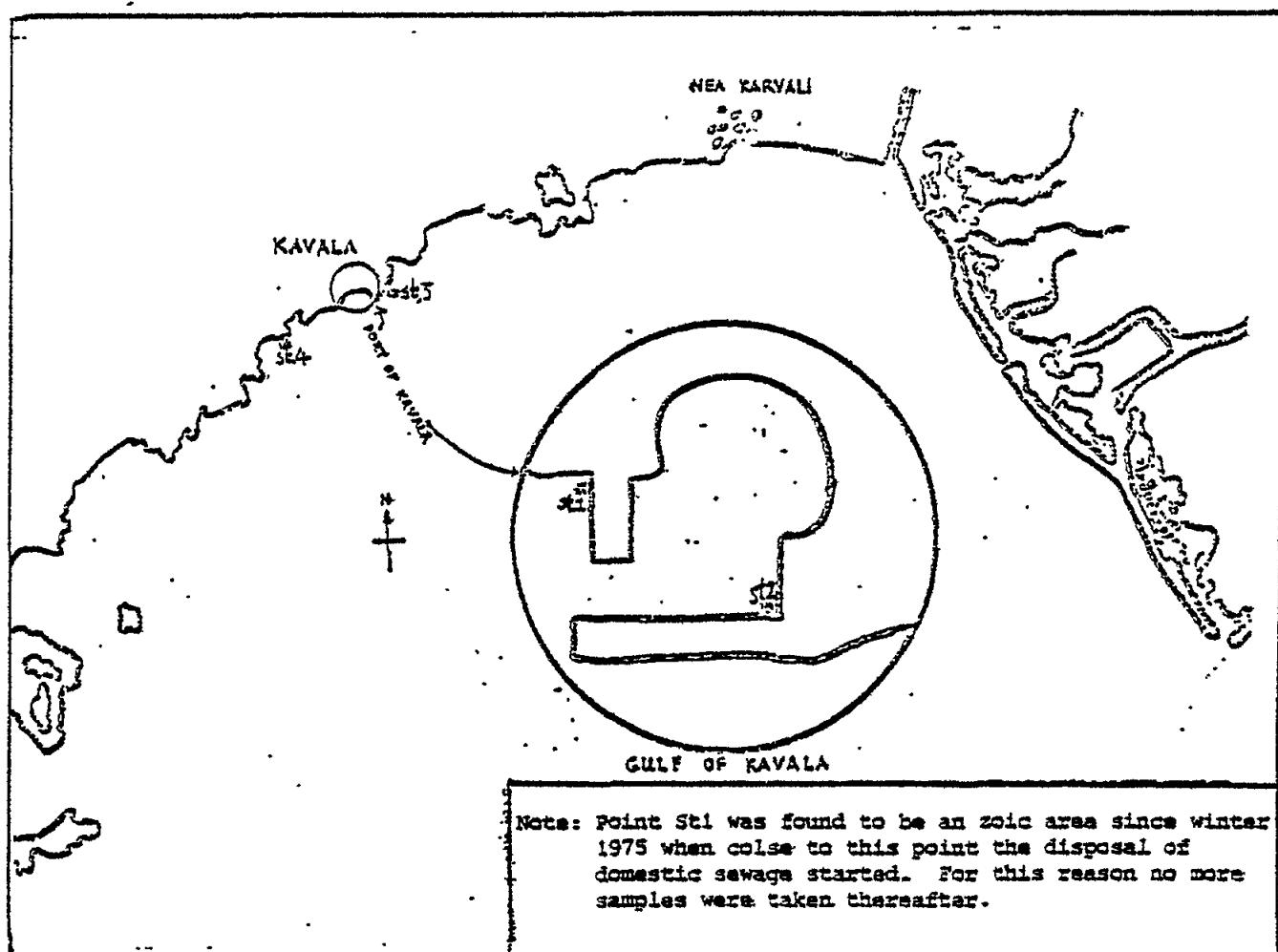


Fig. 2. Sampling sites in the Gulf of Kavala
(Stations St₁, St₂, St₃ and St₄)

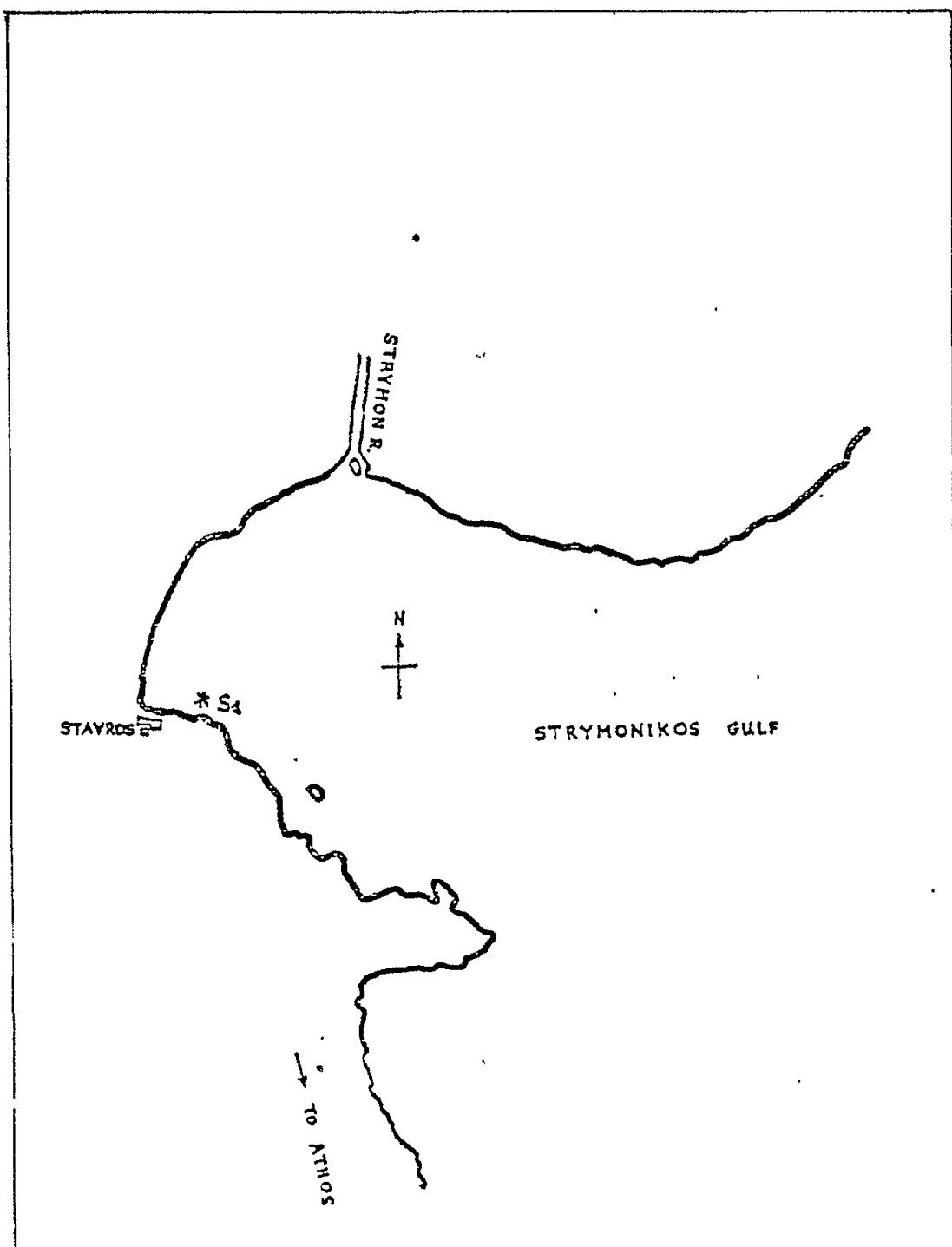


Fig.3. Sampling site in Strymonikos Gulf (S_2)

Table I

Heavy metals concentrations in some organisms from the Northern Aegean Sea.
Mean (µg/kg F.W.), number of analyses (in brackets) and range.

Species	Station	Hg	Cd	Pb
<i>Mitilus galloprovincialis</i>				
Th ₁	53 (18)	4-177	120 (12)	10-283
Th ₂	19 (16)	4- 57	102 (13)	5-403
S ₁	21 (9)	9- 37	13 (7)	8- 19
S ₂	12 (6)	7- 18	45 (5)	27- 60
St ₁	155 (3)	76-282	87 (3)	10-208
St ₂	455 (10)	40-920	52 (8)	15-109
St ₃	46 (9)	4-108	59 (6)	29-143
St ₄	16 (9)	4- 84	181 (7)	34-485
St ₅	24 (5)	12- 33	14 (3)	9- 23
<i>Milllus barbatus</i>				
Th	144 (10)	62-407	125 (9)	58-210
St	104 (8)	41-205	71 (6)	27-158
S	108 (10)	14-194	102 (8)	58-204
<i>Thymus thymus thymus</i>				
Th	335 (2)	50-620	208 (1)	
St	86 (1)		168 (1)	
S	348 (3)	82-890	167 (2)	119-215
<i>Xiphias gladius</i>				
Th	582 (2)	410-755	112 (2)	76-148
<i>Merluccius merluccius</i>				
St	136 (1)		76 (1)	230 (1)
S	50 (2)	38- 62	48 (1)	185 (1)

Research Centre: Institute of Oceanographic and
Fisheries Research
GR-166 04 Hellinikon
GREECE

Principal Investigator: F. VOUTSINOU-TALIADOURI

Period of Reporting: 1976 to January 1980

INTRODUCTION

The first metal determinations in sediments were carried out in October 1974. Following the visit of Mr. O. Lindgren (WHO consultant) in September 1975 marine organisms were also analysed.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

Four species were used for analysis: Mullus barbatus, Parapenaeus longirostris, Mytilus galloprovincialis and Merluccius merluccius.

Pollutants analysed:

The following trace elements were analysed: Pb, Cd, Ni, Co, Cr, Zn, Fe, Mn and Cu. As a mercury analyser was not available, no such analyses were carried out.

Area studied:

All the samples were taken from the Saronikos Gulf, in the northern part of which Athens is situated (Fig. 1). The characteristics of the water are:

Depth: Smallest in the north, where the Elefsis Bay has a maximum of about 30 m only and greatest in the south-west, near Epidavros, where the maximum exceeds 400 m.

Temperature: Between 15 and 25°C in the upper layers, about 14.5-15°C below 200 m.

Salinity: Around 38.5‰

Dissolved oxygen: In general near saturation, at least in the upper layers, but affected by pollution; at times above saturation owing to greatly enhanced photosynthetic activity; often slightly reduced (especially at greater depths) and sometimes low or even absent (central part of Elefsis Bay in summer).

Eutrophication: Greatest in Elefsis Bay where renewal of water is slow and industrial and shipping activities are great, especially in the east. Very high in the zone of the metropolitan sewage outfall, near Pireus harbour. High in the area to the south of the sewage outfall zone and significant elsewhere.

The air temperature over the gulf ranges from 0 to 40°C. The annual rainfall

is below 400 mm, 81% of it from October to March. River run-off is negligible. The predominant wind is northwestern, except in spring, when the sea breeze blows from the south.

Pollution: As estimated by its effect on macrobenthic organisms, it is greatest in Elefsis Bay (especially away from the shore, because of anoxia), and high in the sewage outfall zone, while it is moderate in the neighbouring area immediately to the south of it and generally absent elsewhere.

METHODOLOGY

The specimens were obtained with bottom trawling (Mullus barbatus, Parapenaeus longirostris and Merluccius merluccius) or simple picking (Mytilus galloprovincialis). They were kept in deep freeze until prepared. Then they were lyophilized and digested in concentrated HNO₃ inside Teflon digestion vessels, according to the description given in FAO Fisheries Technical Paper (158). The diluted solutions were processed on a Perkin Elmer 305B AAS equipped with a Deuterium Background Corrector. In case of relatively high metal concentration, the flame was used. Otherwise, the graphite furnace 76B was used. The peak heights were read from the recorder and the results were estimated according to the best fit concentration curve.

Intercalibration exercise:

The centre participated in 4 intercalibration exercises using oyster (MA-M-1), seaplant (SP-M-1), copepod (MA-A-1) and fish (MA-A-2) samples.

RESULTS

All the results are shown as mean values in Tables I, II, III, IV, V and VI. Tables I, II and III indicate the seasonal variations of trace metals in marine organisms, Tables IV and V show the geographical variations and table VI indicates summary of results in three fish species. Histograms in Figs. 2 to 4 give the mean values of the constituents by species and by area. As all samples contained individuals of both sexes, it is not possible to draw any conclusion regarding the relationship between sex and concentrations.

The concentrations of Pb, Cd, Co and Cr in Parapenaeus longirostris are comparable with, or slightly higher, than those in Mullus barbatus. Those of Zn and Cu are 3 and 7 times higher, respectively. The concentrations of Mn and Fe are also higher. In Mytilus galloprovincialis the concentrations of Pb, Co, Cu, Cr and Fe are 2 to 3.5 times higher than those in Mullus barbatus, while Mn, Zn and Cd concentrations are 5, 6 and 7 times higher respectively.

DISCUSSION OF RESULTS

From the results given it appears that there was no significant seasonal or geographical variation in the marine organisms analysed.

By comparing the results obtained with those of other Mediterranean areas (GFCM, Circular No.7, Report No.3, May 1978), it can be seen that the concentration ranges of all metals are similar to those found in fairly clean Mediterranean waters.

PUBLICATIONS

TALIADOURI-VOUTSINOU, F., (1980), Trace metals in marine organisms from the Saronikos Gulf (Greece), *Ves Journées Etud. Pollutions*, pp. 275-280, Cagliari, C.I.E.S.M.

VOUTSINOU-TALIADOURI, F. and SATSMADJIS, J., (1982), Influence of metropolitan waste on the concentration of chlorinated hydrocarbons and metals in *Mullus barbatus*, *Marine Pollution Bulletin*, Vol. 13, No. 8, pp. 166-169

VOUTSINOU- TALIADOURI, F., (in press), Monitoring of metals in some marine organisms from the Saronikos Gulf, *VI^{es} Journées Etud. Pollutions*, Cannes, C.I.E.S.M.

SATSMADJIS, J. and VOUTSINOU-TALIADOURI, F., (1983), *Mytilus galloprovincialis* and *Parapenaeus longirostris* as bioindicators of heavy metal and organochlorine pollution, *Marine Biology*, 76, 115-124

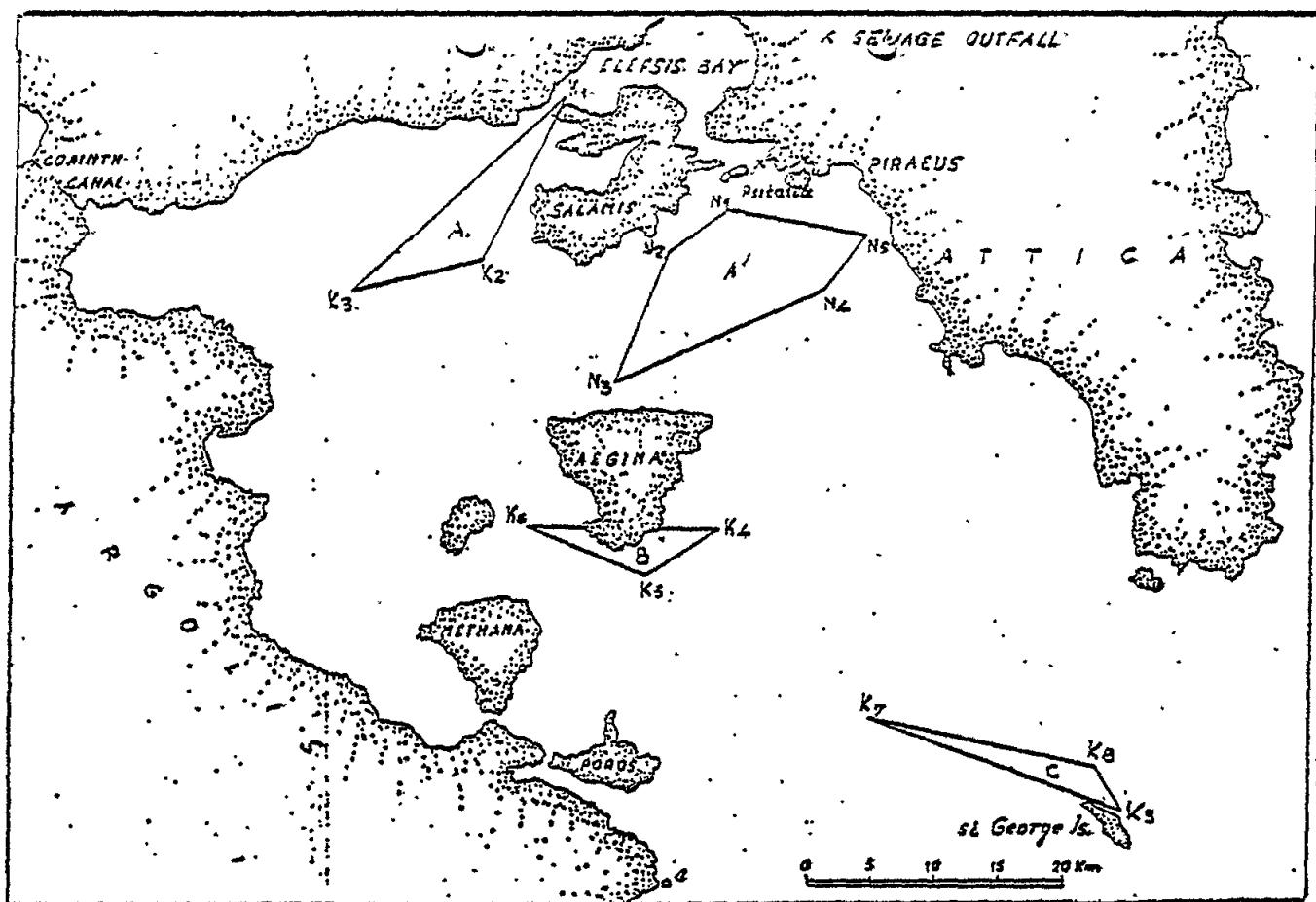


Fig. 1. Sampling areas

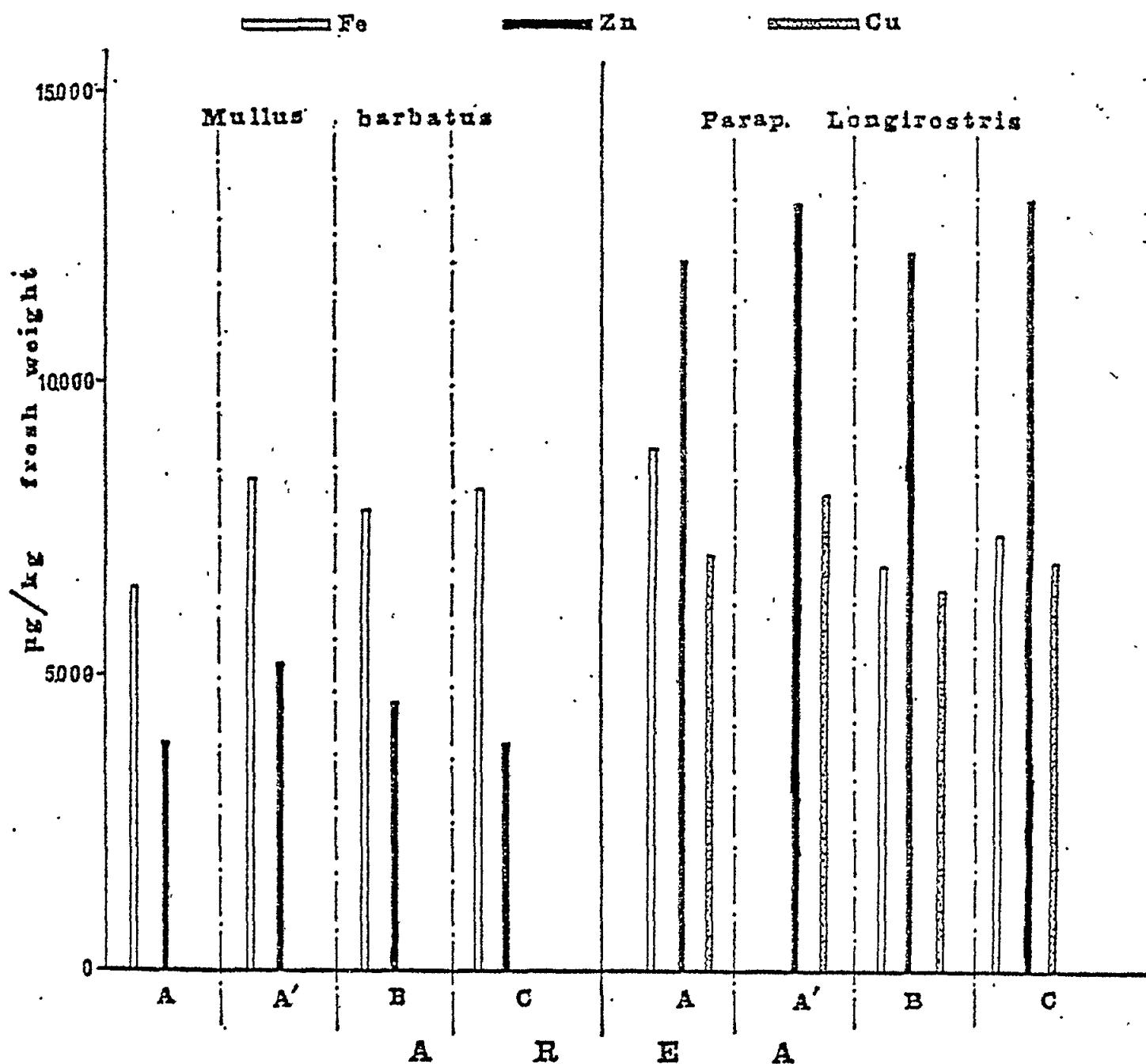


Fig. 2 : Mean concentrations of Fe, Zn and Cu in different areas.

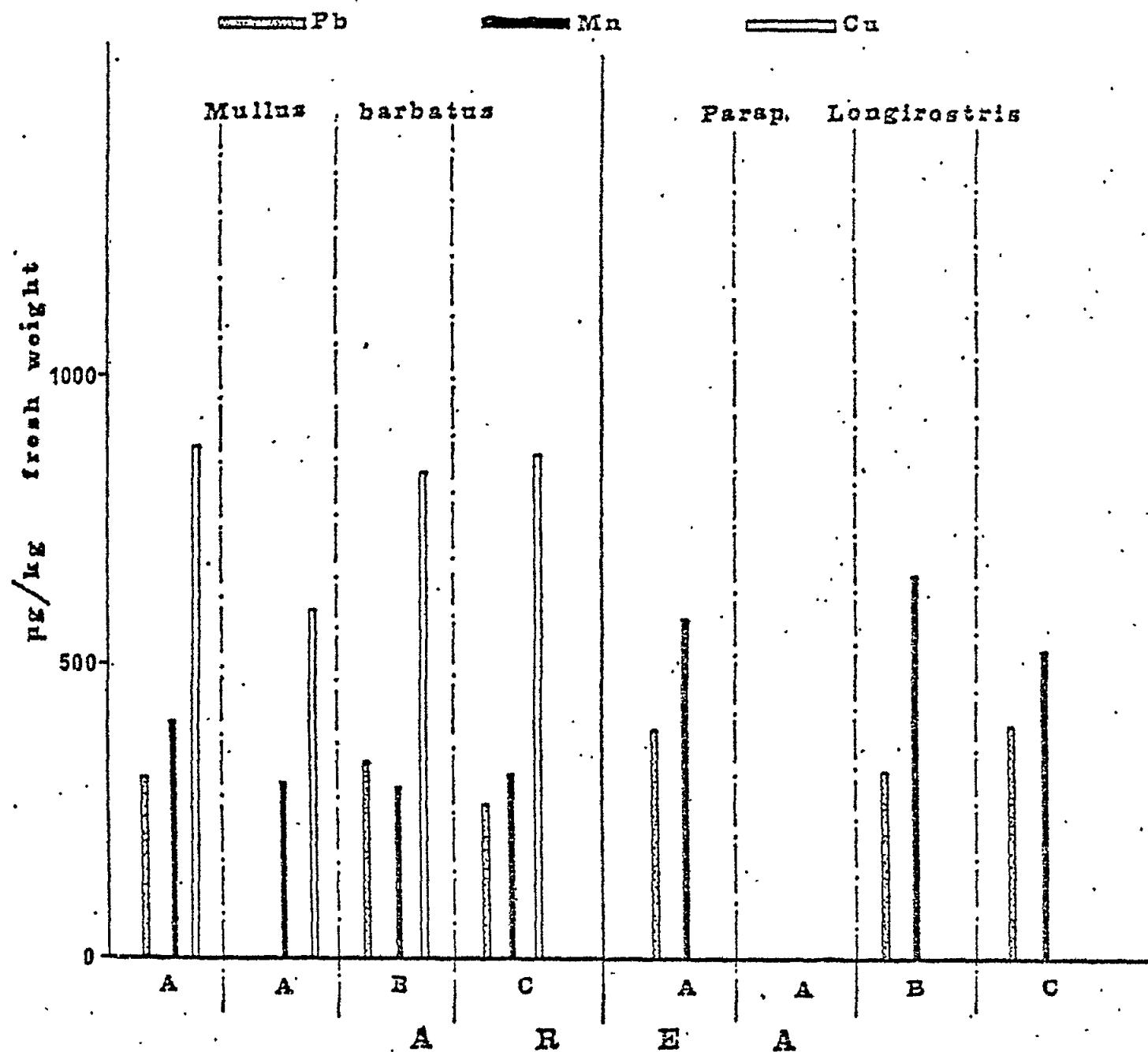


Fig. 3 : Mean concentrations of Pb, Mn and Cu in different areas.

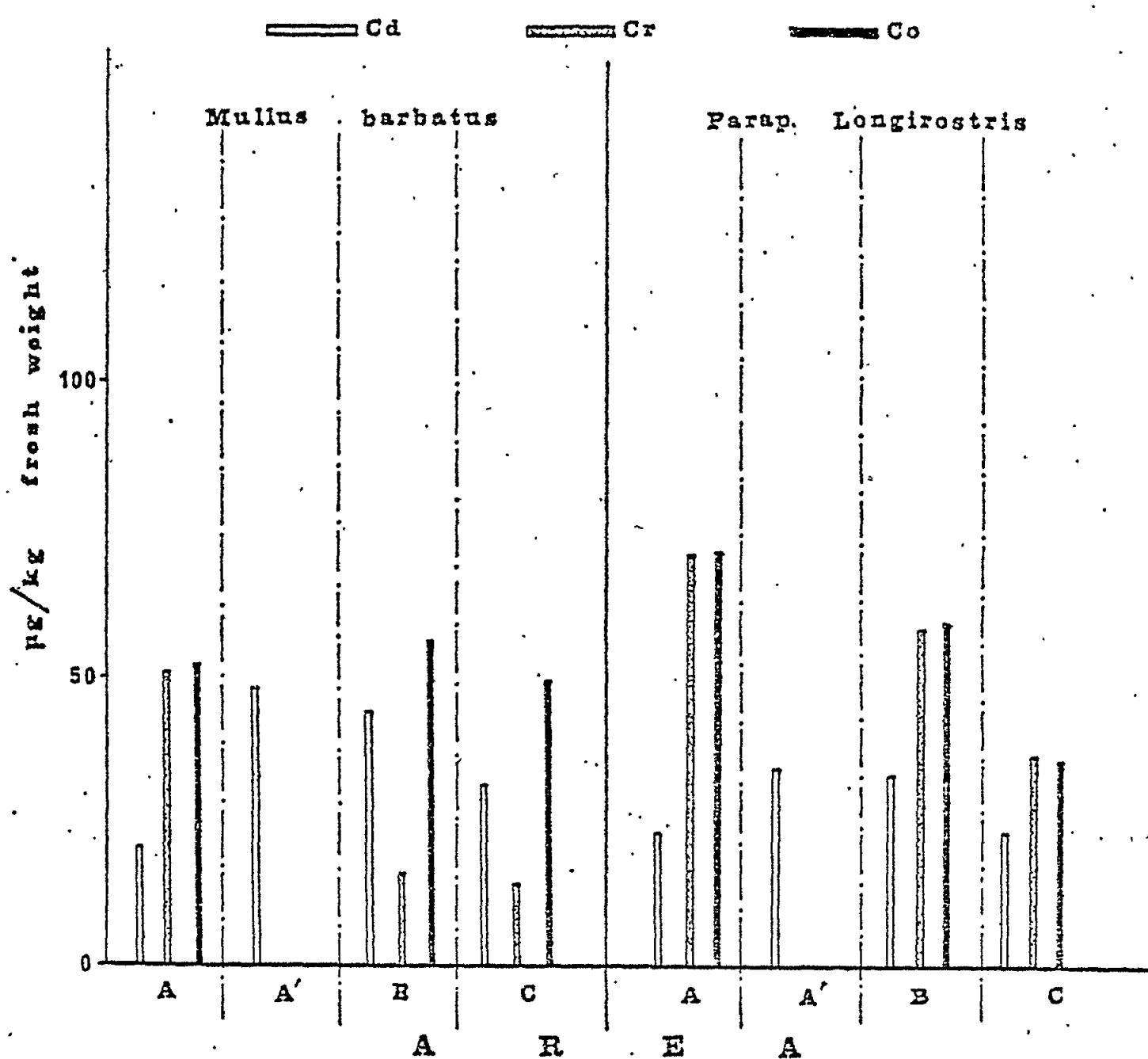


Fig. 4 : Mean concentrations of Cd, Co and Cr in different areas.

T A B L E I
Seasonal means and ranges of trace element
concentrations in Mullus barbatus ($\mu\text{g}/\text{Kg}$ wet weight)

Element	Spring	Summer	Autumn	Winter
	(1976-1978) All 4 Areas	(1976-1978) All 4 Areas	(1975-1978) All 4 Areas	(1975-1978) All 4 Areas
Pb	< 600	307 (250-350)	297 (270-320)	305 (270-340)
Cd	75 (40-90)	70 (23-150)	31 (15-50)	52 (15-120)
Co	< 200	49 (42-59)	52 (47-60)	51 (50-52)
Cr	-	27 (8-68)	35 (12-70)	23 (16-25)
Zn	5100 (3600-6500)	4550 (3600-5700)	3525 (3100-4200)	3900 (3600-4300)
Fe	9050 (8350-10100)	6933 (5700-8000)	6566 (3200-8700)	8091 (5430-10800)
Mn	350 (300-380)	301 (210-425)	317 (200-450)	340 (330-350)
Cu	708 (600-850)	726 (390-1120)	1037 (750-1130)	822 (760-920)

T A B L E II
Seasonal means and ranges of trace element
concentrations in Mytilus galloprovincialis
(μ g/Kg wetweight).

Element	Spring	Summer	Autumn	Winter
	(1976-1978) All 4 Areas	(1976-1978) All 4 Areas	(1975-1978) All 4 Areas	(1975-1978) All 4 Areas
Pb	< 600	-	880	< 600
Cd	110	160	180 (120-200)	70 (<40-120)
Co	< 200	-	40	< 200
Cr	-	-	95	-
Zn	32500	24000	24700 (22100-27000)	14200
Fe	25250	-	16600	23200
Mn	3300	-	1400	2570
Cu	1700	2800	1583 (1300-1900)	1080

T A B L E III
Seasonal means and ranges of trace element
in Parapenaeus longirostris ($\mu\text{g}/\text{Kg}$ wetweight).

Element	Spring (1976-1978) All 4 Areas	Summer (1976-1978) All 4 Areas	Autumn (1975-1978) All 4 Areas	Winter (1975-1978) All 4 Areas
Pb	< 600	365 (310-420)	363 (300-400)	416 (360-420)
Cd	24 (20-26)	26 (20-30)	31 (24-50)	30 (20-35)
Co	< 200	85 (60-110)	63 (50-80)	68 (65-70)
Cr	-	72.5 (65-80)	81 (65-90)	27 (8-45)
Zn	15160 (12400-17200)	11320 (9500-12700)	10950 (9800-12100)	12100 (11600-12800)
Fe	3500 (3100-3800)	8025 (7350-10300)	9467 (8800-10300)	9160 (6400-13780)
Mn	580 (400-800)	540 (500-580)	367 (330-400)	840 (640-1050)
Cu	5257 (4570-5500)	7834 (6300-9800)	7850 (6200-9500)	6223 (5090-7780)

T A B L E IV
Geographical means and ranges of trace element
concentrations in Mullus barbatus ($\mu\text{g}/\text{Kg}$ wet weight).

Element	Area A	Area A'	Area B	Area C	All 4 Areas
Pb	321 (300-340)	< 600	335. (320-350)	263. (250-270)	306 (250-350)
Cd	20. (15-24)	47 (25-70)	44 (15-120)	30. (21-60)	35. (15-70)
Co	51 (42-60)	< 200	55 (50-59)	48 (46-52)	51 (42-60)
Cr	51 (16-70)	-	16 (8-25)	13 (8-23)	27 (8-70)
Zn	3833 (3100-4600)	5220 (4200-6500)	4628 (3200-6200)	3800 (3600-4200)	4370 (3100-6500)
Fe	6610 (5430-8700)	8350	7800 (7100-10100)	8136 (7800-8700)	7724 (5430-10100)
Mn	405 (340-450)	300	292 (200-370)	310 (210-380)	327 (200-450)
Cu	887 (760-1130)	610 (390-760)	833 (420-1120)	856 (600-1300)	796 (390-1300)

T A B L E V
Geographical means and ranges of trace element
concentrations in Parapenaeus longirostris ($\mu\text{g}/\text{Kg}$ wetweight).

Element	Area A	Area A'	Area B	Area C	All 4 Areas'
Pb	387 (310-420)	-	330 (300-360)	400 (390-412)	372 (300-420)
Cd	23 (20-35)	33 (30-50)	32 (30-51)	22 (20-25)	27.5 (20-51)
Co	73 (50-110)	-	64 (60-68)	72 (65-80)	70 (50-110)
Cr	70 (45-90)	-	58 (27-90)	36 (8-65)	55 (8-90)
Zn	12072 (9800-15060)	13133 (9500-17200)	12223 (10600-14640)	13133 (11300-16500)	12640 (9500-17200)
Fe	8906 (3800-13780)	-	6900 (3100-10300)	7466 (3600-8800)	7757 (3100-13780)
Mn	580 (400-1050)	-	653 (330-830)	527 (400-640)	587 (330-1050)
Cu	7044 (4570-9800)	8100 (7600-8600)	6447 (5090-8900)	6950 (5700-9500)	7135 (4570-9800)

T A B L E VI
Summary of Results
Mean values in $\mu\text{g}/\text{Kg}$ (fresh weight)

Species	Area or Station	Cd	Pb	Ni	Fe	Mn	Zn	Cu	Co	Cr
<i>Mullus barbatus</i>	A	67	143	35	4190	259	5520	530	<50	<2
	B	104	216	187	5183	332	5550	450	"	"
	C	221	462	179	5300	344	7140	404	"	"
	N ₂	95	136	30	5595	301	5220	414	"	"
<i>Parapenaeus longirostris</i>	A	149	104	23	2940	576	16075	3779	"	"
	B	191	106	65	7740	533	15790	5986	"	"
	C	99	9	10	8400	1440	17030	2543	"	"
	N ₂	58	278	56	9290	802	16340	3423	"	"
<i>Merluccius merluccius</i>	A	28	105	17	990	204	4315	266	"	"
	B	38	92	125	2715	236	3935	307	"	"
	C	51	65	40	2460	278	4460	362	"	"
	N ₂	113	71	21	1680	233	5945	360	"	"

Research Centre:

Department of Food Hygiene, Veterinary
Faculty
University of Thessaloniki
Greece

Principal Investigator:

A.G. PANETSOS and (from August 1979)
P. KARAOANNOGLOU

Period of Reporting:

February 1977 to March 1981

INTRODUCTION

The Institute has performed studies of total mercury in fish and shellfish of the North Aegean Sea as well as of the lakes and rivers of Greek Macedonia since 1972.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The following species were sampled: Mytilus galloprovincialis, Mullus barbatus, Thunnus thynnus, Xiphias gladius, Merluccius merluccius.

Pollutant analysed: Total mercury.

Areas studied:

The laboratory performs the study and monitoring of total mercury in fish and shellfish of the North Aegean Sea. The area covered is in the vicinity of five main rivers, Aliakmon, Loudias, Axios, Gallikos, Strymon. From this area three main gulfs have been selected for study: Thermaikos Gulf ($40^{\circ} 30' N$ - $21^{\circ} 50' E$), Strymonikos Gulf ($40^{\circ} 50' - 23^{\circ} 60' E$) and Kavala Gulf ($40^{\circ} 55' N$ - $24^{\circ} 24' E$). The gulfs are shallow and provide a very good environment for the cultivation of shellfish (Fig.1).

The Gulf of Thermaikos receives the wastes of the city of Thessaloniki, industrial wastes (west coast) and agricultural wastes (east coast).

The Gulf of Strymonikos receives mainly agricultural wastes, while the Gulf of Kavala receives the wastes of the city of Kavala and agricultural wastes. See Figs. 2 to 4.

METHODOLOGY

Sampling was done by the Laboratory of Zoology, University of Thessaloniki. Samples were stored deep frozen prior to analysis. Samples of about 500 mg were digested for at least 2h at $65-70^{\circ}C$ in a watertub with a mixture of 18N H_2SO_4 and 5.6N HNO_3 (Pirati, et al. 1971, Industria Conserve 46:258). Determination of total mercury (Hg_T) was carried out with flameless AAS, with a Coleman Mercury Analyzer Mas-50.

Intercalibration:

The laboratory has analysed three of the four intercalibration samples provided by the International Laboratory for Marine Radioactivity in Monaco.

RESULTS

Mercury in Mytilus galloprovincialis: The average concentrations in ug/kg fresh weight (FW) are presented in Table I. There is an indication of a decrease since 1977 in Thermaikos Gulf and Strymonikos Gulf, which may be attributed to the measures taken against pollution.

Mercury in Mullus barbatus: The average concentrations in ug/kg FW are presented in Table II. There seems to be the same trend of decreasing concentrations as for Mytilus galloprovincialis. The average concentrations are in the range from 42 to 381 μ g/kg FW.

Mercury in Thunnus thynnus and Xiphias gladius. Only a few samples of these species have been analysed (Tables III and IV). In addition some samples of Merluccius merluccius have been analysed (Table V).

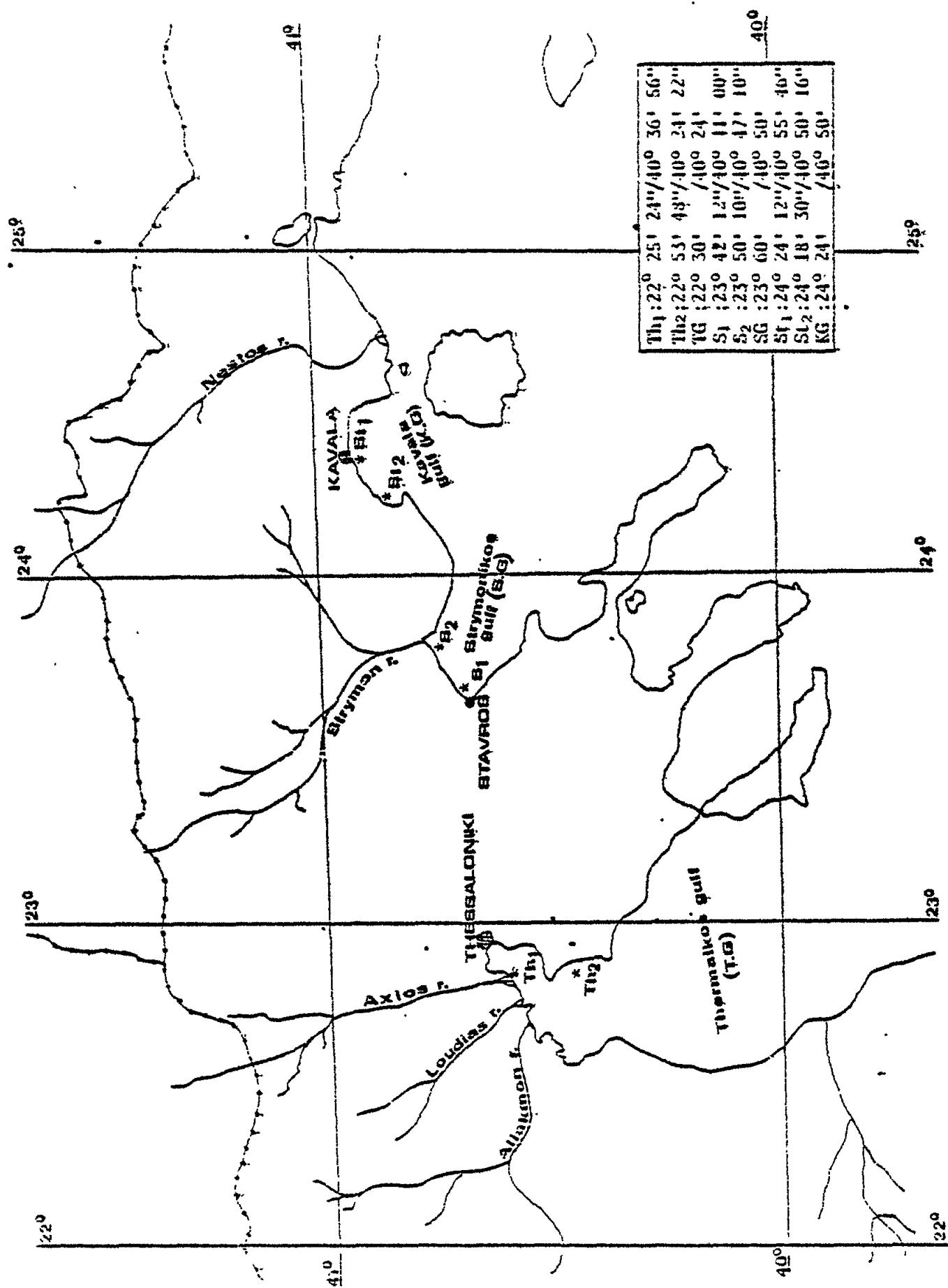


Fig. 1. Areas studied

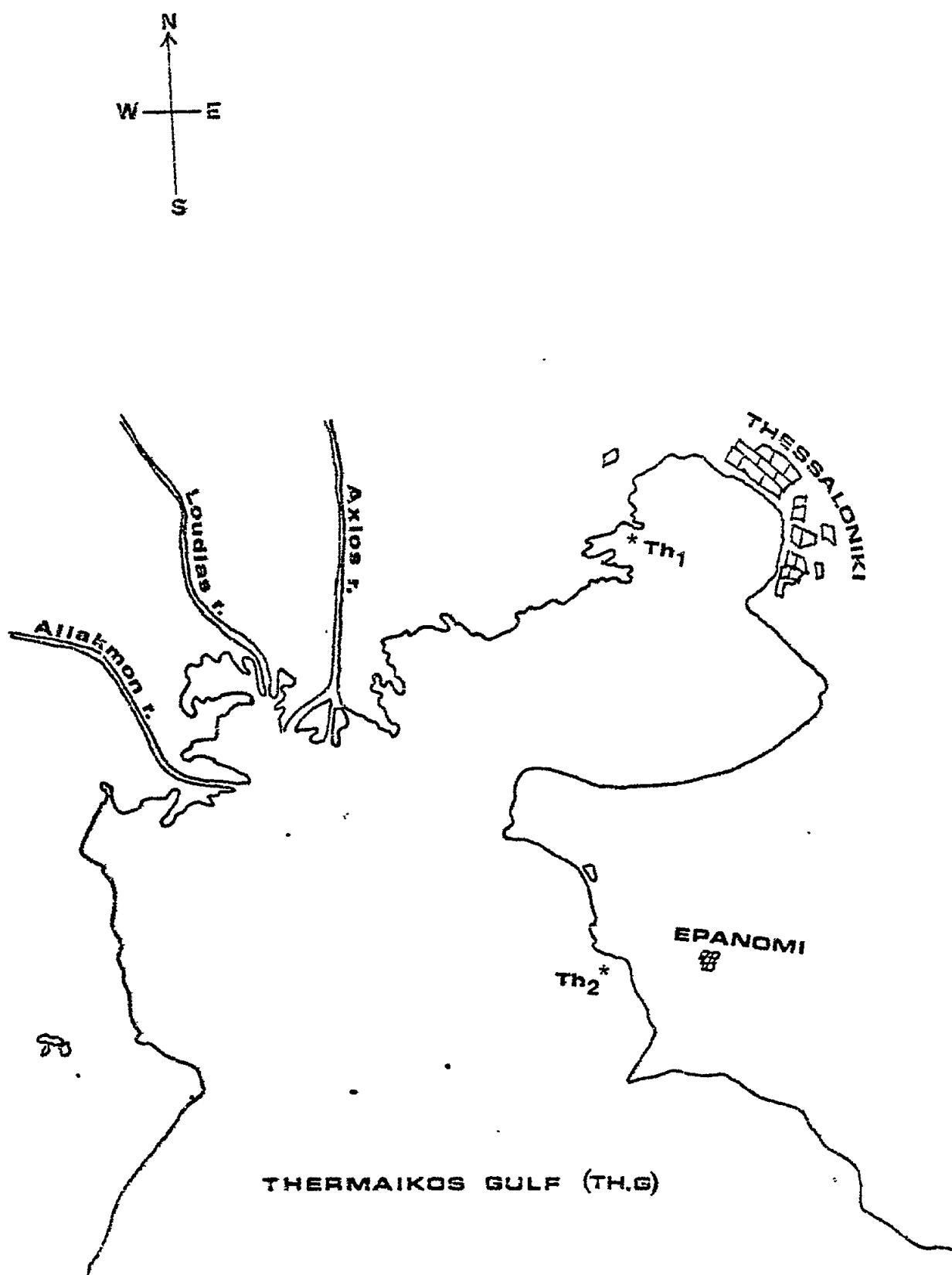


Fig. 2. Sampling sites in Thermaikos Gulf (Th₁ and Th₂)

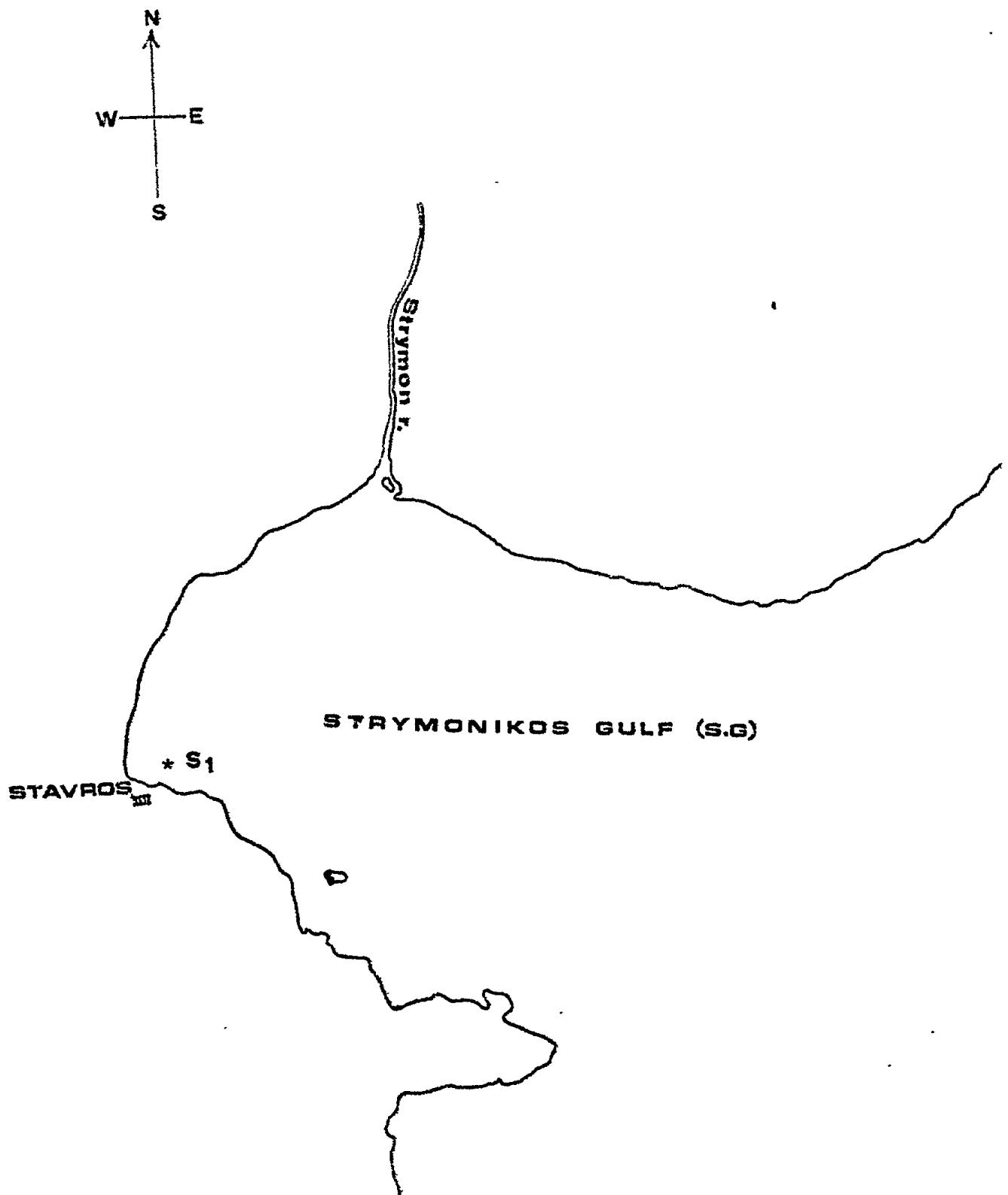


Fig.3. Sampling sites in Strymonikos Gulf (S₁)

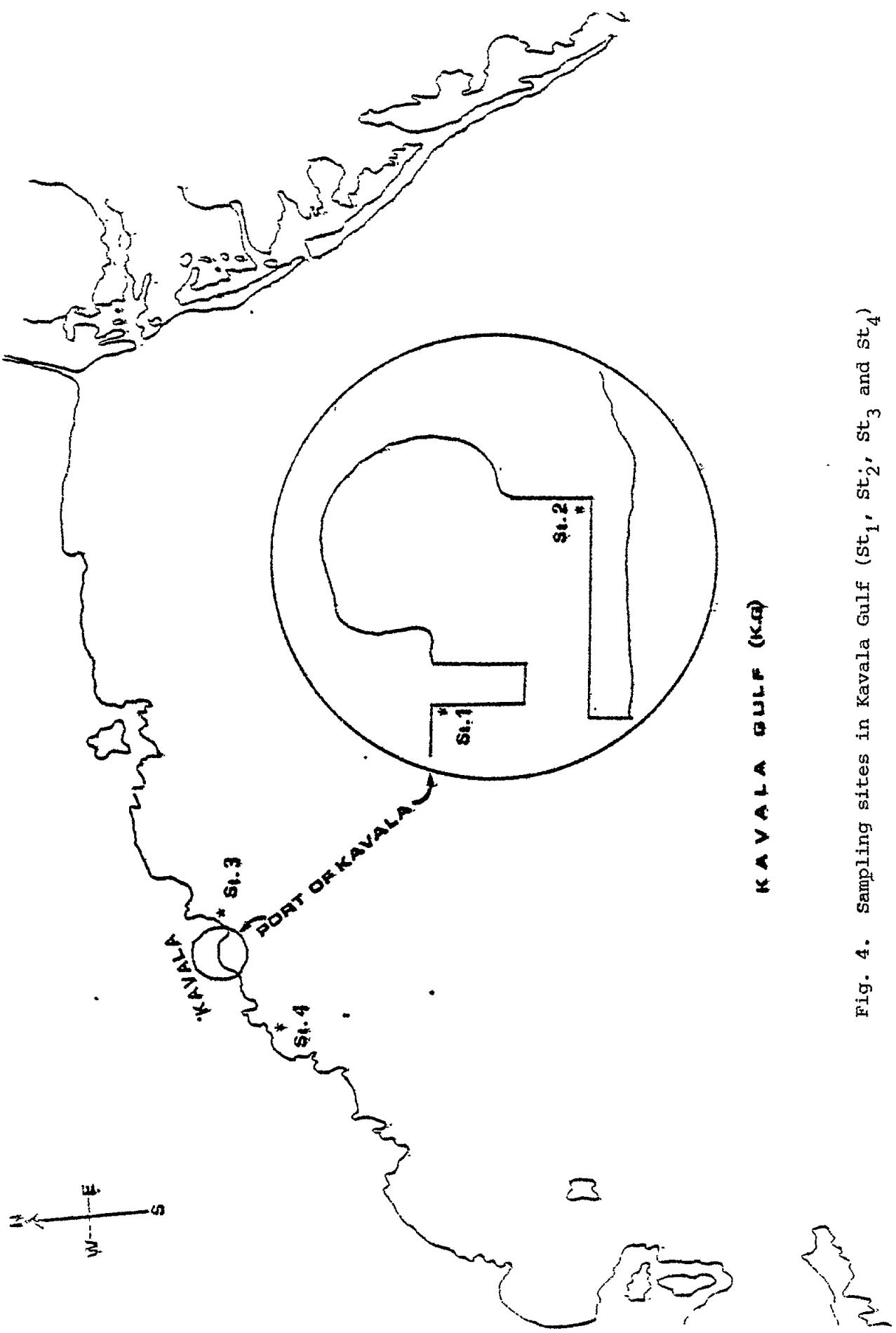


TABLE I
Heavy Metals (Hg) in *Mytilus galloprovincialis*

SAMPLING AREA	1975			1976			1977			1978			1979			1980		
	Number of samples	\bar{x} µg/kg																
Thermaikos Gulf	6	108.5	15	85.66	0	297.37	4	75.25	5	44.49	4	10.75	42					
Strymonikos Gulf	9	335.5	11	116.45	4	424.75	7	97.57	12	47.08	4	13.75	46					
Kavala Gulf	-	-	-	-	0	294.87	-	-	-	-	4	16.00	12					
TOTAL	14		26		20		11		17		12		100					

TABLE II
Heavy Metals (Hg) in *Mullus barbatus*

SAMPLING AREA	1975			1976			1977			1978			1979			1980		
	Number of samples	\bar{x} µg/kg																
Thermaikos Gulf	-	-	1	45.00	4	233.25	2	60.59	4	58.00	1	62.00	12					
Strymonikos Gulf	-	-	3	80.65	4	381.50	3	75.00	4	42.25	1	76.00	15					
Kavala Gulf	-	-	3	250.33	-	"	1	86.00	4	44.50	1	25.00	9					
TOTAL	-		7		0		6		12		3		36					

Heavy Metals (U.S.) in Human Health

TABLE IV.
Heavy Metals (lignite) in *Xanthias gladius*

Heavy Metals (Hg⁺) in *Hericium erinaceus* mycelium

SAMPLING AREA	1975			1976			1977			1978			1979			1980			TOTAL
	Number of samples	μg/kg of samples																	
Theimakos Gulf	-	-	-	-	-	-	-	-	-	-	2	41.00	-	-	-	-	-	-	2
Aegeanikos Gulf	-	-	-	-	-	-	-	-	-	-	2	41.50	1	39.00	3	1	39.00	3	
Kavala Gulf	-	-	-	-	-	-	-	-	-	-	2	51.0	2	36.50	4	2	36.50	4	
TOTAL	-	-	-	-	-	-	-	-	-	-	6	-	3	-	-	3	3	9	

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

Principal Investigator: O. OREN

Period of Reporting: October 1975 to December 1979

INTRODUCTION

Studies on heavy metals in fish, sediments and water had already started in the Institute in 1974 (Roth and Hornung, 1977 and 1977a). With the signature of the agreement for the pilot project the work was intensified. As a result of the studies, it was found that certain species of fish caught along the shore of Israel are able to concentrate larger quantities of pollutants, especially mercury, than the rest of the species investigated. Because of the fact that the level of mercury in one fish species, Upeneus moluccensis, reached concentrations above the maximum permissible quantity (1.00 ppm), this fish, from a certain size (age) onwards, is prohibited to be marketed. In another fish species, Holocentrum rubrum, the concentration of mercury is also considerable, and above the maximum permissible quantity.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The species of fish and other organisms were selected according to the recommendations contained in the Operational Document for the pilot project, and, in addition, several other species of fish of commercial importance in Israel were analysed. The fish examined are the following: Saurida undosquamis, Synodus saurus, Trachurus mediterraneus, Mullus barbatus, Mullus surmuletus, Upeneus moluccensis, Boops boops, Pagellus erythrinus, Pagellus acarne, Dentex filosus, Dentex macroptalmus, Pagrus ehrenbergii and Conger conger. All these are trawl fish.

Pollutants analysed:

The pollutants analysed were: mercury, cadmium, lead, copper, zinc and nickel. Because of the lack of the proper recorder for the carbon rod atomizer, the majority of the analysis of the minor elements could not be completed.

Areas studied:

The areas sampled are shown in Fig. 1. The physical conditions of the sampling sites were not determined at the time of sampling, and it is assumed that "normal" conditions prevailed, e.g. that the water temperatures and salinities did not differ very much from the mean temperatures and salinities at the specific seasons of sampling.

METHODOLOGY

As mentioned previously, the samples were collected by commercial trawl nets at predetermined sampling stations. Fish samples for analyses in the field

and in the laboratory were prepared by the methods recommended in FAO Fisheries Technical Paper (158). The technique of Holak *et al.* (1972) was used for the mercury analysis, and the other metals were determined according to the procedure described earlier (Roth and Hornung, 1977).

Intercalibration exercise:

The following intercalibration samples were analysed: oyster (MA-M-1), seaplant (SP-M-1), copepod (MA-A-1) and fish (MA-A-2).

RESULTS

Mercury: Means and ranges of total mercury concentration in 18 species of trawl fish for the years 1975-79 are shown in Table I. From this table it can be seen that the range for all the species during 1975-79 varied from 8 to 122 µg/kg (fresh weight). The highest mean values of mercury are observed in Upeneus moluccensis (262-511 µg/kg). The range of mercury in this species is close to, and sometimes exceeds, the permissible level established by the U.S. FDA in 1978 for human consumption. Mullus barbatus and Mullus surmuletus belong to the same Mullidae family as Upeneus, but the mean mercury values for these species are much lower (116-141 µg/kg and 86-179 µg/kg). The reason for this phenomenon remains unclear. All the other species listed in Table I have low mercury concentrations. No increase could be noted with the oncoming years.

Other metals: The concentration of cadmium, lead, nickel, copper and zinc in five species of fish are given in Table II. When comparing these values with those reported earlier (Table III), there is almost no difference in the results for the listed species.

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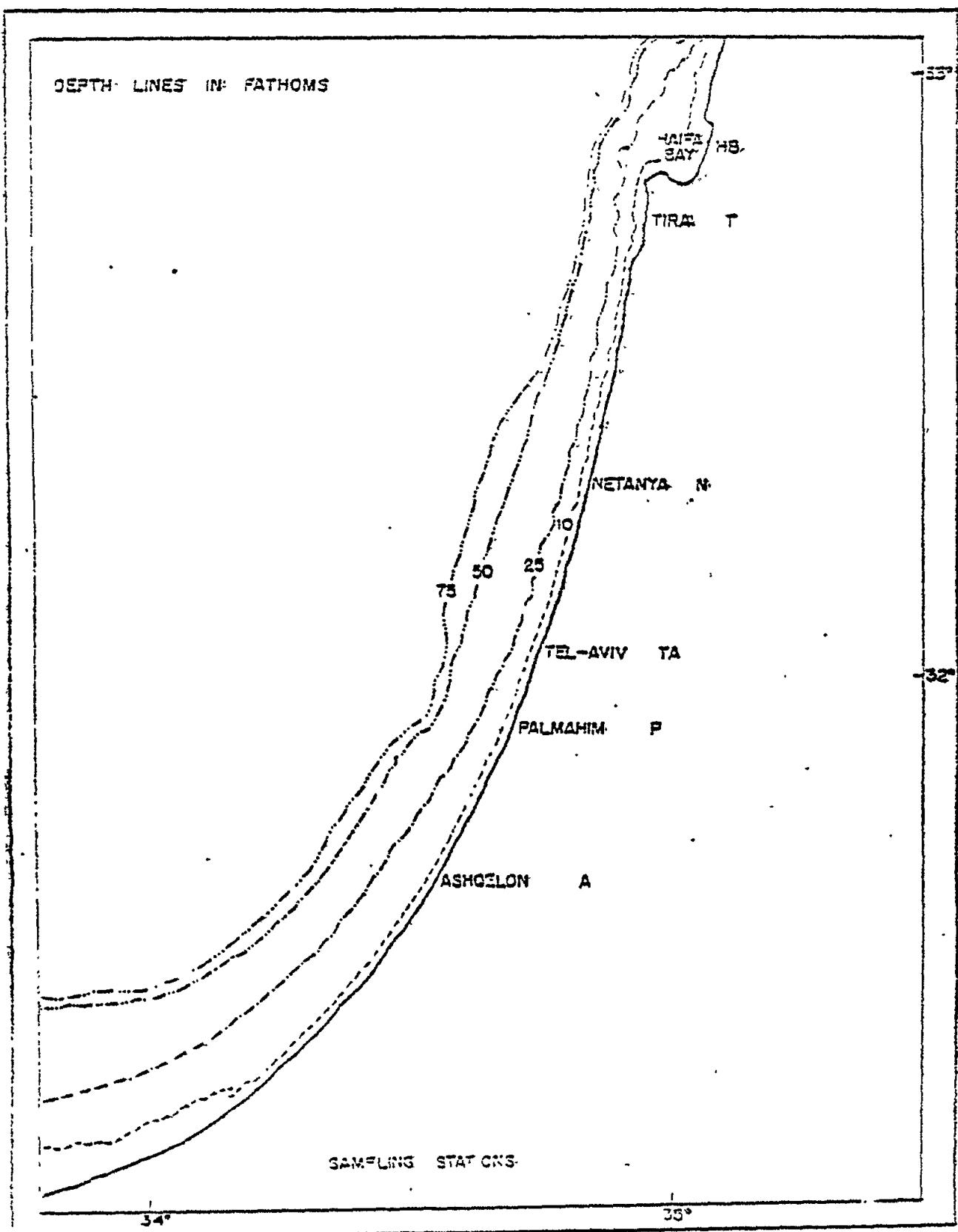


Fig. 1 Sampling sites.

Table I

Total mercury concentration (in $\mu\text{g/kg}$ fresh weight) in the Mediterranean trawl fishes of Israel
 (means and ranges for each species) during the years 1975-1979
 (Number of specimens shown in parenthesis)

Species	1975	1976	1977	1978	1979
<i>Saurida undulata</i>	-	91 ± 39 49 - 123 (16)	145 ± 113 45 - 649 (86)	159 ± 83 66 - 381 (42)	119 ± 82 42 - 495 (56)
<i>Synodus aculeatus</i>	-	-	-	-	123 ± 32 88 - 152 (3)
<i>Merluccius merluccius</i>	42 ± 30 10 - 74 (8)	-	258 (1)	51 ± 22 31 - 74 (4)	209 ± 71 127 - 254 (3)
<i>Trachurus mediterraneus</i>	-	100 ± 60 46 - 165 (10)	141 ± 111 35 - 391 (31)	42 ± 8 35 - 52 (8)	57 ± 90 8 - 343
<i>Mullus barbatus</i>	141 ± 66 28 - 221 (51)	121 ± 44 62 - 216 (255)	114 ± 52 38 - 217 (125)	132 ± 106 35 - 475 (64)	116 ± 59 47 - 267 (25)
<i>Mullus surmuletus</i>	-	86 (9)	-	-	179 ± 47 90 - 316 (51)
<i>Upeneus moluccensis</i>	-	262 (13)	511 ± 285 113 - 1019 (75)	429 ± 268 95 - 945 (50)	455 ± 298 94 - 1122 (56)
<i>Boops boops</i>	-	250 ± 207 68 - 432 (9)	64 ± 35 40 - 89 (3)	±	66 ± 8 60 - 72 (2)
<i>Pagellus erythrinus</i>	-	198 ± 102 84 - 280 (20)	238 ± 166 92 - 805 (71)	172 ± 92 53 - 393 (42)	202 ± 70 102 - 419 (39)
<i>Pagellus acarne</i>	-	-	216 ± 114 112 - 337 (4)	-	-
<i>Dentex macrophthalmus</i>	-	-	-	-	385 ± 100 220 - 480 (6)
<i>Dentex filamentosus</i>	-	-	-	-	140 ± 22 99 - 178 (10)

Table I (continued)

Species	1975	1976	1977	1978	1979
<i>Sphyraena</i> <i>chrysopteraenia</i>	420 (5)	-	303 176 - 397 (3)	114	-
<i>Sphyraena</i> <i>argentea</i>	-	164 (2)	200 -	107 304 157 - 452 (2)	209
<i>Epinephelus</i> <i>albus</i>	-	-	-	99 (1)	-
<i>Chelidonichthys</i> <i>lucerna</i>	-	-	-	86 (4)	-
* <i>Cynoscion</i> <i>nebulosus</i>	-	-	-	-	-
* <i>Pagrus</i> <i>merluccius</i>	-	-	-	-	298 ± 0 (2)
					311 ± 123 127 ± 560 (11)

* Species found in the sampling for the first time

Table II

Heavy metal concentrations (mean values in $\mu\text{g}/\text{kg}$ fresh weight) in
Israel Mediterranean trawl fishes during April and August 1979.
(Number of specimens is shown in parentheses.)

Species	Total length Range (cm)	Total Hg ($\mu\text{g}/\text{kg}$)	Cd ($\mu\text{g}/\text{kg}$)	Pb ($\mu\text{g}/\text{kg}$)	Cu ($\mu\text{g}/\text{kg}$)	Zn ($\mu\text{g}/\text{kg}$)	Mg ($\mu\text{g}/\text{kg}$)
Saurida undosquamis							
April	No specimens						
August	13.2 - 30.6	119 (56)	20 (5)	290 (5)	460 (5)	3750 (5)	260 (5)
Trachurus mediterraneus							
April	22.0 - 23.0	326 (2)	81 (2)	300 (2)	576 (2)	8162 (2)	261 (2)
August	9.6 - 19.8	31 (21)	60 (4)	290 (4)	490 (4)	5140 (4)	140 (4)
Mullus barbatus							
April	13.5 - 18.0	119 (18)	49 (18)	311 (18)	535 (18)	6313 (18)	106 (18)
August	9.4 - 13.2	108 (7)	37 (7)	410 (7)	640 (7)	5040 (7)	167 (7)
Upeneus moluccensis							
April	11.2 - 16.0	405 (6)	50 (6)	357 (6)	833 (6)	5846 (3)	75 (6)
August	9.1 - 19.2	461 (50)	48 (6)	430 (6)	615 (6)	5203 (6)	120 (6)
Pagellus erythrinus							
April	13.0 - 15.8	214 (4)	43 (4)	474 (4)	179 (4)	4550 (4)	170 (4)
August	11.3 - 18.7	201 (35)	35 (4)	525 (4)	259 (4)	4732 (4)	211 (4)

Table III
 Heavy metal concentration (mean values in $\mu\text{g}/\text{kg}$ fresh weight) in Israel Mediterranean trayl fishes
 from October 1975 to March 1978
 (Number of specimens is shown in parenthesis)

Species	Range length (cm)	Total Hg ($\mu\text{g}/\text{kg}$)	Cd ($\mu\text{g}/\text{kg}$)	Pb ($\mu\text{g}/\text{kg}$)	Cu ($\mu\text{g}/\text{kg}$)	Zn ($\mu\text{g}/\text{kg}$)	NI ($\mu\text{g}/\text{kg}$)
<u>Saurida undosquamis</u>	12.3 - 31.3	150 (144)	12 (41)	510 (41)	452 (41)	3910 (41)	276 (41)
<u>Merluccius merluccius</u>	17.5 - 25.0	100 (13)	-	-	-	-	-
<u>Trachinus mediterraneus</u>	13.0 - 26.4	110 (49)	49 (10)	401 (10)	701 (10)	6027 (10)	198 (10)
<u>Upeneus moluccensis</u>	8.9 - 20.6	470 (138)	45 (13)	455 (13)	1150 (13)	6730 (13)	205 (13)
<u>Boops boops</u>	14.8 - 19.8	160 (12)	53 (9)	190 (9)	700 (9)	4820 (9)	49 (9)
<u>Pagellus acorus</u>	13.5 - 16.2	220 (5)	-	-	-	-	-
<u>Pagellus erythrinus</u>	9.7 - 20.7	200 (126)	22 (25)	393 (25)	835 (25)	5820 (25)	209 (25)
<u>Sphyraena chrysotaenia</u>	20.6 - 26.7	330 (8)	-	-	-	-	-
<u>Sphyraena sphyraena</u>	21.9 - 31.0	190 (19)	35 (2)	260 (2)	1010 (2)	6350 (2)	75 (2)
<u>Chelidonichthys lucernus</u>	17.0 - 18.5	90 (4)	-	-	-	-	-

Research Centre: Environmental Protection Division, CNEN
LA SPEZIA
Italy

Principal investigator: M. BERNHARD

Period of reporting: 1975 to 1979

INTRODUCTION

The work was carried out in collaboration with the Institute for Applied Physical Chemistry and the Marine Station Fiascherino of the Nuclear Research Center (KFA), Juelich (FRG). Sampling and sample preparation were undertaken jointly. The chemical analyses were conducted by KFA. Prior to the participation in MED POL II both institutions had been active in radioecological studies concerning heavy metals as carriers of radioisotopes, and were familiar with the problems concerning sampling, sample preparation and analysis. Samples of tunas were collected in collaboration with Prof. Renzoni, University of Siena, who also analysed some of the tuna samples.

After the UNEP/FAO (GFOM) expert consultation (Rome 1975) had identified mercury and cadmium as the most important metal pollutants for monitoring, the centre concentrated its work on these elements. The analysis of cadmium revealed, however, that the levels found in marine organisms from the Mediterranean were much lower than anticipated. All levels were near the detection limit of about 20 µg Cd/kg FW. These low levels excluded the possibility that even heavy consumers of fish would reach the tolerable intakes set for cadmium.

Therefore our attention focused entirely on the Hg levels. The concentration on the Hg levels was furthermore justified because, besides an apparent health problem, the high Hg levels also presented an acute legal problem.

Practically all tuna and swordfish caught in the Mediterranean are above, and often very much higher, than the legal limits.

The problem is not, however, restricted to tuna and swordfish; other marine organisms also have Hg levels that are higher than the legal limits. Therefore, the centre investigated the Hg levels in marine shellfish and fish offered on the Italian market in order to obtain an idea as to which species have levels higher than the legal limits.

Earlier publications had indicated that Hg levels in Mediterranean fish were higher than those from the Atlantic.

In the course of the investigation the specimens from the Italian coastal waters were compared with specimens of the same species for the Atlantic (Strait of Gibraltar).

METHODOLOGICAL CONSIDERATIONS

Selection of species:

Two criteria guided the selection: Pelagic species such as anchovy, mackerel, sardine, tuna, etc., being remote from local pollution sources, would give an

indication of the Hg levels over wider areas; tuna probably of a large part of the Mediterranean. On the other hand coastal and benthic species would give an indication of local contamination.

The pelagic species studied are listed in Table I and the benthic and coastal species in Table II. For comparison also some data from the North Sea were included.

Pollutants analysed:

After finding only very low levels the cadmium analyses were discontinued and only mercury was determined.

Areas studied:

This investigation concerns trawling areas around La Spezia, and during 1976 near the Isola della Maddalena (N. Sardinia) as shown in Figs. 1 and 2 and in the Venice-Chioggia area.

Mussels were collected at stations A and C and Ulva in station B (Fig. 1). In addition samples were taken at several other locations at various times.

METHODOLOGY

The procedures of sampling and sample treatment as described in FAO Fisheries Technical Paper No. 158 were followed where applicable.

Materials not described were treated as follows: Ulva was collected from rocks, washed briefly with distilled water and stored in plastic bags at -18°C. Sepia, Octopus, Loligo and Eledone were stored after sampling in plastic bags at -18°C. Sample preparation consisted in removing the skin under similar conditions as described in FAO Fisheries Technical Paper No. 158. (Bernhard 1976)

Shrimps were prepared as outlined in paragraph 5.2.4 of Bernhard (1976) but with the precautions and instruments as stated in 5.1.4. Hg determinations were made with an automated Perkin-Elmer AAS using the cold vapour technique as described by Stoeppler, et al. (1976).

Intercalibration:

The centre participated in the IAEA intercalibration of all four samples; oyster (MA-M-1), sea plant (SP-M-1), copepod (MA-A-1) and fish (MA-A-2) and in an intercalibration exercise between the USA, Canada, and Federal Republic of Germany. In addition NBS standards "bovine liver" and "orchards leaves" were analysed. Also an interlaboratory comparison with Prof. Renzoni at the University of Siena was carried out.

RESULTS

Samples were collected regularly in the two areas, La Spezia and Venice, for two years starting in spring 1976, but due to an overload of the analytical capacity in KFA not all samples could be analysed. In addition samples were collected near Maddalena in 1976 and during sampling trips to the Strait of Gibraltar. For comparison, a few results from the North Sea are also reported.

Mercury in Mytilus galloprovincialis:

The analysis of mercury concentration in single specimens showed an interspecimen variance of 42 to 62%. This means that differences between samples have to be greater than about 60% to be significant at a 66% level. Thus, no significant differences could be detected between the samples collected (Table II).

Table II shows also that the mussels from the Mediterranean have similar levels to mussels collected in non-Mediterranean locations.

Mercury in Mullus barbatus:

The coefficient of variation for pre-treatment and analysis of Mullus barbatus is about 10%. Since mercury concentrations are expected to increase with the size of the specimens a comparison of means is allowed only if specimens of exactly the same size are compared. Otherwise, the correlations of size versus Hg concentrations have to be compared. Fig. 3 shows that the wide spread of the individual Hg values does not allow a distinction to be made between different locations. Table II gives mean and range of the different samples.

Mercury in Thunus thynnus and Xiphias gladius:

Tunas were collected from various parts of the Western Mediterranean (Sicily, Sardinia, La Spezia, Palermo, and the Strait of Gibraltar).

The weight of these specimens ranges from very small tunas, only a few months old (0.23 kg), to large specimens older than 15 years (450 kg). Plotting the Hg concentrations against the size revealed that data are divided into two distinct populations (Fig. 4). In one population the Hg concentration is strongly correlated with body weight. Tunas heavier than about 100 kg form a second population with Hg concentrations 1/4 to 1/3 that of tunas of equal weight from the first population. This second population has only a weak Hg-concentration versus size relationship. The highest value was about 4000 ug Hg/kg FW. Tunas caught in the Strait of Gibraltar migrating in and out of the Mediterranean all belong to the second 'low Hg' population. Two specimens of Xiphias gladius were analysed. One had a level of about 1800 ug Hg/kg FW (Table I).

Mercury in other marine organisms:

Mercury in pelagic fish: Anchovy, mackerel and sardines were collected near La Spezia, Maddalena and in the Strait of Gibraltar. Plots of the Hg-concentrations versus size showed that, for example, sardines from the Italian coast had significantly higher Hg levels than specimens from the Strait of Gibraltar (Fig. 5). Table I shows that pelagic fish other than tuna and swordfish, e.g. Trachurus trachurus, can reach considerable Hg levels.

Mercury in benthic and coastal organisms. Specimens of 24 species other than Mytilus galloprovincialis have been analysed. Their Hg concentrations, together with some measurements carried out by the KFA group in the North Sea are shown in Table II.

The highest Hg levels were observed in Sepia officinalis, but also other species had considerable levels. Level-size regressions are different in the various locations (Figs. 6 and 7).

DISCUSSION OF RESULTS

The range of Hg levels in mussels does not significantly differ from the levels reported by other authors for the Mediterranean and Atlantic coast of Europe (for recent reviews Bernhard 1978, Bernhard and Renzoni 1980). The significance of the data for Mullus barbatus is not yet clear. As Renzoni (pers. com.) has shown, the correlation between Hg levels and size depends on still unknown factors, therefore only further research will tell us how to interpret the data obtained.

The Hg levels in tunas and in other pelagic fish allow the following interpretation. The Mediterranean is known to be a geochemical anomaly for mercury. It might serve as an indication to bear in mind that 65% of the known world reserves of exploitable mercury are located in the Mediterranean which occupies only 1% of the earth surface.

Apparently these high environmental Hg levels are reflected in the tuna and other pelagic fish. The migration of tuna can explain the two different populations. The low level population migrates into the Mediterranean only for spawning while it is feeding on low level pelagic fish in the Atlantic. The high level population stays in the Mediterranean feeding on high level pelagic fish.

In fact the levels of other pelagic fish such as anchovy, sardines and mackerel are also significantly higher around Italy which has several Hg inputs (Monte Amiata and volcanos).

The high levels in tunas which migrate over long distances cannot be due to anthropogenic contamination which, although marked in some local areas, does not raise the Hg level at a distance of more than about 10 km. Similarly the high Hg levels encountered in swordfish and in other pelagic fish (anchovy, mackerel and sardines) are of natural origin. The levels in Mediterranean tunas are the highest reported for tunas but not the highest found in teleost fish.

The marlins of Hawaii and Australia can reach up to 15000 µg Hg/kg FW. The Hg levels in benthic and coastal marine organisms are more difficult to interpret. Certainly also their levels are due, in the majority of cases, to natural sources and not to anthropogenic input. This has been shown by Renzoni and Baldi (1973) who found high levels in fish caught far away from possible anthropogenic sources.

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TABLE I
MERCURY CONCENTRATION AND BIOLOGICAL DATA IN PELAGIC MARINE ORGANISMS FROM THE MEDITERRANEAN AND ATLANTIC

Species	No. of specimens	Hg-T concentration (µg/kg fresh weight)		Fork length (cm)		Body weight (g)		Sampling area and date		Ocean
		\bar{x}	range	\bar{x}	range	\bar{x}	range	\bar{x}	range	
<i>Belonis belone</i>	2	210	165—270	52.0	48.5—55.5	173.7	158.0—	190.0	Maddalena 0.6.76	Med.
<i>Loligo vulgaris</i>	10	320	85—530	85—	130	96.7	17.2—	24.4	Tarigier 07.76	All.
<i>Sardina pilchardus</i>	10	100	85—	110—	330	14.8	14.0—16.5	74.4	Ostend 10.76	North Sea
	26	220	160—	160—	475	16.3	15.5—17.0	35.4	124.1	
	9	300	5—	30	50	13.2	12.0—14.9	47.1	50.4	La Spezia 06.76
	28	105	70—	70—	140	11.1	10.5—13.0	27.3	57.0	Maddalena 06.76
	20	380	210—	210—	590	16.4	16.0—17.5	16.1	37.2	Ned.
<i>Engraulis encrasicolus</i>	16	70	50—	50—	95	13.4	12.3—14.3	39.5	21.0	La Spezia 09.76
	10	75	45—	45—	95	19.5	17.3—24.2	17.6	34.3—	Ned.
<i>Scomber japonicus</i>	9	340	130—	130—	510	19.9	14.5—21.5	71.1	4.2—	Med.
<i>Scomber scombrus</i>	15	80	45—	45—	125	29.0	26.5—31.5	87.0	20.4	Med.
	10	330	160—	160—	550	31.1	28.0—33.5	265.6	47.2	All.
	5	420	180—	180—	550	36.5	35.0—39.0	312.3	37.2	All.
<i>Trachurus trachurus</i>	5	1255	645—	645—	2210	25.2	24.5—25.5	588.3	133.3	North Sea
	3	725	315—	315—	1400	29.3	28.5—31.0	225.0	1060	Helpoland 09.76
<i>Sarda sarda</i>	10	460	180—	180—	815	46.9	44.0—52.0	333.3	1060	North Sea
<i>Xiphias gladius</i>	2	1260	620—	620—	1790	—	—	1355.0	1980	All.
								67500	56000	Ned.
								—	—	Trapani 06.76

TABLE II
MERCURY CONCENTRATION AND BIOLOGICAL DATA IN BENTHIC MARINE ORGANISMS FROM THE MEDITERRANEAN AND ATLANTIC

Species	No. of specimens	Hg-T concentration ($\mu\text{g}/\text{kg}$ fresh weight)		Length ^a (cm)		Body weight (g)		Sampling area and date	Ocean
		\bar{x}	range	\bar{x}	range	\bar{x}	range		
<i>Portunus</i> spec.	15	40	20–65	3.0	2.5–3.5	7.0	2.9–9.7	Carrara 04.76	Med.
<i>Penaeus kerathurus</i>	10	100	20–185	12.9	11.0–14.0	16.7	10.8–22.9	Carrara 04.76	Med.
<i>Squilla mantis</i>	20	150	65–460	12.7	11.0–15.5	27.3	18.6–49.2	Chioggia 09.76	Med.
<i>Mytilus galloprovincialis</i>	30	25	Composite sample	4.8	4.3–5.0	4.2	2.3–5.3	Tino Isle 10.75	Med.
	14	40	15–70	6.0	4.0–8.0			Palmaria Isle 06.76	Med.
	25	65	40–95	5.2	4.8–5.7			La Spezia 04.76	Med.
	10	160	120–215	6.2	5.5–7.5	20.2	14.48–27.83	Maddalena 02.76	Med.
<i>Mytilus edulis</i>	20	110	50–210	6.9	6.0–7.5	26.6	18.96–32.43	off German Coast 10.76	North Sea
	14	85	45–145	5.1	4.0–6.2	11.7	6.69–19.45	off Dutch Coast 10.76	North Sea
	42	50	25–90	4.2	3.7–4.7	12.7	9.78–16.87	Zeeland 10.76	North Sea
	20	90	60–135			287.1	253.6–314.4	Ostend 10.76	North Sea
<i>Eledone</i> spec.	3	400	340–490					La Spezia 06.76	Med.
<i>Octopus vulgaris</i>	5	288	80–710					Maddalena 06.76	Med.
	2	125	65–165			1046.0	402.8–1691.0	Maddalena 06.76	Med.
	6	115	50–255			3860.0	175.5–719.9	Ceuta 07.76	All.
	4	115	40–175			312.0	261.0–346.5	Carrara 09.76	Med.
<i>Sepia officinalis</i>	4	340	110–620			221.0	139.0–285.2	La Spezia 06.76	Med.
	8	610	180–1090					Maddalena 06.76	Med.
	8	200	135–285			121.6	54.0–160.1	Maddalena 06.76	Med.
	34	155	60–275	6.5	3.8–10.0	42.3	10.7–135.3	Chioggia 09.76	Med.
	15	125	60–290	12.3	10.5–14.0	256.7	157.4–353.2	Ceuta 07.76	All.
	13	80	45–115	16.8	14.5–21.5	557.2	331.9–1000	Scheveningen 10.76	North Sea
<i>Reja asterias</i>	3	335	175–540					Maddalena 76	Med.
<i>Atherina</i> spec.	ca. 30	110	55–210	\sim 5 composite sample		~2.5		Maddalena 02.76	Med.

TABLE II (continued)

<i>Boops boops</i>	10	11.0	70—265	16.0	15.2—16.7	59.2	48.8	72.1	Tangier 07.76
<i>Grenabrus lineatus</i>	10	12.0	65—270	18.3	14.6—23.2	99.2	49.3	203.0	Ceuta 07.76
<i>Diplodus annularis</i>	20	42.0	170—680	13.1	11.0—21.5	41.6	27.7	103.5	Maddalena 02.76
<i>Muraena maena</i>	10	21.0	80—310	18.0	16.0—20.0	100.8	76.7	129.4	Maddalena 06.76
<i>Aterlucius merluccius</i>	18	23.5	120—425	12.4	11.5—13.5	55.4	36.7	80.1	Maddalena 06.76
<i>Mullus barbatus</i>	4	17.0	120—240	17.1	16.2—18.0	90.4	74.0	102.2	Maddalena 02.76
<i>Muraena merluccius</i>	13	13.0	75—395	21.3	18.0—34.0	103.0	63.2	347.0	Maddalena 06.76
<i>Mullus barbatus</i>	.0	21.0	40—765	13.1	10.8—16.0	43.1	23.8	75.2	La Spezia 03.76
<i>Muraena merluccius</i>	10	10.0	45—220	14.5	13.0—16.5	49.3	31.9	76.0	La Spezia 05.76
<i>Muraena merluccius</i>	5	21.0	115—330	11.9	10.5—13.5	24.4	17.3	32.8	La Spezia 06.76
<i>Mullus barbatus</i>	10	7.0	45—125	12.7	11.5—14.0	35.5	27.4	47.3	Carrara 10.75
<i>Mullus surmuletus</i>	21	8.0	20—190	9.8	8.5—12.5	18.4	9.9	35.2	Carrara 04.76
<i>Mullus surmuletus</i>	5	20.5	165—245	14.0	13.2—14.5	58.3	46.8	64.0	Maddalena 02.76
<i>Obtala melanura</i>	10	24.5	80—405	15.7	13.5—20.5	78.3	45.5	139.5	Maddalena 06.76
<i>Pogonias cromis</i>	10	24.0	90—560	13.4	10.5—17.0	48.8	18.7	92.4	Tunis 05.76
<i>Pogonias cromis</i>	10	28.0	50—615	16.0	12.5—21.5	77.3	36.7	168.5	Tangier 07.76
<i>Scorpaena scorpaena</i>	8	15.0	60—320	~12	~12	~12	~12	~12	Maddalena 07.75
<i>Scorpaena scorpaena</i>	6	9.0	70—110	14.8	14.0—15.5	51.0	42.2	62.2	Trapani 06.76
<i>Scorpaena scorpaena</i>	4	28.0	190—390	18.4	16.5—21.5	117.5	75.2	212.52	Ceuta 07.76
<i>Obtala melanura</i>	6	48.0	365—640	20.0	18.5—21.0	173.4	117.5	219.2	Maddalena 06.76
<i>Pogonias cromis</i>	8	14.5	60—230	17.7	16.0—19.0	142.0	124.4	173.6	Maddalena 06.76
<i>Pogonias cromis</i>	15	20.5	50—500	14.6	13.5—15.5	72.7	56.0	92.0	Maddalena 06.76
<i>Phycis blennoides</i>	4	12.5	70—150	25.8	23.5—29.0	205.2	142.0	315.3	Maddalena 06.76
<i>Scorpaena scorpaena</i>	12	24.0	130—325	13.8	12.5—15.0	77.5	59.6	99.7	Maddalena 06.76
<i>Scorpaena porcus</i>	1	3.0	—	13.0	—	58.0	—	—	Maddalena 06.76
<i>Serranus scriba</i>	15	70.5	500—1040	13.7	11.5—15.0	61.2	46.6	81.7	Maddalena 06.76
<i>Solea vulgaris</i>	30	45	15—115	16.3	10.8—21.0	60.2	16.3	127.1	Cagliari 07.76
<i>Trachinus draco</i>	11	11.0	65—285	18.4	16.0—20.5	110.0	73.0	154.6	Ostend 10.76
<i>Uranoscopus scaber</i>	7	53.0	115—810	25.0	23.0—27.0	125.5	81.0	163.6	Maddalena 06.76
<i>Uranoscopus scaber</i>	2	20.0	115—270	17.5	17.5—18.0	135.3	31.7	139.0	Maddalena 02.76
<i>Uranoscopus scaber</i>	4	27.5	140—500	22.7	21.0—24.0	221.0	157.1	276.8	Maddalena 06.76

*Crustacean length: rostrum to uropod; *Mytilus* spec. and sepias: shell length; fishes: fork length.

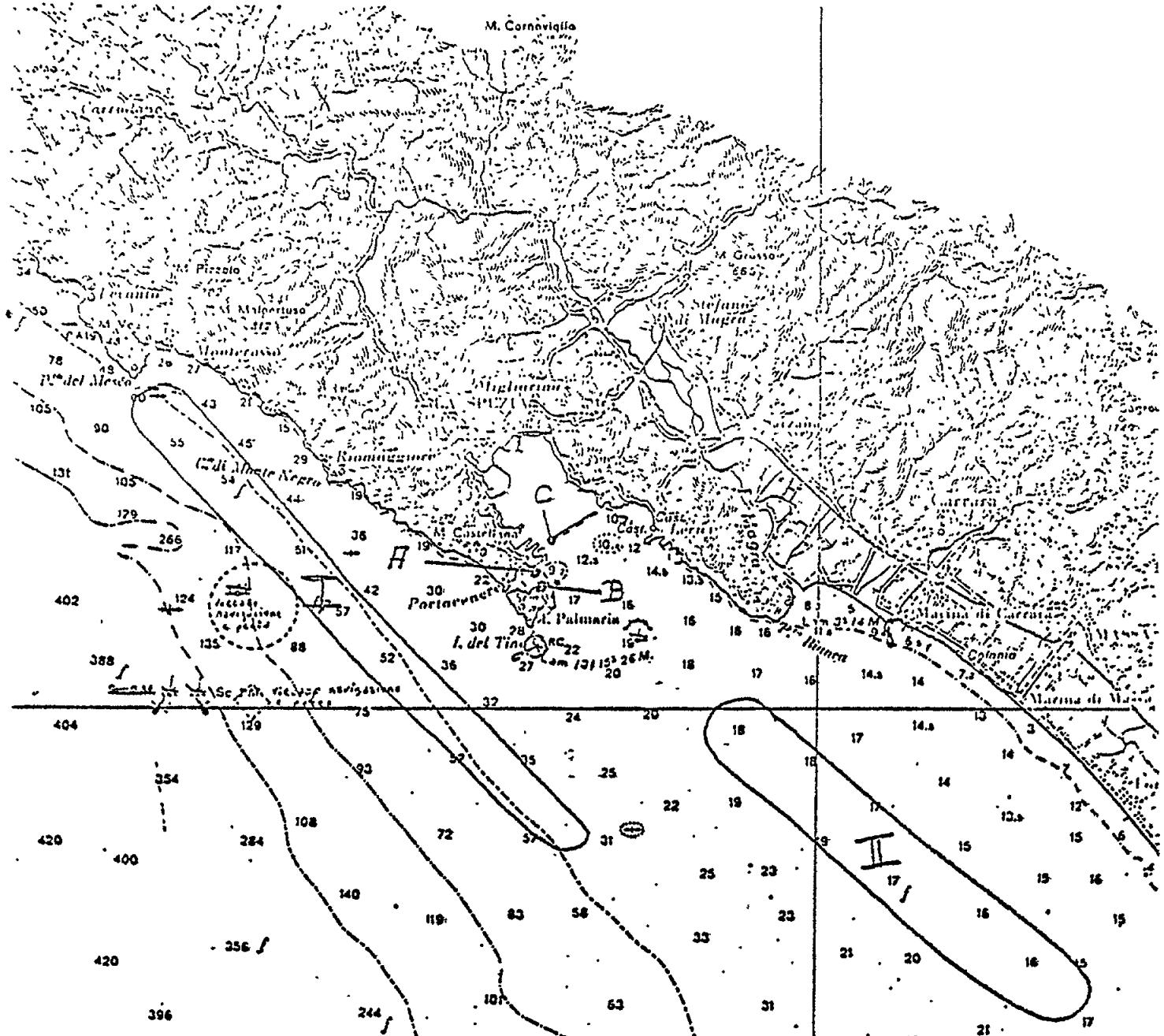


Fig. 1 Trawling areas and sampling stations near La Spezia

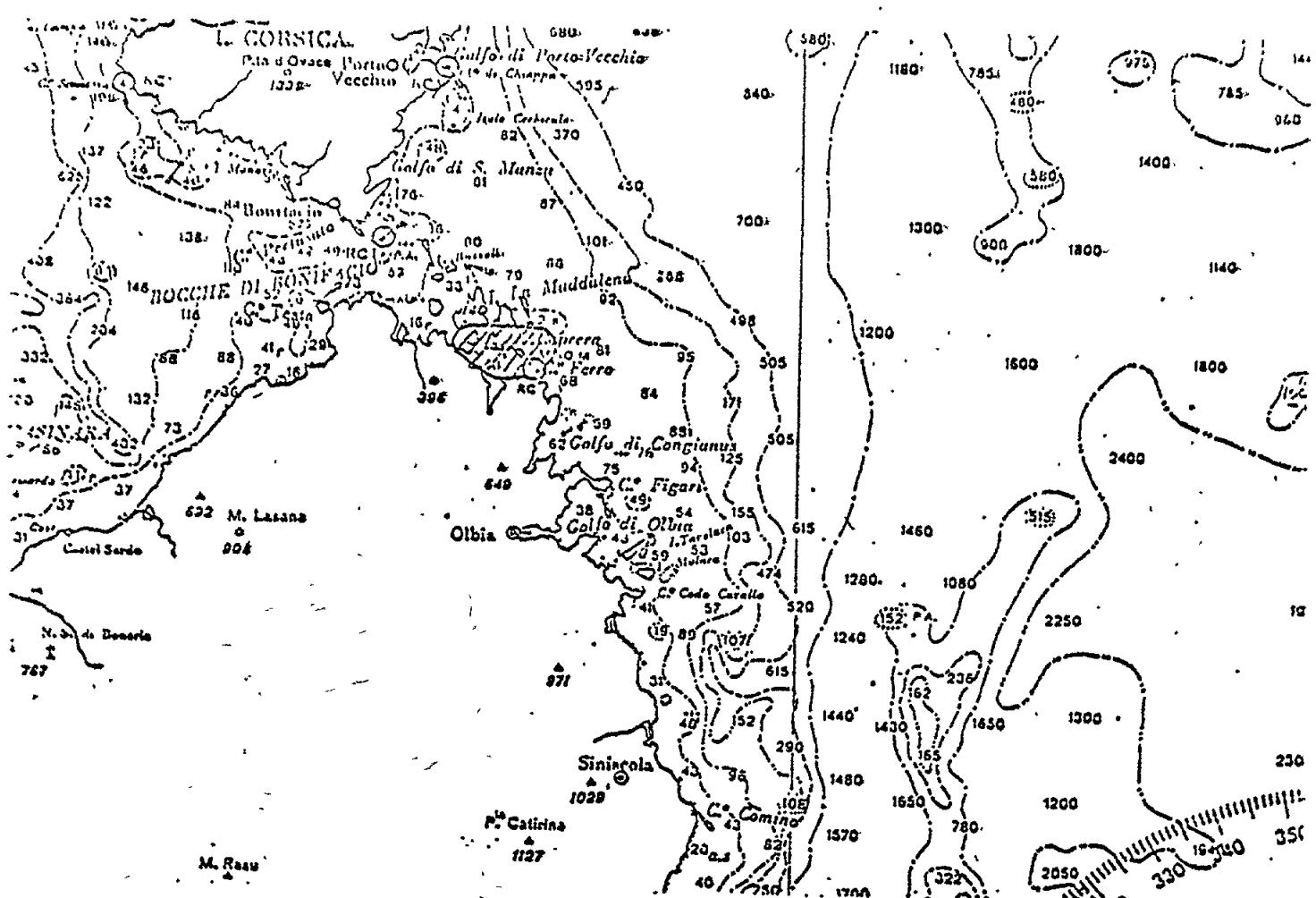


Fig. 2. Trawling and sampling area of Maddalena

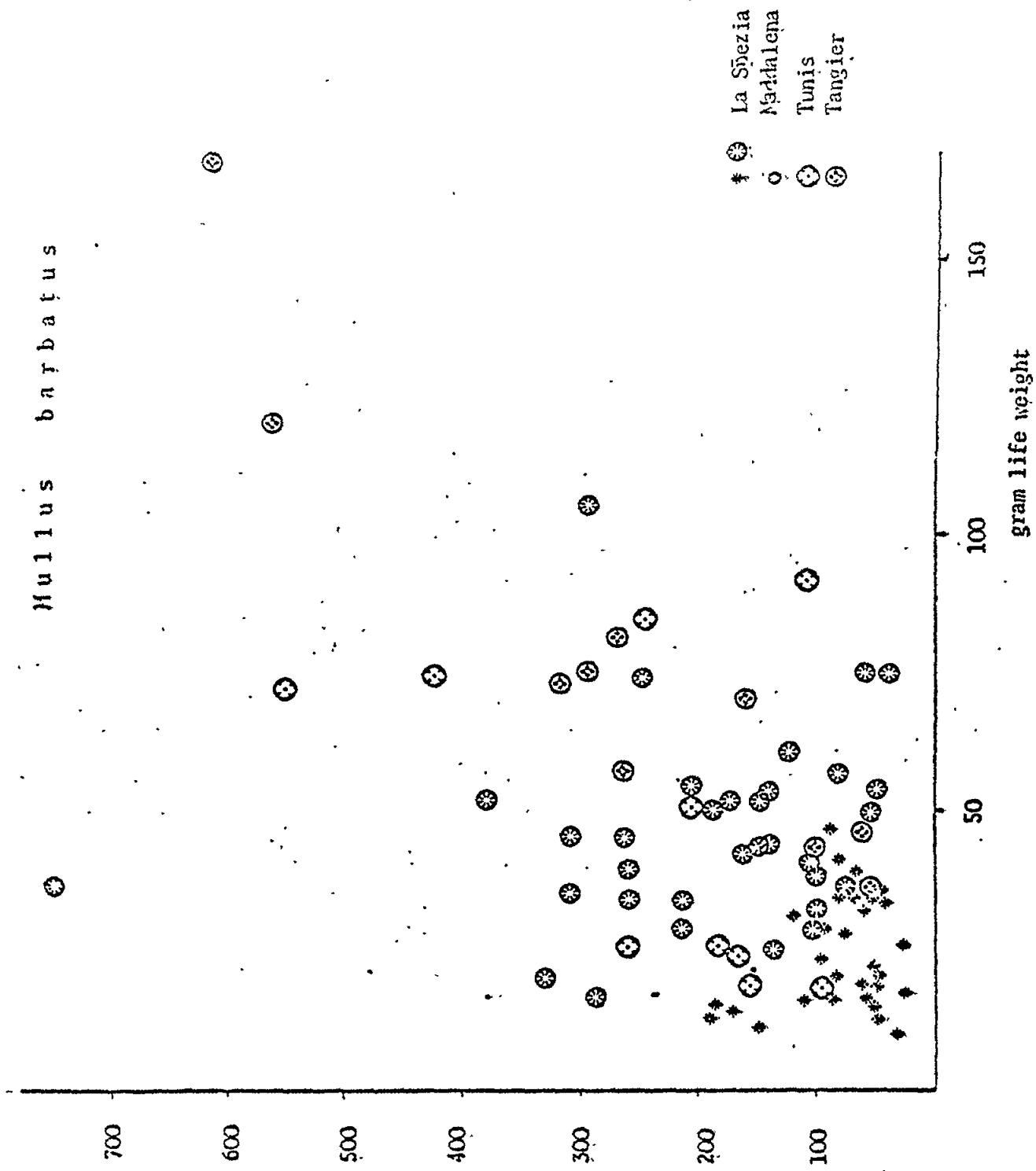


Fig. 3 Hg concentration versus size in *M. barbatus* from La Spezia, Maddalena, Tunis and Tangier

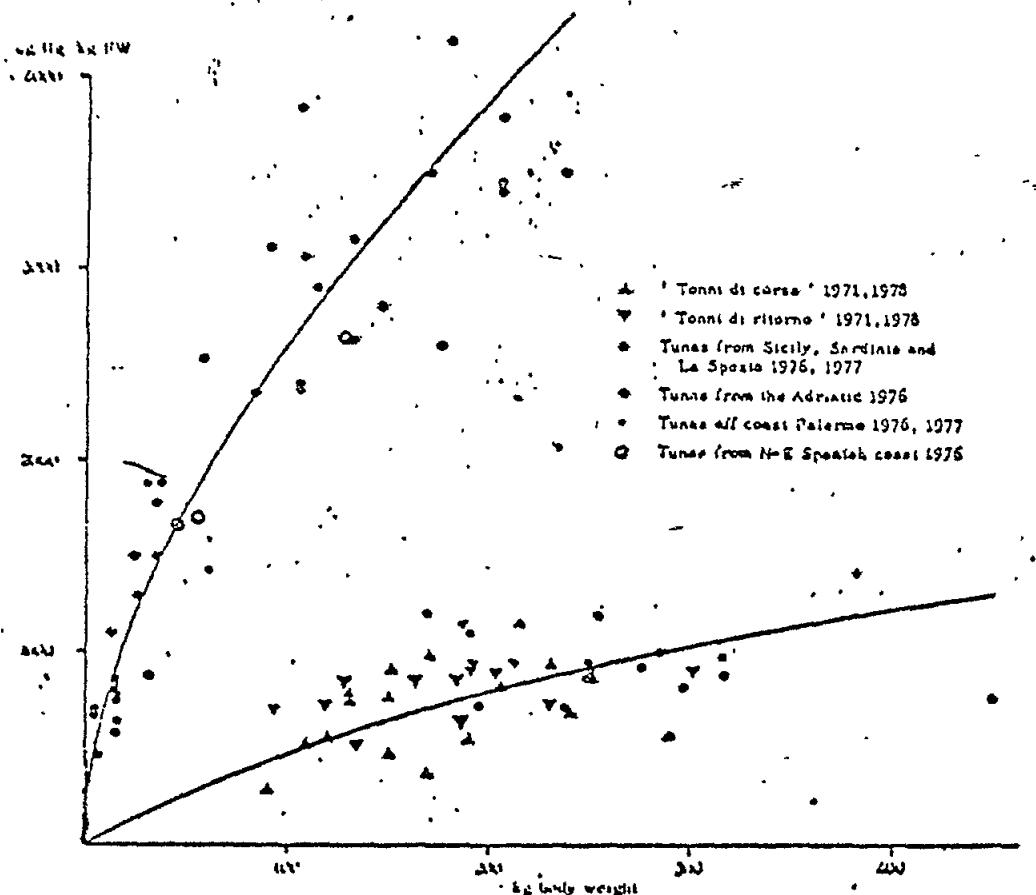


Fig. 4 Mercury concentration versus weight in *Thunnus thynnus* from various locations in the Mediterranean.

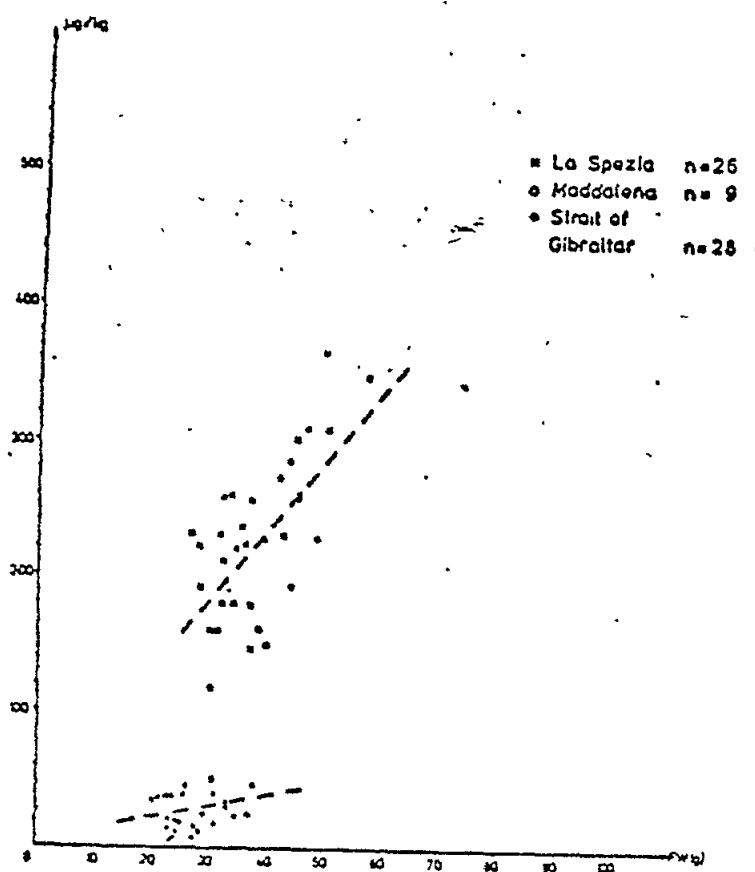


Fig. 5 Hg-T/weight correlation for *Sardina pilchardus*. La Spezia and Maddalena: $y = 5.46x + 27.48; r = 0.60$. Strait of Gibraltar: $y = 0.74x + 7.59; r = 0.28$.

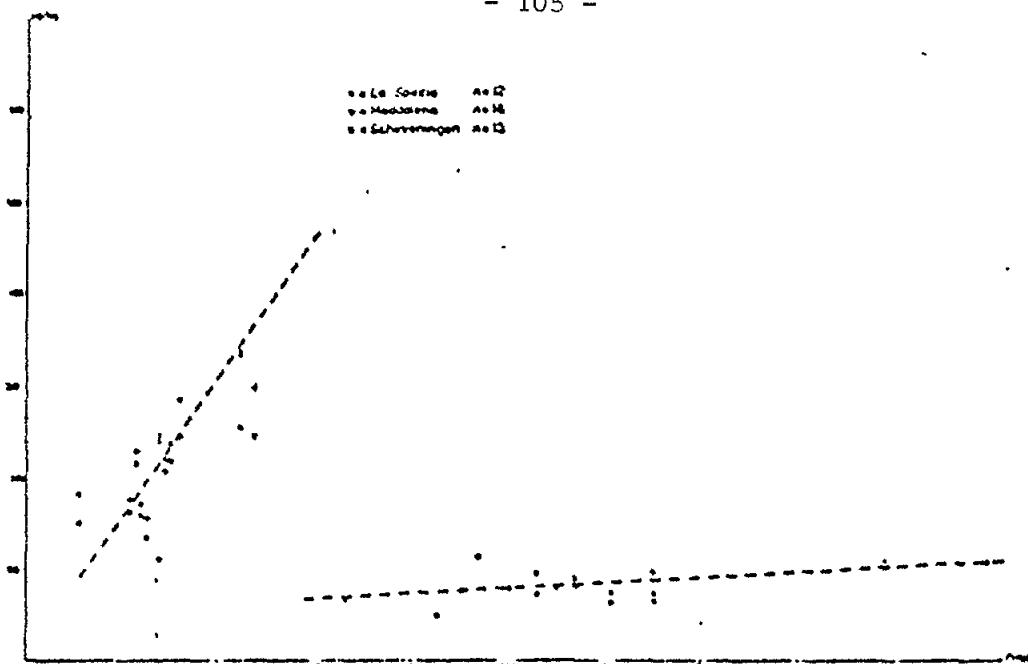


Fig. 6 Hg-T/weight correlations for *Sepia officinalis*, I. La Spezia and Maddalena: $y = 1.505x + 7.383; r = 0.805$; Scheveningen: $y = 0.053x + 51.03; r = 0.498$.

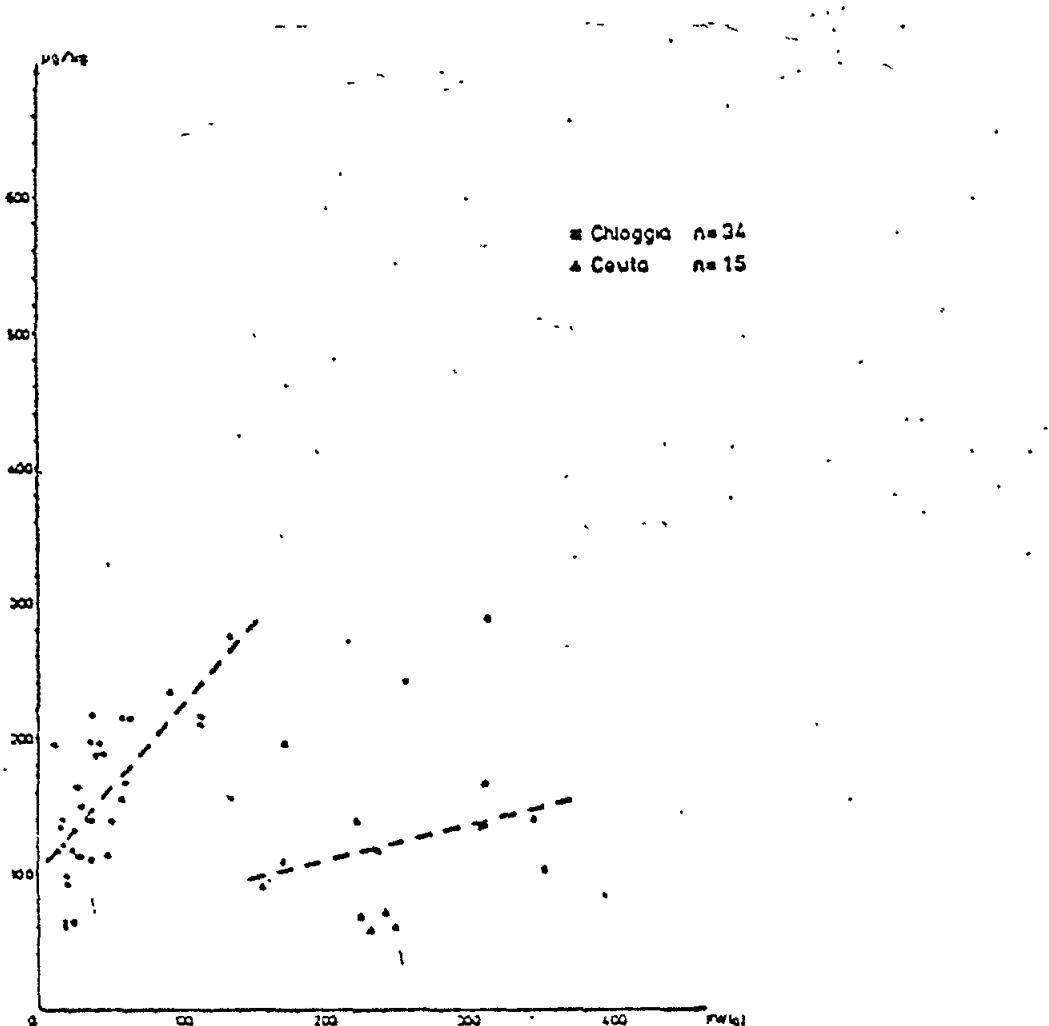


Fig. 7 Hg-T/weight correlations for *Sepia officinalis*, II. Chioggia: $y = 1.22x + 101.69; r = 0.71$. Ceuta: $y = 0.263x + 57.56; r = 0.278$.

Centre de Recherche:

Gruppo di Ricerca Oceanologica (G.R.O.G)
Università di Genova
GENOVA
Italie

Chercheur principal:

R. CAPELLI

Période couverte par le rapport: Décembre 1976 à décembre 1980

INTRODUCTION

Le Centre de Recherche Océanologique - Genova (G.R.O.G.) a été créé à Genova dans le but de rassembler en une seule unité des disciplines diverses telles que Chimie, Physiologie, Hydrobiologie, Pisciculture et Sédimentologie, de façon à disposer de tous les composants nécessaires pour affronter le problème complexe de la recherche marine.

L'activité du G.R.O.G. a commencé par la campagne océanographique de novembre 1974 (N.O. BANNOCK), après laquelle l'Institut de Chimie Générale a commencé son activité en entreprenant l'étude de la présence des métaux en traces dans les organismes marins. En 1976 le Groupe de recherche a adhéré au projet MED POL II et en même temps il a entrepris son activité dans le domaine des projets du C.N.R. (Océanographie et fonds marins). Comme suite à cette participation, notre attention s'est tournée vers les espèces qui avaient été choisies dans les deux programmes.

CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces:

Les espèces prises en considération ont été les suivantes : Mullus barbatus, Engraulis encrasiculus, Nephrops norvegicus, Mytilus galloprovincialis et Sarda sarda.

Polluants analysés:

Les métaux déterminés ont été : Hg (total), Hg (méthyl-mercure), Cd, Pb, Cu, Mn et Zn.

Zone étudiée:

La zone dans laquelle le Groupe a effectué ses recherches est celle du nord de la Mer Ligurienne et particulièrement celle qui va de la Punta del Mesco (est de Gênes) à Savona (ouest de Gênes). Dans la Fig. 1 sont représentées les localités où l'échantillonnage a été fait. Les moules ont été recueillies sur le promontoire de Portofino (zone très éloignée des centres industriels et urbains) et sur l'île des pétroliers qui est située au large de Gênes-Pegli, à deux milles environ de la côte (zone très près du port de Gênes et de la zone industrielle). Les localités où les moules ont été récoltées sont indiquées sur la Fig. 1 avec la lettre C. Les anchois ont été pêchés avec des filets près de la côte; les rougets et les langoustines ont été pris à la traîne et avec chalut respectivement au delà de l'isobathe des 50 et 500 mètres et dans deux zones qui vont de Camogli à punta del Mesco et de Gênes à Savona (Fig. 1, B et A).

METHODOLOGIE

La conservation des échantillons a été effectuée par congélation à -25°C. La préparation des échantillons a été effectuée conformément aux instructions dans FAO, Document technique sur les pêches, N°. 158 (1977).

La méthodologie analytique :

Environ 25 grammes de substance sont traités avec 50ml de HNO₃ 90%. On laisse réagir à froid (2-3 heures) et après on chauffe jusqu'à la solubilisation complète de la matière organique. Après refroidissement on ajoute 10 ml d'eau distillée et l'on chauffe jusqu'à ce que les vapeurs rouges disparaissent.

Toutes ces opérations sont effectuées sous reflux. La détermination de teneur en métaux a été effectuée sur la solution filtrée et portée à 100 ml (avec de l'eau distillée) à l'aide d'un spectrophotomètre d'absorption atomique, en employant une flamme air-acétylène. La détermination de la teneur en Hg total a été effectuée au moyen de la spectrophotométrie sans flamme. Afin de réduire les possibilités d'erreur, on a estimé opportun d'utiliser la méthode des additions. En outre, pour éliminer les erreurs dues à l'absorption moléculaire, on a employé une lampe au deutérium. Afin de contrôler nos méthodes analytiques, des échantillons d'"orchard leaves" du NBS ont été minéralisés et analysés suivant le même procédé. Cette opération de contrôle a été répétée périodiquement au cours de l'année.

En ce qui concerne le méthyl-mercure la méthodologie que nous avons employée est la même que nous avons mise au point, (Capelli, et al., 1979).

Programme d'intercalibration :

Le centre de recherche a effectué les intercalibrations prévues.

RESULTATS

Les résultats obtenus sont résumés par les Tableaux I, II, III, IV, V. Dans le cas des moules, les valeurs ont été reportées comme minimum, maximum, moyenne et déviation standard pour chacune des zones et pour chaque année.

Pour les autres organismes marins, on a considéré les valeurs concernant une zone à l'est et à l'ouest de Gênes de façon à mettre en évidence les variations; de plus, on reporte la moyenne de toutes les valeurs (Golfe de Gênes) et la déviation standard correspondante, afin de pouvoir comparer les résultats obtenus pour des années différentes. On ne fera que certaines considérations sur les valeurs obtenues jusqu'à présent. Enfin la table n°. V qui a été présentée aux ves Journées d'Etudes sur les pollutions marines en Méditerranée (Cagliari, 9-13 octobre 1980), reporte les diagrammes relatifs à la distribution de fréquences pour la concentration des métaux dans les organismes examinés. Cette table résume et montre les données que nous avons jusqu'au mois de Mars 1980.

DISCUSSION DES RESULTATS

En examinant les résultats on peut mettre en évidence certaines indications de caractère général :

Pour tous les organismes examinés il y a une accumulation de mercure (total) correspondant à l'augmentation de la taille (longueur ou poids). L'augmentation est particulièrement évidente chez la pélamide (Sarda sarda) et chez la langoustine (Nephrops norvegicus). En outre, dans les langoustines il semble qu'il y ait un minimum pour le mercure pendant l'été. Pour aucun des autres métaux étudiés il n'a été constaté de mécanisme d'accumulation. La teneur en mercure chez les langoustines (pêchées à 13-15 milles de la côte et à la profondeur de 400-600 mètres) est probablement plutôt d'origine naturelle qu'humaine. Afin d'avoir une évaluation de l'apport naturel en comparaison de l'apport humain, dans la campagne océanographique de septembre 1980, nous avons effectué un carottage des sédiments dans les zones où les langoustines ont été pêchées (les données sont encore en élaboration).

En 1979 également les moules récoltées près de l'Ile des pétroliers (à deux milles au large de Gênes-Pegli) accusent des valeurs semblables à celles du Promontoire de Portofino.

Comme les moules échantillonnées près de la côte ont des valeurs bien plus élevées, ces résultats sembleraient prouver que deux à trois milles sont déjà suffisants pour faire diminuer notablement l'influence de la pollution. Une telle justification devrait être complétée par des analyses sur la matière en suspension et par des mesures éventuelles de courants.

Pour ce qui concerne les anchois, la diminution de la teneur en mercure total, remarquée pour l'année 1978, n'a été constatée ni pour l'année 1979 ni pour l'année 1980. Il serait opportun de voir si une telle diminution a été aussi remarquée pour les autres unités opératives qui agissent en Mer Tyrrhénienne ou s'il ne s'est agi que d'une situation locale.

La teneur en Cd et Pb trouvée dans les poissons est inférieure à la limite que permet de révéler la méthode analytique que nous employons.

Les premiers résultats sur le méthyl-mercure montrent pour la Sarda sarda un pourcentage qui varie de 60 à 95% du mercure total dans le filet, alors que dans le foie, le pourcentage de mercure sous la forme de méthyl-mercure semble descendre à 40-50%. Chez le Nephrops le méthyl-mercure est présent suivant des pourcentages qui varient de 69 à 85%. Ces chiffres ne sont donnés qu'à titre indicatif car ils présentent des valeurs obtenues à l'aide d'analyses en nombre encore limité. L'intention est de poursuivre en 1980 la détermination du méthyl-mercure et de la mettre en rapport avec le sélénium dès que la méthode pour la détermination du Se sera parfaitement déterminée.

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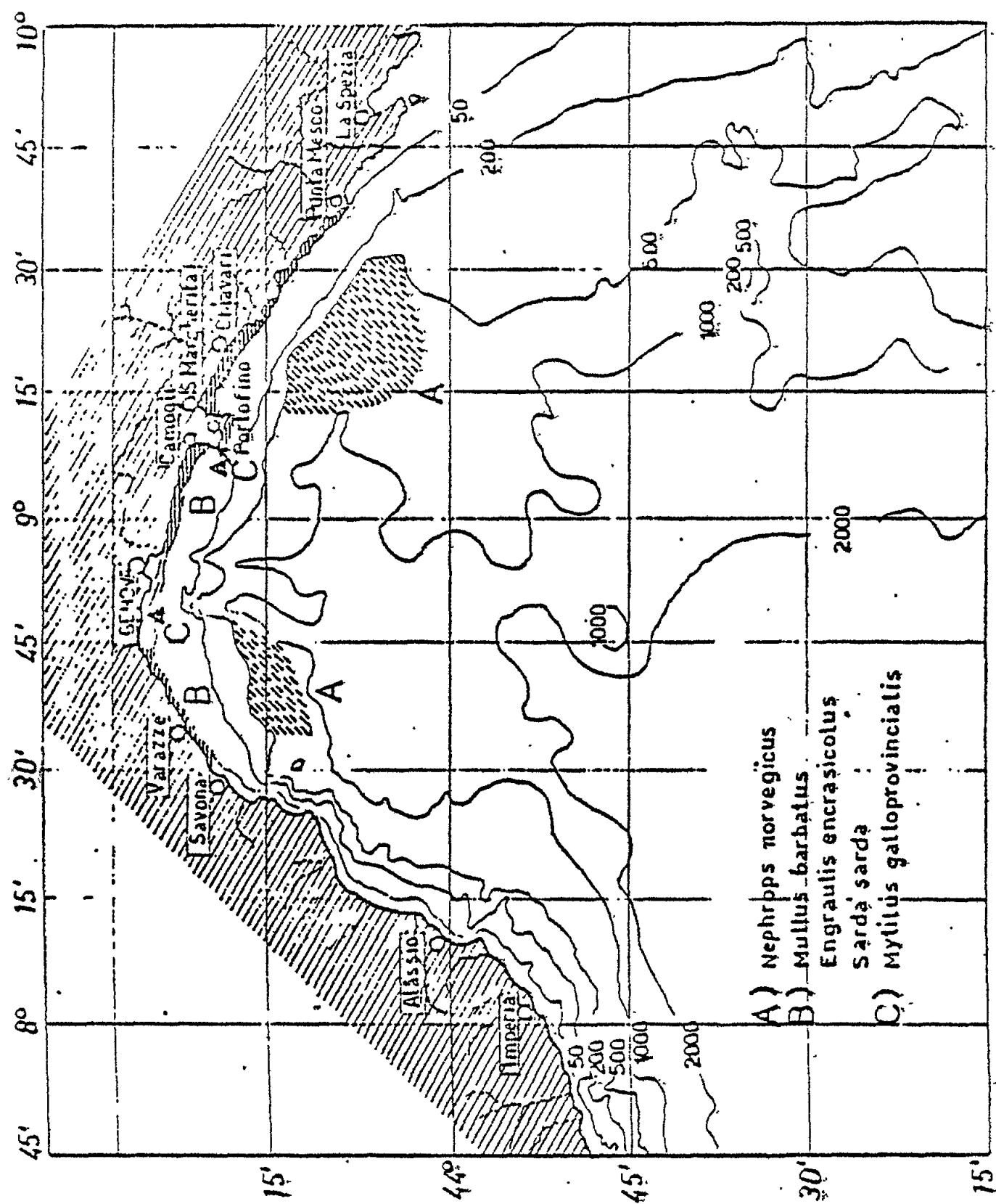


Fig. 1. Zone de prélèvement des échantillons

GOLF DE GENÈS - concentrations des métaux ($\mu\text{g}/\text{kg}$ poids frais) dans la partie molle de *MYTILUS galloprovincialis*

Tableau II
GOLFE DE GÊNES = concentrations des métaux ($\mu\text{g}/\text{Kg}$ poids frais) dans le filet
ENGRaulIS encrasiculus

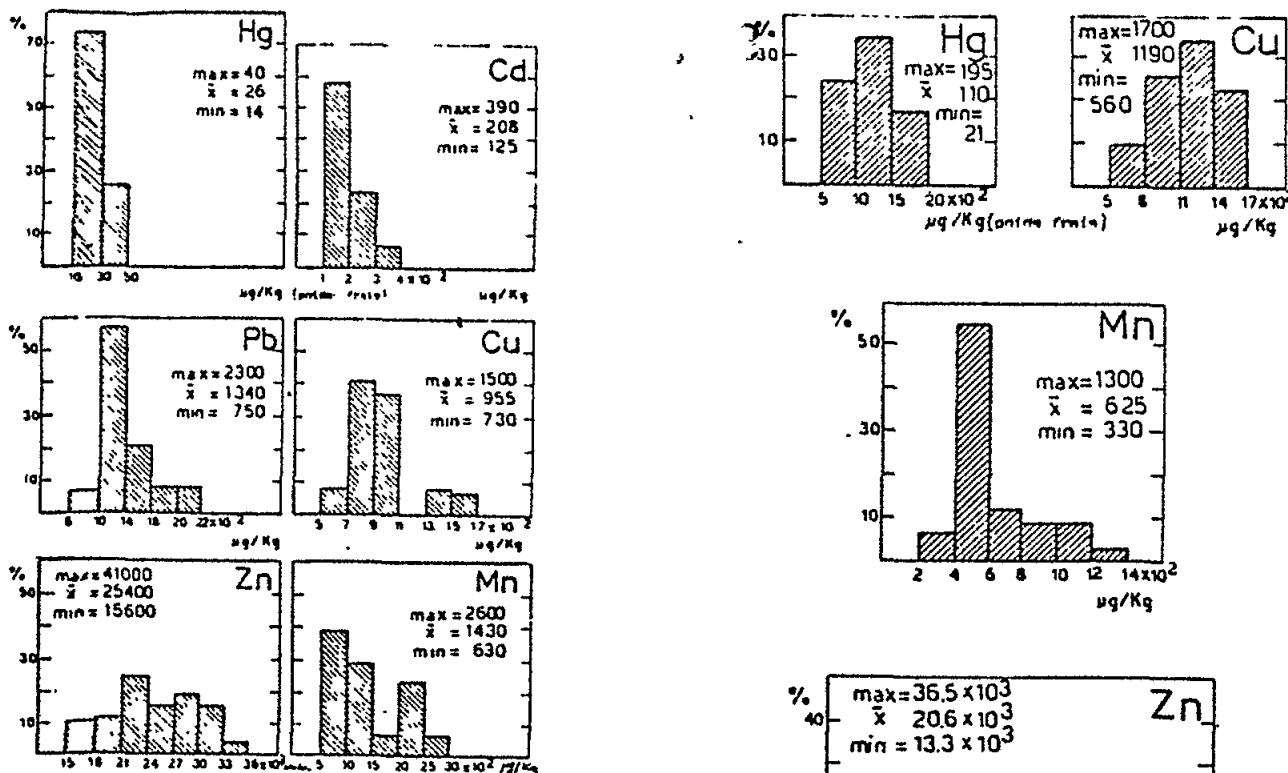
TABLÉAU III. - Concentrations des métaux ($\mu\text{g}/\text{kg}$ poids frais) dans le filet Golfe de Génes

MULLUS barbatus.

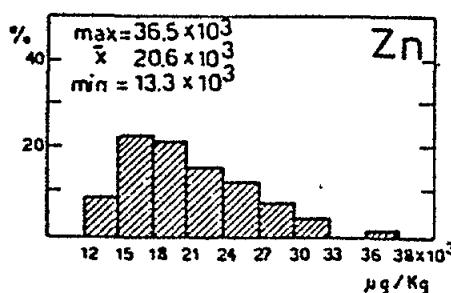
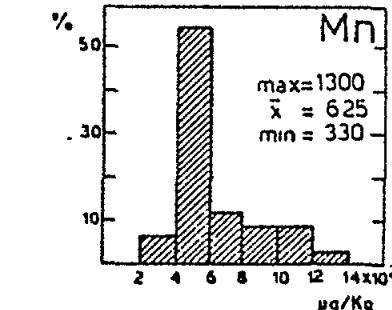
Tableau IV
GOLFE DE GÊNES - concentrations des métaux (µg/Kg. poids frais) dans la partie molle
NEPHROPS norvegicus

Lieu	Année	Hg	min max	Cd	min max	Pb	min max	Cu	min max	U	min max	Zn	min max
Golfe de Gênes 1977		560 ± 735		< 80	< 300	5160 ± 770		3970 ± 6000	930 ± 2160	12000 ± 16000	11950 ± 10500	12930 ± 10500	1580 ± 250
Golfe de Gênes 1978	$\bar{x} \pm 1\sigma$	370 ± 650	500 ± 120	< 80	< 300	4300 ± 8200	4320 ± 1660	1710 ± 160	1710 ± 160	1260 ± 2600	1320 ± 2600	11450 ± 15000	11950 ± 2970
Golfe de Gênes 1979	$\bar{x} \pm 1\sigma$	485 ± 1060	745 ± 215	< 80	< 300	805 ± 200	6320 ± 1840	4520 ± 9200	4520 ± 9200	1260 ± 2600	1260 ± 2600	11400 ± 1600	12760 ± 1240
Ouest de Gênes 1979	$\bar{x} \pm 1\sigma$	485 ± 1060	805 ± 200	< 80	< 300	6750 ± 1820	6730 ± 1740	1700 ± 140	1700 ± 140	1890 ± 500	1890 ± 500	11400 ± 1600	12810 ± 1140
Est de Gênes 1979	$\bar{x} \pm 1\sigma$	375 ± 840	600 ± 165	< 80	< 300	6670 ± 1770	6670 ± 1770	4650 ± 8950	1260 ± 160	1260 ± 160	1260 ± 160	11900 ± 1400	11900 ± 1400

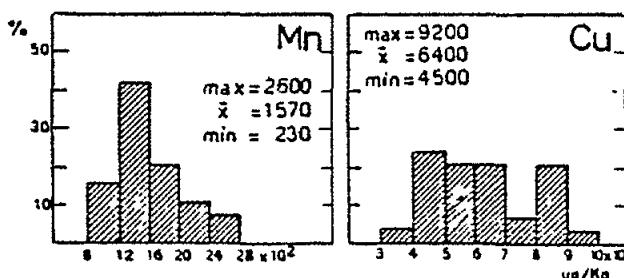
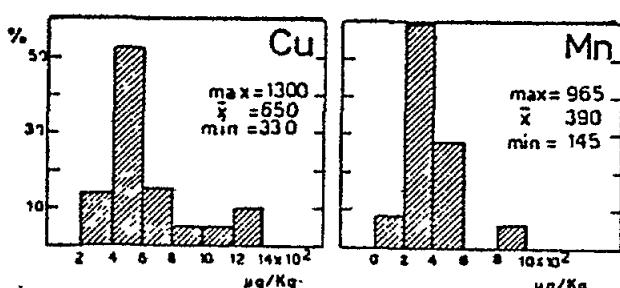
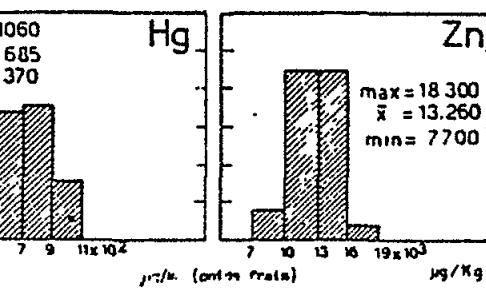
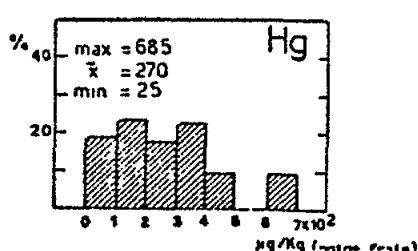
Tableau V



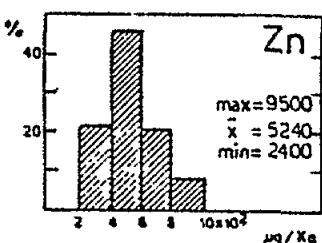
— Distribution de fréquences pour la concentration des métaux dans les moules (*Mytilus galloprovincialis*).



— Distribution de fréquences pour la concentration des métaux dans les moules (*Mytilus galloprovincialis*).



— Distribution de fréquences pour la concentration des métaux dans les rougets (*Mullus barbatus*). — Distribution de fréquences pour la concentration des métaux dans les langoustines (*Nephrops norvegicus*).



Research Centre: Istituto di Zoologia e di Anatomia
 Comparata
 Stazione di Biologia Marina
 MESSINA
 Italy

Principal Investigator: L. MOJO

Period of Reporting: November 1976 to September 1979

INTRODUCTION

In 1976 the Institute signed an agreement with FAO-UNEP, for participation in the pilot project MED II, employing the funds of the National Council of Research (CNR).

The Marine Biological Station has been interested in fishery investigation for a long time. The research carried out by Prof. Bolognari and Prof. Cavallaro disclosed the impoverishment of the bottom in the Straits of Messina (see list of references).

The Institute of Zoology has two research-boats at its disposal: R/B Colapesce, 13m. length and R/V Algesiro, 26m. length, equipped for oceanographic research and for fishery purposes.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The choice of the species has been made as suggested by FAO. We have sampled the following: Mytilus galloprovincialis, Mullus barbatus and Thunnus thynnus thynnus. Two other species: Engraulis encrasiculus and Nephrops norvegicus, were also examined, as requested by the National Council of Research.

Pollutants analysed:

The following metals have been examined: Hg, Cd and Pb.

Areas studied:

The areas where the samples have been selected are defined by the geographical co-ordinates included in the Log-Forms; they refer to zones in the Italian seas adjoining the coasts of Sicily and Calabria (Fig.1). The samples were taken in the areas where commercial fishing is practised, employing professional tools and means.

METHODOLOGY

The samples from the fishing areas were treated in the laboratory according to the FAO Fisheries Technical Paper No.158 (1977). First, the biological parameters were obtained; then specimens of the same size were grouped in numbers of ten for each sample. From these samples the muscular or soft tissues were taken and normalized to the same weight. From each sample, using a mechanical homogenizer at checked speed, an homogeneous substance was

achieved from which only two grammes were taken. Then the two grammes of the homogeneous substance were put in a container of teflon closed in a steel digester, heated on a thermostat plate with the minimum quantity of HNO_3 , "suprapur" needed for the complete digestion of the organic substance. The complete digestion was subdivided into two periods: one of predigestion at ambient temperature and the other of digestion at a temperature of 100°C for three hours.

To obtain a curve of the performance it was necessary to prepare some standards by the addition method. The nitric solution obtained after the digestion was brought up to the required volume with redistilled, deionised H_2O and analysed by the AAS without flame, using a AAS Perkin Elmer 306, supplied by a graphite furnace HGA 76 and an accessory for the determination of the mercury with cold vapour (11).

Intercalibration exercise:

The research centre participated in four intercalibration exercises. The following samples were analysed: oyster (MA-M-1), sea-plant (SP-M-1), copepod (MA-A-1) and fish (MA-M-2).

RESULTS

Mytilus galloprovincialis:

All the samples of this species were collected in the same area (Area 1), because it was impossible to collect this species in other areas.

Hg in M. galloprovincialis shows, on average, low level of accumulation, in spite of the big size of the specimens sampled; Hg average level is 86 $\mu\text{g}/\text{kg}$ of fresh weight (F.W.), Cd average value is 38 $\mu\text{g}/\text{kg}$ F.W. Pb contents seem to be really high, but the average value of 562 $\mu\text{g}/\text{kg}$ F.W. is probably due to the vicinity of the sampling to the town of Siracusa.

Mullus barbatus:

Hg average value in specimens collected in Area 2 is 268 $\mu\text{g}/\text{kg}$ F.W.

Lower levels have been noted in the samples collected in other areas and, particularly, in the samples collected in the zone of St. Eufemia (Area 4). Cd general average level is 47 $\mu\text{g}/\text{kg}$ F.W. and, also in this case, Area 4 seems to be less polluted. Pb accumulation is homogeneous in all the areas and the medium value is 180 $\mu\text{g}/\text{kg}$ F.W.

Thunnus thynnus thynnus:

During the research the species sampled were mostly young tuna. The average level of Hg (180 $\mu\text{g}/\text{kg}$ F.W.) is homogeneous in all the areas. Cd average level (25 $\mu\text{g}/\text{kg}$ F.W.) is low, especially if compared with Cd contents in M. barbatus and also there are no differences between the different areas. Consideration should also be given to the migratory characteristic of this species; this does not permit any relation to be established between the sampling area and the metal contents in the tissues. Pb average content is 220 $\mu\text{g}/\text{kg}$ F.W.

Engraulis encrasiculus:

The average concentration of heavy materials in this species is homogeneously distributed in the different areas: Hg concentration is 139 µg/kg F.W. and Cd average is 24 µg/kg F.W. Pb content in the specimens sampled in Area 3 (244 µg/kg F.W.) is the highest, but it is probably due to the vicinity of the Milazzo refinery.

Nephrops norvegicus:

Heavy metals content in this species is higher than in all the other species sampled, especially in samples collected in Area 1 and Area 3 in the vicinity of the towns of Catania and Milazzo. The highest Hg content was found in specimens collected in Area 1 (average value: 295 µg/kg F.W.) while the highest Pb value was found in samples of Area 3 (average value: 840 µg/kg F.W.). Also Cd concentration in specimens collected in Area 3 is quite marked (average value: 67 µg/kg F.W.). Cd concentration in the specimens collected in the other two areas is lower (average value: 27 µg/kg F.W.). Near the city of Messina (Area 2) no specimen of this species was found.

DISCUSSION OF RESULTS

The final results of this experience disclosed the possibility of comparing the values of pollution by heavy metals found in the species examined with the values reported by other authors for the same or nearby areas (6, 7, 8, 9, 10). Comparing our data with the values found in other Italian seas (Ligurian Sea and Northern Adriatic Sea), (12,13) it is possible to note a lower degree of pollution.

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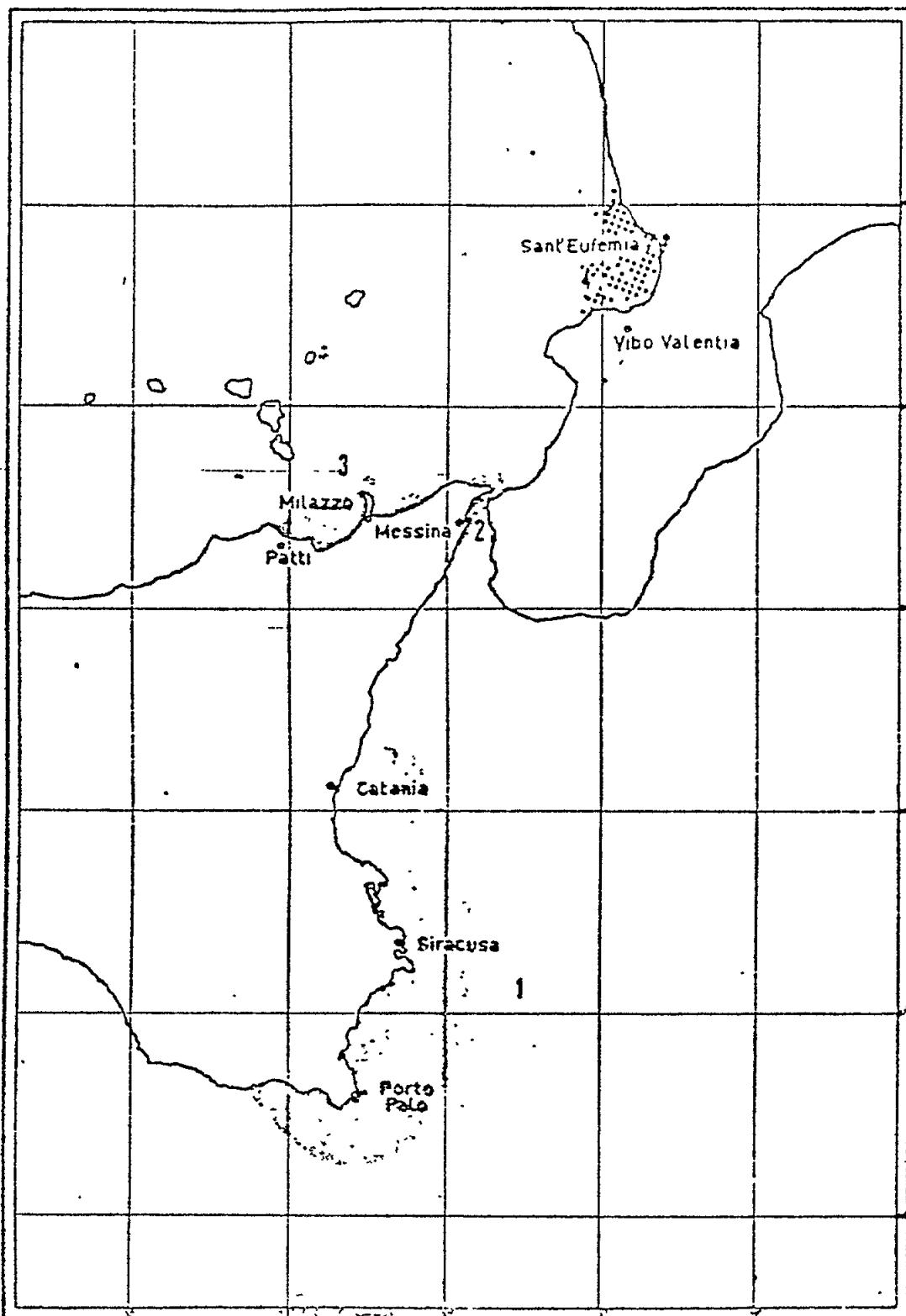


Fig. 1. Areas studied

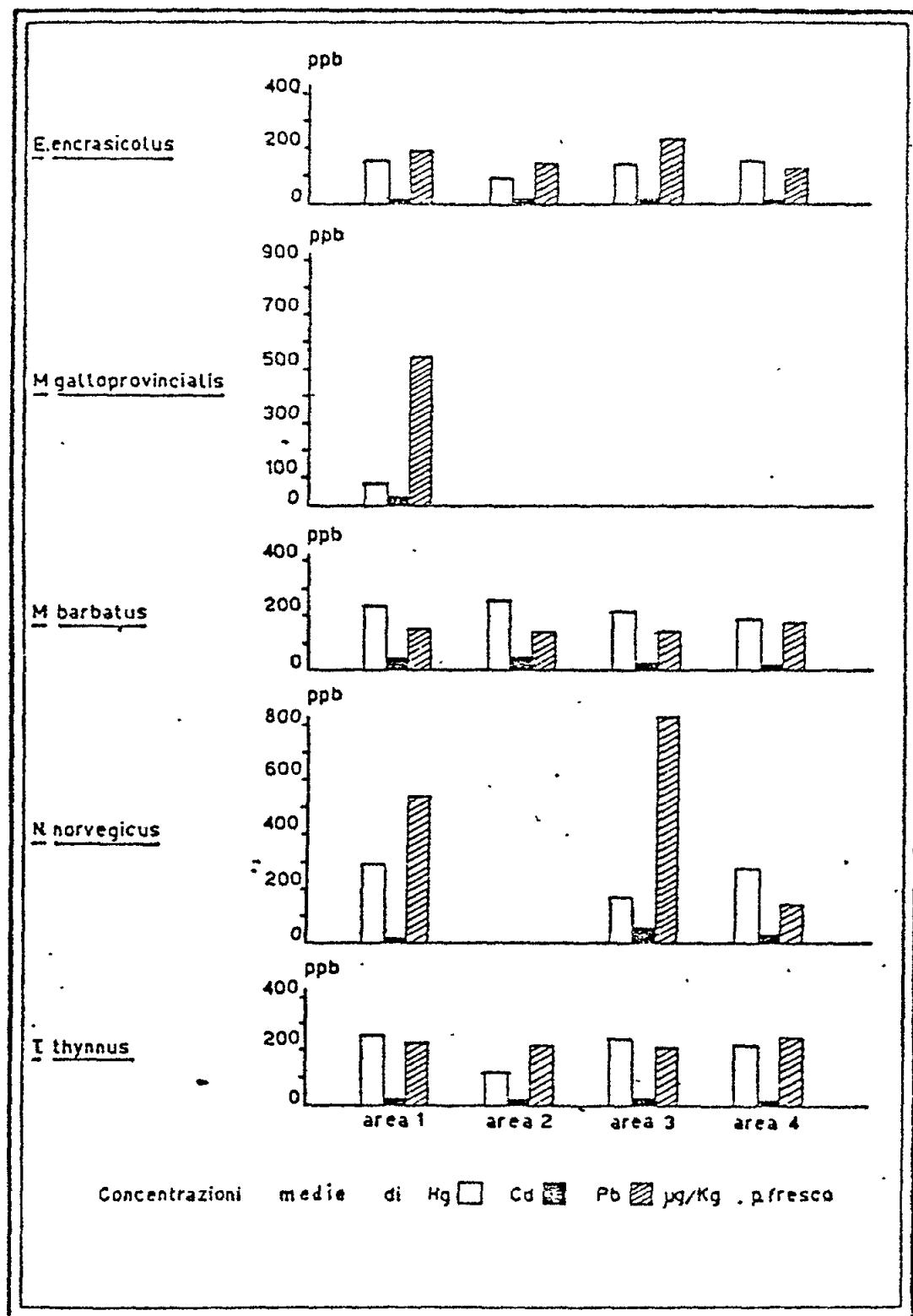


Fig. 2. Results of analyses

Research Centre:

Centro di Radiochimica e Analisi
per Attivazione del CNR
Istituto di Chimica Generale e Inorganica
Università di Pavia
Italy

Principal Investigator:

E. ORVINI

No final report was submitted by the Centre.

Results from 1976 were reported at the Mid-term Expert Consultation (Dubrovnik, 2-13 May 1977) and published in the Compilation of Progress Reports submitted by Research Centres Participating in the Pilot Projects MED II and MED III (FIR: PM/77/7, p.3 and 20; April 1977).

Research Centre: Istituto di Anatomia Comparata
Università di Siena
Italy

Principal Investigator: A. RENZONI

Period of Reporting: Winter 1976 to Winter 1979

INTRODUCTION.

The interest of the Research Centre in the distribution of mercury in the aquatic environment and its effects on biota (man included), began in 1972 (Renzoni and Bacci, 1973; Renzoni, *et al.*, 1973., Bacci, *et al.*, 1976). The "Progetto Finalizzato Oceanografia e Fondi Marini - Sottoprogetto Inquinamento Marino" of the National Research Council (CNR) and the Joint FAO(GFCM)/UNEP Co-ordinated Project MED POL, have provided financial support to carry out a study on the presence of Hg, Cd, Pb, Cu, Mn, Zn, and, later on, Se in marine organisms.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The following organisms were selected: Mytilus galloprovincialis, Mullus barbatus, Nephrops norvegicus, Engraulis encrasicolus, Xiphias gladius and Thunnus thynnus thynnus.

Pollutants analysed:

Hg (total), Cd, Pb, Cu, Mn, Zn and, in a few samples of Mullus barbatus, also Se.

Area studied:

In the northern Tyrrhenian Sea, around the Archipelago Toscano (Fig. 1), the following species were taken: M. galloprovincialis, at sampling stations M₁, M₂, M₃ and M₄ (only from intertidal sites); M. barbatus, at T₁, T₂ and T₃; N. norvegicus, at S₁, S₂ and S₃, and X. gladius and E. encrasicolus from the Archipelago Toscano area.

METHODOLOGY

Fish and crustaceans were caught by trawl nets, and mussels by hand. All samples, with the exception of the mussels, were carried to the laboratory at a temperature of about 4°C and later on kept deep-frozen (-20°C); mussels were kept in clean sea-water for 36 hours. Weight and length were measured according to the FAO Fisheries Technical Paper No. 158. Sub-samples were taken at the moment of the analyses for determination of the water content (24 h at 105-110°C). Typical values of the ratio fresh weight/dry weight in the material analysed are: M. galloprovincialis: 5 (all data normalized) for soft part; M. barbatus: 4,287 for muscle; N. norvegicus: 4.459 for muscle; E. encrasicolus: 4,100 for muscle; X. gladius: 3,860 for muscle.

* Results for this species reported elsewhere (see reference)

Pre-treatment of the samples for the analysis of the trace metals was made by the pressure wet decomposition system described by Stoeppler and Backaus (1978). Composite samples (pools) were made only for mussels (20-50 specimens).

Determinations were carried out by a Perkin-Elmer AAS (Model 300S), with a D₂ automatic background compensator and recorder. Mercury was atomized by the cold vapour technique according to the Italian official method (Gazz. Uff. Rep. It. No. 328, 28 December 1971, pp 8263-5), which has been slightly modified; zinc (and sometimes copper and manganese) by the air-acetylene flame, without extraction and concentration procedures; cadmium and lead (and sometimes copper and manganese) by an electrothermal system (Varian CRA 90). Because of the long time needed for the determinations, the electrothermal system was replaced by the NaDDC-MIBK extraction and concentration procedure described by Julshamn and Braekkan (1975), followed by flame determinations.

Interferences on specificity were eliminated by the D₂ automatic background compensator; interferences on sensitivity were eliminated by the method of addition, before pre-treatment.

The precision of the method was satisfactory: between 3% as coefficient of variation (C.V.) for Zn and 20% (C.V.) for Pb, calculated on 10 replicates of the same sample before decomposition.

Intercalibration exercise:

Accuracy of the methodology was evaluated through the participation in the intercalibration exercises organized by the International Laboratory of Marine Radioactivity of the IAEA (Monaco).

RESULTS

Heavy metals in Mytilus galloprovincialis:

All data are expressed in µg/kg fresh weight (F.W.). The water content is 80% of the fresh weight (fresh weight/dry weight = 5).

Mercury (Table I): No significant variation with size or season was observed. Results from sampling stations M₂ and M₃ are quite constant and very close to the lower values reported by De Wolf (1975) in mussels (M. edulis and M. galloprovincialis) from the West European coast. Higher results are obtained from sampling station M₁ (up to 400 µg/kg F.W.), located near the mouth of the Arno river. Mussels from sampling station M₄ show average concentrations higher than those from sampling station M₁ (up to 1,830 µg/kg F.W.). However, these anomalous values are limited to a very small area; about 50 m south-west, mercury concentrations becomes 100-150 µg/kg F.W., as at the M₂ and M₃ sampling sites.

Cadmium (Table II): The concentrations are around 150 µg/kg F.W., without evident variations in size, season and station. The data obtained are similar to the lowest values reported by Fowler and Oregoni (1976); their overall average weight is about 2 times higher.

Lead (Table III): Samples from sampling stations M₁ and M₄ show low concentrations. Higher values were found at station M₂ (from 980 to 1,700 µg/kg F.W., with an exceptional value of 12,700) and at station M₃ (from

1,900 to 5,200 $\mu\text{g}/\text{kg}$ F.W.). Values are lower than those reported by Fowler and Oregioni (1976) in the same species from the north-west Mediterranean. Favretto and Tunis (1974) found a 4,200 $\mu\text{g}/\text{kg}$ dry weight (840 $\mu\text{g}/\text{kg}$ fresh weight, with 80% water content) in specimens from the Gulf of Trieste.

Copper (Table IV): No significant differences between the 4 stations and no variations in size and season were found. Quite similar values are reported by Fowler and Oregioni (1976) and about 2 times lower than those reported by Phillips (1976a).

Manganese (Table V): Values are very irregular, ranging from 1,200 to 20 300 $\mu\text{g}/\text{kg}$ F.W.

Zinc (Table VI): This element presents a quite regular distribution at the four stations, without significant variation of sampling site, season or body size. Similar values are reported by Fowler and Oregioni (1976), and somewhat higher, in M. edulis from Australian coasts, by Phillips (1976b).

Heavy metals in Mullus barbatus:

Mercury (Table I): The data are rather scattered, but the average values are generally high. A normalization of the results, only on the body weight basis, is very difficult, even with samples from the same sampling area. This would seem to show that the mercury bio-availability is quite different in various sub-parts of the sampling area.

Cadmium (Table II): All results are below the detection limit (25 $\mu\text{g}/\text{kg}$ F.W.), in good agreement with the findings of Topping (1973a) and Harms (1975) in other teleosts from Scottish waters.

Lead (Table III): All values are below the detection limit (100 $\mu\text{g}/\text{kg}$ F.W.) and like cadmium, in good agreement with the findings of Topping (1973a) and Harms (1975).

Copper and manganese (Tables IV and V): Data are regular and homogeneous, without differences between stations, seasons and body weight. For Cu, similar results are reported by Topping (1973a) in other teleosts from Scottish waters.

Zinc (Table VI): As for copper, about the same values were found during the sampling period in all stations. Similar results were observed in M. surmuletus (GFCM, 1978) and in other teleosts (Topping, 1973a).

Selenium: The analysis was carried out on only 60 specimens from sampling stations T. Average values obtained are 690 $\mu\text{g}/\text{kg}$ F.W. ($n = 11$, S.D. = 131, summer 1978) and 680 $\mu\text{g}/\text{kg}$ F.W. ($n = 49$, S.D. = 312, fall 1978). Because of the irregular distribution of the data on mercury concentration in the same specimens, a correlation between selenium and mercury concentration is not evident.

Heavy metals in Xiphias gladius:

Mercury: Results of the 4 specimens analysed are 750 (body weight 13 kg), 750 (b.w. 14 kg), 2 100 (b.w. 34 kg) and 4,300 $\mu\text{g}/\text{kg}$ F.W. (b.w. 51 kg).

Cadmium and lead: All values are below the detection limits.

Heavy metals in Engraulis encrasiculus:

Mercury (Table I): Overall average is around 150 µg/kg F.W., about two times higher than the overall average of E. encrasiculus caught in the Straits of Gibraltar (Baldi, et al., 1978). A slight increase of mercury concentration with the body size has been observed and reported elsewhere (Bacci, et al., 1979).

Cadmium and lead (Tables II and III): All data are below the detection limits.

Copper, manganese and zinc (Tables IV, V and VI): Average values range from 380 to 1,730 µg/kg F.W. for copper, and from 370 to 1,120 µg/kg F.W. for manganese. Higher concentrations are obtained for Zinc (11,000 - 22,000 µg/kg F.W.), which is in accordance with the findings of Ciusa, et al. (1974) in the same species from the Ligurian Sea.

Heavy metals in Nephrops norvegicus:

Mercury (Table I, Fig. 2): The averages are generally high (up to 1,920 µg/kg F.W.). Specimens of the same sex and of the same body weight, caught in different seasons, present very similar mercury concentrations, even if coming from different sampling stations. A plot of average values for mercury concentrations in males and in females of 10 g body weight classes, against body weight, shows that the sex and the body weight are important factors for the mercury levels (Fig. 2). In the same body weight class, values are higher in females. Males grow faster than females (Vives and Suau, 1963; Farmer, 1973) and if we assume an equal mercury intake and an equal bioaffinity for this element in both sexes, the level of mercury should be the same at the same age. The age (time of exposure) appears to be a more important factor than the body weight.

Cadmium and lead (Tables II and III): All data are below the detection limits. Similar results are reported by Topping (1973a) in N. norvegicus (homogenate of whole body) from Scottish waters.

Copper, manganese and zinc (Tables IV, V and VI): Data are quite regular, without variations between sampling stations, seasons, sexes or body sizes. Typical values are about 6,000 for copper, 1,300 for manganese and 15,000 µg/kg F.W. for zinc.

DISCUSSION OF RESULTS

Mercury: The soft parts of mussels, the muscles of the Norwegian lobster and of the fish are, fundamentally, useful material for mercury monitoring. Results demonstrate anomalous environmental levels. In the area studied mercury shows:

- predominant low levels along the coast (mussels);
- higher and quite scattered levels in the continental shelf (striped mullet);
- high and more regular levels in the bathyal zone, without significant differences between the three sampling stations (Norwegian lobster).

This indicates that bio-available mercury is derived mostly from natural sources since only in a few sites of the area studied does industrial contamination occur. (Renzoni, et al., 1973; Baldi, et al., 1979).

Cadmium: The concentrations in mussels, which can be considered as useful for monitoring of cadmium (see Phillips, 1977), show low environmental levels of this element. Considering a provisional tolerable weekly intake of 400-500 ug of cadmium (FAO/WHO, 1978), no risks for human consumption of fishery products from the area studied exist.

Lead: Results obtained for mussel indicate a low environmental level of this element. Considering a provisional tolerable weekly intake of 3 mg of lead (FAO/WHO, 1978), no risks for human consumption of fishery products from the area studied exist at present.

Copper: Differences were found between species, rather than between stations or seasons. Because of the criticism expressed on the mussel as a biological indicator for copper as pollutant (Phillips, 1976a), a contamination by this element in the studied area cannot be excluded; however, it seems unlikely. The levels found, similar to those from other areas, do not appear to be toxic to man.

Manganese: Striped mullet and Norwegian lobster present typical values. Other data are difficult to interpret.

Zinc: As for copper, the differences are between the species, rather than between sampling stations or seasons. Results obtained with mussels demonstrate no environmental pollution by zinc.

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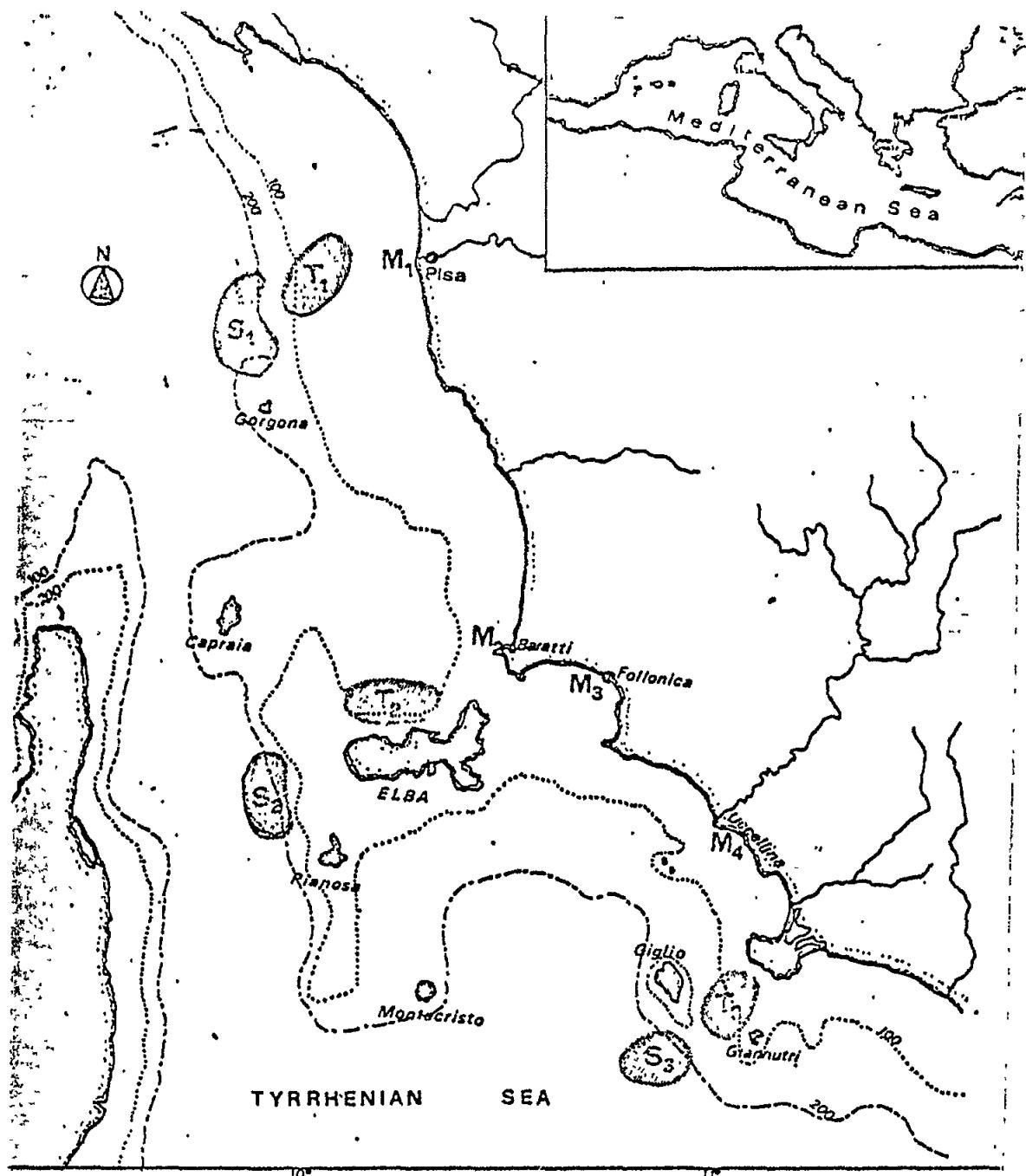


Fig. 1. Sampling area.

Stat.	M ₁	M ₂	M ₃	M ₄	T ₁	T ₂	T ₃	S ₁	S ₂	S ₃
Lat.	43° 40'	42° 59'	42° 54'	42° 37'	43° 40'	42° 51'	42° 20'	43° 31'	40° 45'	42° 16'
Long.	10° 16'	10° 30'	10° 47'	11° 05'	10° 02'	10° 14'	11° 04'	09° 56'	09° 57'	10° 50'

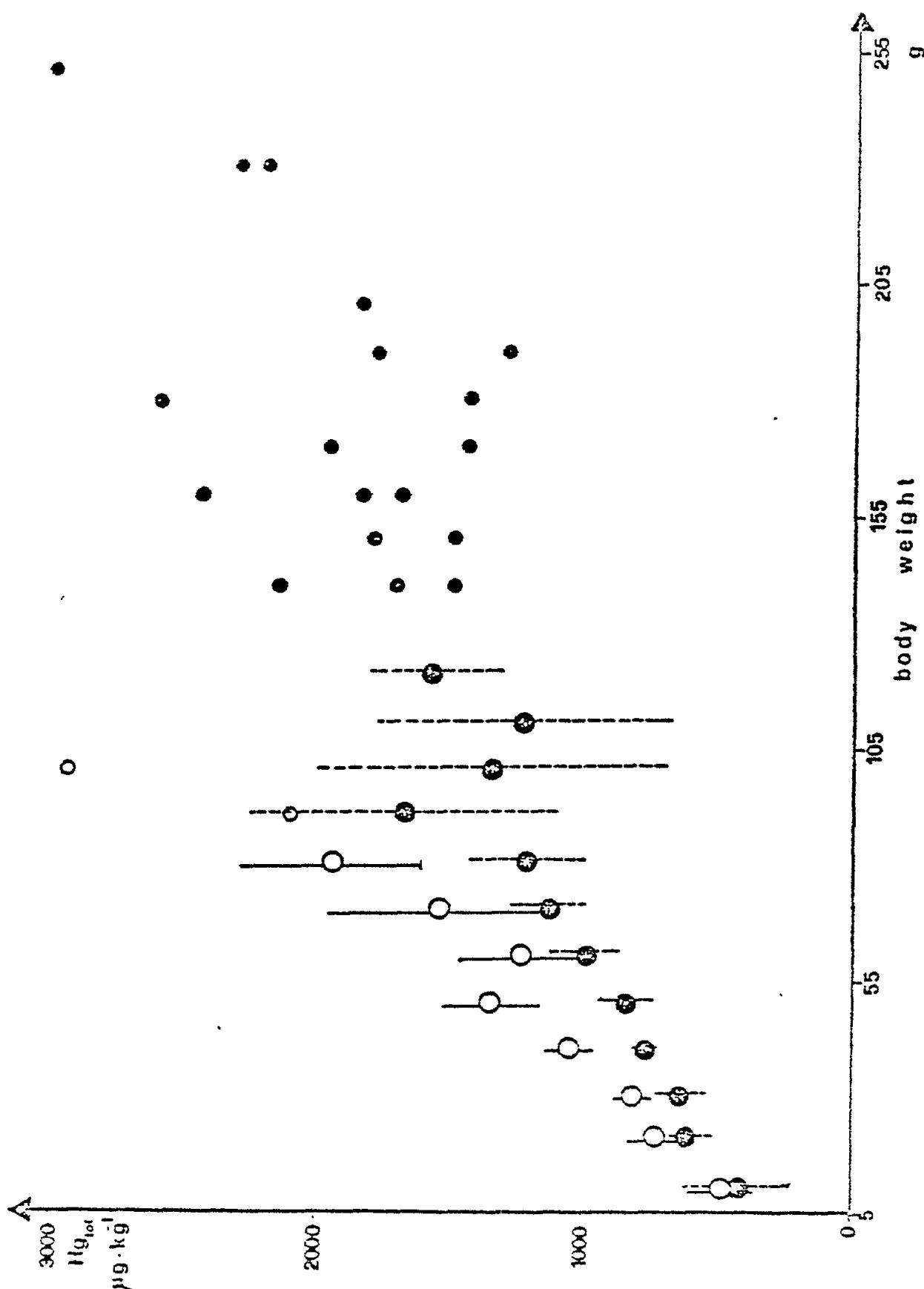


Fig. 2 - Total mercury concentration in the muscle of *N. norvegicus* against body weight. O females; ● males. Averages and 95% confidence limits of 10 g body weight classes. Little circles: single values.

Tab. 1 - Total mercury concentration in biological samples from the Northern Tyrrhenian Sea, in $\mu\text{g}/\text{kg}$ fresh weight.
In brackets the number of specimens (or pools, only for *M. galloprovincialis*) analyzed.

Hg	<i>N. norvegicus</i> * <i>E. gracilis</i>				<i>M. berbis</i>				<i>M. galloprovincialis</i>						
	S_1	S_3	T_1	T_3	M_1	M_2	M_3	M_4	\bar{x}	S.D.	n	\bar{x}	S.D.	n	
7261	\bar{x}	S.D.	\bar{x}	S.D.	\bar{x}	S.D.	\bar{x}	S.D.	\bar{x}	S.D.	n	\bar{x}	S.D.	n	
WINTER	330 (19)	450 (20)	680 390 (20)	200 80 (13)	110 60 (17)	1220 350 (18)	1240 830 (24)	160 50 (1)	205 50 (5)	920 400 (7)			1830 370 (5)		
SPRING	820 (24)	930 330 (27)	170 70 (30)	420 140 (10)	1590 900 (19)	190 (2)			190 (2)						
SUMMER	670 250 (30)	120 30 (10)	270 340 (25)	1350 760 (24)	2500 1680 (15)	400 (3)			90 40 (4)			520 (3)			
FALL	480 180 (30)	430 140 (10)	110 20 (16)	520 450 (16)	1220 620 (24)	610 1130 (21)	250 (3)		130 50 (4)			530 110 (.5)			
WINTER	1160 580 (51)	970 260 (32)	160 40 (7)	920 970 (39)	1270 1030 (16)	540 310 (18)	370 50 (4)	160 70 (5)	190 60 (4)	460 130 (4)					
SPRING	1310 730 (31)	1090 410 (22)	160 50 (7)	190 580 (34)	190 190 (5)	750 (5)			180 (3)			300 (1)			
SUMMER	1110 380 (42)	1320 700 (16)	150 40 (42)	1010 650 (15)	1800 910 (25)	1550 1010 (16)	100 20 (4)	150 40 (4)	140 40 (5)	540 30 (4)					
FALL	1470 530 (46)	710 350 (33)	200 60 (16)	1820 1010 (14)	2020 1030 (41)	2810 2600 (5)	200 (3)	100 (3)	100 (3)	180 (3)					
WINTER		1070 230 (25)													
SPRING	1280 390 (22)	190 30 (16)	400 230 (14)	570 890 (43)		290 (3)			140 (3)			1100 200 (4)			
SUMMER	940 510 (6)	840 490 (16)	150 50 (7)	1240 680 (32)	1370 380 (11)	730 (6)						130 (1)	580 120 (4)		
FALL		1230 210 (7)				4980 860 (6)	1190 250 (9)	280 (2)	80 (3)	110 (3)					
WINTER		1210 220 (6)				910 310 (6)									

* Data from sampling station S_2 :

winter '76.

fall '77.

196 20

Tab. II - See Tab. I.

Cd	<i>M. morvegicus*</i>				<i>E. murinus</i>				<i>M. barbatus</i>				<i>M. galloprovincialis</i>				
	<i>S₁</i>	<i>S₃</i>	<i>T₁</i>	<i>T₂</i>	<i>T₃</i>	<i>M₁</i>	<i>M₂</i>	<i>M₃</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>X</i>	<i>Y</i>	<i>Z</i>
1976	<i>X</i>	<i>Y</i>	<i>X</i>	<i>X</i>	<i>X</i>	<i>X</i>	<i>X</i>	<i>X</i>	<i>X</i>	<i>Y</i>	<i>Y</i>	<i>X</i>	<i>Y</i>	<i>Y</i>	<i>X</i>	<i>Y</i>	<i>Y</i>
WINTER	<20 (4)	<20 (20)	<20 (13)	<20 (13)	<20 (13)	<20 (10)	<20 (23)	<20 (18)	<20 (18)	<20 (7)	60 (7)	20	60 (2)	20	70 (3)	20	70 (4)
SPRING	<20 (25)	<20 (15)	<20 (10)	<20 (10)	<20 (15)	<20 (10)	<20 (15)	<20 (15)	<20 (15)	100 (3)	90 (4)	90 (2)	90 (2)	90 (2)	100 (5)	100 (4)	100 (4)
SUMMER	<20 (16)	<20 (10)	<20 (10)	<20 (10)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (10)	100 (3)	130 (4)	130 (4)	130 (3)	130 (3)	130 (4)	130 (5)	130 (4)
FALL	<20 (30)	<20 (10)	<20 (10)	<20 (10)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (9)	160 (4)	170 (5)	170 (5)	170 (4)	170 (4)	150 (4)	150 (4)	150 (4)
WINTER	<20 (5)	<20 (32)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (5)	180 (3)	130 (3)	130 (3)	130 (3)	130 (3)	100 (1)	100 (1)	100 (1)
SPRING	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (10)	<20 (16)	<20 (16)	<20 (16)	180 (4)	60 (4)	450 (4)	60 (5)	150 (5)	40 (5)	100 (3)	40 (3)
SUMMER	<20 (16)	<20 (6)	<20 (42)	<20 (10)	<20 (10)	<20 (14)	<20 (16)	<20 (16)	<20 (16)	130 (3)	100 (3)	100 (3)	300 (3)	300 (3)	220 (3)	220 (3)	220 (3)
FALL	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)	<20 (16)								
WINTER																	
SPRING																	
SUMMER																	
FALL																	
WINTER																	

* Data from sampling station S₂; winter 1976 and fall 1977; <20.

Tab. III - See Tab. I.

Pb	<i>M. moreoticus</i> *				<i>E. variegatus</i>				<i>M. barbatus</i>				<i>M. galloprovincialis</i>			
	<i>S₁</i>	<i>S₃</i>	<i>T₁</i>	<i>T₂</i>	<i>T₁</i>	<i>T₂</i>	<i>T₃</i>	<i>M₁</i>	<i>M₂</i>	<i>M₃</i>	<i>M₄</i>	<i>S₁</i>	<i>S₃</i>	<i>T₁</i>	<i>T₂</i>	<i>T₃</i>
8261 WINTER	<200 (4)	<200 (20)	<200 (3)	<200 (3)	<200 (10)	<200 (23)	<200 (46)	<200 (18)	<200 (18)	<200 (2)	<200 (3)	<200 (3)	<200 (3)	<200 (3)	<200 (3)	<200 (3)
SPRING 8261	<200 (25)	<200 (15)	<200 (3)	<200 (15)	<200 (10)	<200 (45)	<200 (10)	<200 (45)	<200 (45)	<200 (3)	980 (2)	2630 (2)	<200 (3)	<200 (3)	2420 (5)	80
SUMMER 8261	<200 (16)	<200 (10)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (3)	1130 (4)	290 (3)	3270 (3)	<200 (4)	1020 (5)	210 (4)
FALL 8261	<200 (30)	<200 (10)	<200 (32)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (9)	1020 (5)	210 (4)	5240 (4)	330 (4)	160 (4)	160 (4)
WINTER 8261	<200 (51)	<200 (32)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (5)	480 (4)	250 (3)	2230 (3)	850 (4)	900 (3)	3600 (3)
SPRING 8261	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (10)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (3)	1700 (4)	1700 (3)	3210 (5)	680 (3)	250 (3)	250 (3)
SUMMER 8261	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (3)	1700 (3)	1900 (3)	430 (3)	430 (3)	430 (3)	430 (3)
FALL 8261	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (3)	1700 (3)	1700 (3)	1700 (3)	1700 (3)	1700 (3)	1700 (3)
WINTER 8261	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (16)	<200 (3)	1700 (3)	1700 (3)	1700 (3)	1700 (3)	1700 (3)	1700 (3)
SPRING 8261	<200 (6)	<200 (10)	<200 (7)	<200 (7)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	680 (2)	1110 (3)	1000 (3)	1000 (3)	1000 (3)	1000 (3)
SUMMER 8261	<200 (6)	<200 (10)	<200 (7)	<200 (7)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	1110 (3)	1110 (3)	1110 (3)	1110 (3)	1110 (3)	1110 (3)
FALL 8261	<200 (6)	<200 (7)	<200 (7)	<200 (7)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	1110 (3)	1110 (3)	1110 (3)	1110 (3)	1110 (3)	1110 (3)
WINTER 8261	<200 (6)	<200 (7)	<200 (7)	<200 (7)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	<200 (6)	1110 (3)	1110 (3)	1110 (3)	1110 (3)	1110 (3)	1110 (3)

* Data from sampling station S₂: Winter 1976 and Fall 1977: <200.

Tab. IV - See Tab. I.

* Data from S₂:

Tab. V - See Tab. I.

Mm	<i>M. norvegicus*</i>						<i>M. emarginatus</i>						<i>M. berbatus</i>						<i>M. galloprovincialis</i>												
	S ₁	S ₂	T ₁	T ₂	T ₃	M ₁	M ₂	M ₃	M ₄	S ₁	S ₂	S ₃	T ₁	T ₂	T ₃	M ₁	M ₂	M ₃	M ₄	S ₁	S ₂	S ₃	T ₁	T ₂	T ₃	M ₁	M ₂	M ₃	M ₄		
9 ⁶⁵ F	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	x	50	
WINTER	1360 (14)	490	1160 (20)	950	1120 (13)	290				320 (11)	60	8200 (5)		4150																	11600 (3)
SPRING	1570 (16)	560	1520 (15)	490	200 (10)	50	270 (13)	410	710 (16)	280	16900 (2)																		15300 (4)		
SUMMER	1190 (16)	350			240 (15)	80	300 (10)	70	430 (15)	110	20100 (3)																		3860 (5)		
FALL	1610 (13)	710	2520 (10)	4400	270 (16)	60	370 (8)	140	330 (5)	190	7900 (3)																	4400 (4)			
WINTER	1210 (49)	530	960 (46)	370	210 (46)	70	310 (16)	70	360 (9)	130																					
SPRING	1580 (16)	620	1280 (16)	360	340 (14)	140			160 (5)	110																			1200 (1)		
SUMMER	1320 (16)	780	1030 (16)	480	660 (31)	240	290 (10)	90	270 (16)	70	220 (16)	60	3570 (3)															3300 (4)			
FALL	1600 (16)	930	1380 (15)	600	380 (46)	60	330 (13)	110	300 (16)	130	280 (5)	30	3330 (3)															1330 (3)			
WINTER																															
SPRING																															
SUMMER	1510 (6)	230	1440 (10)	490	390 (7)	90				250 (6)	40																	1010 (2)			
FALL																													6500 (3)		
WINTER	1670 (6)	210			370 (8)	80	310 (6)	70																			12230 (3)				
																													10400 (2)		

* Data from S₂
winter 1976 x S.D. n.
fall 1977 1360 460 14

Tab. VI - See Tab. I.

Zm	<i>M. mormgeicus</i>				<i>E. berusculus</i>				<i>M. barbatus</i>				<i>M. galloprovincialis</i>			
	S ₁	S ₃	T ₁	T ₃	M ₁	M ₂	M ₃	M ₄	S ₁	S ₃	T ₁	T ₃	M ₁	M ₂	M ₃	M ₄
	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.
967 WINTER	11950 (14)	1810 (20)	12690 (20)	10800 (13)	5190 (10)	1020 (13)	3110 (16)	580 (16)	24710 (7)	16500 (7)	19150 (2)	16500 (2)	31050 (4)	9280 (2)		
	15460 (6)	2190 (15)	14350 (15)	1630 (13)	3180 (10)	490 (23)	910 (16)	960 (16)	36400 (8)	24300 (3)	29630 (3)	21150 (5)	3540 (3)	31100 (3)		
567 SPRING	16170 (16)	2250 (15)			4890 (45)	930 (40)	3570 (45)	410 (45)	24300 (3)	24300 (3)	29630 (3)	21150 (5)	3540 (5)	31100 (3)		
	23710 (13)	4410 (10)	16720 (10)	2310 (10)	4760 (16)	610 (16)	4820 (16)	830 (16)	31450 (3)	31450 (3)	31450 (4)	29470 (3)	22380 (4)	3210 (4)		
667 FALL	14510 (5)	2800 (16)	13740 (16)	1200 (16)	3510 (16)	440 (16)	3560 (16)	530 (16)	30530 (3)	30530 (3)	31030 (4)	29470 (3)	31030 (4)	22380 (4)		
	15360 (16)	2270 (16)	16530 (16)	1750 (16)	3830 (16)	520 (16)	3850 (16)	430 (5)	3850 (5)	51670 (3)	35030 (3)	35030 (3)	31700 (1)	31700 (1)		
867 SUMMER	16300 (16)	2570 (16)	15660 (16)	1120 (42)	3660 (10)	1000 (42)	3920 (16)	900 (16)	30200 (4)	4420 (4)	31400 (4)	2550 (4)	37890 (5)	8140 (5)	28330 (3)	
	16600 (16)	2190 (16)	15760 (16)	2220 (16)	47060 (14)	4210 (16)	430 (14)	3110 (16)	650 (16)	4280 (5)	470 (3)	37970 (3)	31300 (3)	41570 (3)		
667 WINTER																
	SPRING															
667 SUMMER	15110 (6)	1690 (6)	15010 (10)	1660 (7)	44270 (7)	4350 (7)	33390 (6)	370 (6)					41370 (3)	30060 (4)		
	FALL												48950 (2)	28270 (3)		
WINTER													26330 (3)	26330 (3)		
													33370 (2)	33370 (2)		

* Data from S₂:

winter 1976 \bar{x} S.D. n
fall 1977 26150 3120 14

Research Centre: Marine Research Centre
 National Council for Scientific Research
 Jounieh - Lebanon

Principal investigator: H.H. KOUYOUMJIAN

Period of reporting: 1977 - 1978

INTRODUCTION

This is the first time that such an exercise has been attempted by a governmental organization. In fact, the Marine Research Centre was partially organized in order to have on a national level the capability to undertake such activities.

METHODOLOGICAL CONSIDERATIONS

The species sampled were: Mullus barbatus, Patella vulgata and Euthynnus alleteratus.

We had difficulty in finding Thunnus or Xiphias. Euthynnus was used instead.

Pollutants analysed:

The pollutants analysed were: mercury, cadmium, copper and lead.

Areas studied:

Fish samples were brought in from two main areas along the Lebanese coast - Jounieh area (near Beirut) and Tripoli (north of Beirut).

The following give an idea of the prevailing hydrographical conditions. These data were recorded in the Jounieh area during these studies. Data from Tripoli is not expected to be significantly different.

pH range	7.13 - 8.28
Water temperature (°C)	13.00 - 29.0
Salinity (°/oo)	33.72 - 41.42

The above-mentioned are the range for mean annual values. As regards general water circulation in our area, it should be mentioned that the major currents fall within the current pattern of the eastern Mediterranean.

METHODOLOGY

Samples were brought in by selected fishermen under the supervision of the research assistant. They were then processed and kept in deep-freeze until analysis. Methodology was based on the guidelines described in FAO, Fisheries Technical Paper No. 158 (FIRI/T158), 1976.

Samples have been collected since 1977. Because of obvious reasons thus far we have only been able to analyse fish samples for 4 metallic pollutants.

RESULTS

The accompanying Table I shows seasonal mean values of mercury, cadmium, lead and copper in Mullus barbatus. Inspection of the results does not show any significant difference between the Tripoli and Jounieh areas, nor do we observe any gross seasonal differences. It must be pointed out that these observations are only based on 1977-78 data; future samples (preserved in deep-freeze) might show significant differences both with regard to season and location.

Values reported do not differ from values reported from other Mediterranean zones, and appear to be acceptable as regards fish.

Table 1. MEAN SEASONAL VALUES OF HEAVY METALS IN *Mullus barbatus* (Values in µg/kg. FW)

Research Centre: Department of Chemistry
University of Malta
MSIDA
Malta

Principal Investigator: A.P. STORACE

Period of reporting: September 1976 to March 1981

INTRODUCTION

The Department of Chemistry had not carried out monitoring of metals before participating in the pilot project. As a result of this participation, the analytical techniques have been refined and the difficulties involved in metal analysis at low levels have been largely overcome.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

Composite samples of the first priority organism, Mullus barbatus, were analysed at approximately three-monthly intervals from September 1976 to July 1980, except for December 1977 and 1978 and June 1979.

The other first priority organism, Mytilus galloprovincialis, was not available and the approved substitute, Lithophaga lithophaga, was used instead. The first analyses were carried out with the February 1978 samples, and subsequently in July and October 1978, March, June and October 1979, and January, April, July and October 1980.

No samples of *Thunnus Thynnus* or its substitute could be provided. Since tuna is a migratory species, the analysis of specimens from Maltese waters should, however, not differ substantially from those of other centres.

Two samples of Trachurus mediterraneus (September and December 1976) and Merluccius merluccius (December 1976) were analysed at the beginning of the programme.

Pollutants analysed:

All of the organisms were analysed for cadmium and total mercury. Specimens of Mullus barbatus from September 1976 to June 1977 were also analysed for Cu, Mn and Zn. From September 1977, lead was also included. All Lithophaga lithophaga samples were analysed for the six elements mentioned above. Since the digested sample solutions were not always sufficient for the analysis of all six elements, work was carried out in the following order of priority:

- (a) Cd, Pb, and Hg;
 (b) Cu, Mn and Zn.

Areas studied:

Fish were caught at a depth of about 180 m at 7 km off the coast. The approximate co-ordinates of the site, indicated by A in Fig. 1 are 35°55'N and 14°15'E. This site can be considered as a clean area. Two additional samples of Mullus (September and December 1976) were caught off Grand Harbour, which is indicated in Fig. 1 and has the co-ordinates 14°31.3'S and 35°54'N.

Lithophaga were sampled from Lazzaretto Creek (14°30'E and 35°54'N), indicated by L in the figure. The site is in a small harbour into which sewage overflow occurs periodically, especially in summer.

METHODOLOGY

Samples were stored in a freezer at -25°C. The procedures given in FAO Fisheries Technical Paper No. 158 were used for the dissection of specimens. One unspiked and three spiked samples (1.5 g fresh weight each) were digested in 4 ml of concentrated nitric acid at 160°C in a teflon bomb. The solutions were then transferred to 10 ml volumetric flasks and for Mullus, usually analysed directly. For Lithophaga samples, a five-fold dilution was required for Cd and Zn analysis.

All Cd and Hg analyses were carried out with flameless atomic absorption spectrophotometry using the Varian AAS 1250A and CRA-90 (for Cd) and the model 64 (for Hg). Pb was determined by the CRA-90 or using an air-acetylene flame according to the levels encountered. Cu, Mn and Zn were determined by an air-acetylene flame using the Varian AAS 1250A or a Perkin Elmer 303.

Most of the results were obtained by the method of standard additions and linear regression. In those cases where the standard additions were too low, the results were obtained by comparison with aqueous standards.

The 95% confidence limits were derived from $t \cdot S.E.(X)$ where

$$\begin{aligned} S.E.(X) &= \frac{\sigma}{b} \left\{ \frac{1}{m} + \frac{1}{n} + \frac{(Y - \bar{y})^2}{b^2 S_{xx}} \right\}^{\frac{1}{2}} \\ &= \left[\frac{1}{n-2} \left(\frac{1}{r^2} - 1 \right) \left\{ \frac{S_{xx}}{m} + \frac{S_{xx}}{n} + \frac{(Y - \bar{y})^2}{b^2} \right\} \right]^{\frac{1}{2}} \end{aligned}$$

$$\text{where } \sigma^2 = \frac{S_{yy} - b^2 S_{xx}}{n-2},$$

$S_{xx} = \sum x^2 - (\sum x)^2/n$ with corresponding expressions for S_{yy} and S_{xy} ,

$$b = S_{xy}/S_{xx},$$

Y = the mean absorbance of m readings of the blank solution,

\bar{y} = the mean absorbance of n standard solutions,

and $r^2 = S_{xy}^2/S_{xx} S_{yy}$, the coefficient of determination.

The individual readings were checked before regression for outliers by Grubbs' formula

$$\frac{\text{Extreme} - \text{Overall mean}}{\text{Overall standard deviation}}$$

It can be seen that the confidence limits are strongly dependent on slight departures of r^2 from 1 because of the term $(\frac{1}{r^2} - 1)$.

(r^2 is a measure of the linearity of the observed readings of each standard addition series). There is, for example, a five-fold increase in the contribution of this term to the total error when r^2 goes from 0.99 to 0.95. Incomplete homogenization is probably the main cause of deviations from linearity, at least with Lithophaga, where the high levels encountered should give low errors.

Intercalibration Exercise:

The Department participated in the intercalibration analysis of the seaplant (SP-M-1), the copepod (MA-A-1) and the fish (MA-A-2) samples.

RESULTS

Heavy metals in Lithophaga lithophaga:

The following results were obtained from 11 composite samples involving 62 specimens.

Element	Mean	Standard	Range	
Cd	591	365	330	- 1590
Hg	248	250	79	- 960
Cu	5560	2430	3140	- 10500
Mn	5650	4540	2220	- 14000
Pb	26400	9210	12000	- 40000
Zn	113000	31200	60000	- 160000

Units are in $\mu\text{g}/\text{kg}$ fresh weight

The dry weight of Lithophaga is about 20% of the fresh weight. To convert the above results to $\mu\text{g}/\text{kg}$ dry weight, multiply them by 5. The results are comparable with those for Mytilus galloprovincialis from polluted areas. Some values are given overleaf.

Element	Level	Site	Reference
Cd	6 800 µg/kg D.W. 1 900 µg/kg D.W.	La Spezia N.W. Med.	IRPTC 1/, p.294 "
Hg	1 740 µg/kg F.W. (max.)	Marseille	GFCM 2/, p.11
Zn	381 mg/kg D.W. 250 mg/kg D.W. 11.9-29.9 mg/kg F.W.	La Spezia Sicily Saronikos	IRPTC, p. 451 " p. 454 GFCM, p. 15
Pb	50 mg/kg D.W. 27 mg/kg D.W.	La Spezia Sicily	IRPTC, p. 575 "

D.W. = dry weight

F.W. = fresh weight

1/ International Register for Potential Toxic Chemicals

2/ GFCM Circular No. 7 (Report No. 3) FAO, May, 1978

It was expected that the levels of pollutants should increase in summer because of sewage overflow. This seems to be confirmed by the January 1980 sample, which has the lowest Zn and Pb levels, and the Mn, Cd and Hg levels are in the lower part of the observed ranges. The highest Zn and Pb levels in Lithophaga were observed in September 1979. This sample also had the highest Hg and Cu levels.

Heavy metals in Mullus barbatus:

Element	Mean	Standard Deviation	Range	F 1/
CD	20.3	12.5	8 - 49	29.1
Hg	148	88.1	32 - 380	1.68
Cu	850	641	360 - 2700	6.54
Mn	255	161	100 - 580	22.2
Zn	4170	884	2700 - 5800	27.1
Pb	Below detection limit			

Units are µg/kg fresh weight

1/ see text below

The above averages are lower than the Lithophaga values by the factor indicated under column F.

The Mullus samples are obviously far less polluted than Lithophaga but the concentrations are not as low as the results from Turkey (below) indicate. No seasonal variation is evident but the constant F factor for Cd and Zn suggests a common pollution source (Zn is almost always accompanied by Cd). These correlations should be interpreted with caution because of the analytical errors, particularly in determining the low levels of Cd in Mullus.

Some values from other Centres are given below:

Element	Level	Site
Cd	0-590 µg/kg 50 µg/kg F.W. 0.2-2 µg/kg D.W.	Port Vendres Saronikos Turkey
Hg	30 µg/kg 1 740 µg/kg 60-320 µg/kg F.W. 0.1-0.44 µg/kg D.W.	Cap Bar Marseille Saronikos Turkey
Cu	2.4-33 µg/kg D.W.	Turkey
Mn	2.3-5.8 µg/kg D.W.	Turkey
Zn	2 570 - 4 050 µg/kg F.W. 3.6-32 µg/kg D.W.	Saronikos Turkey

Source: GFCM Circular No. 7 (Report No. 3), pages 11, 14-17 and 26-27, FAO, May, 1978.

Heavy metals in other marine organisms:

Five single specimens of Trachurus mediterraneus caught in September and December 1976 were analysed for cadmium and total mercury. A composite sample of Merluccius merluccius (December 1976) was analysed for Cd, Hg, Cu, Mn and Zn. The analyses were carried out largely to gain experience in the methodology since samples of Mullus were limited. The levels of Cd and Hg in one Trachurus sample were higher than the range observed for Mullus. With Merluccius Cd and Zn were higher than observed in Mullus. However, with the limited amount of data, these observations cannot be regarded as a definitive trend.

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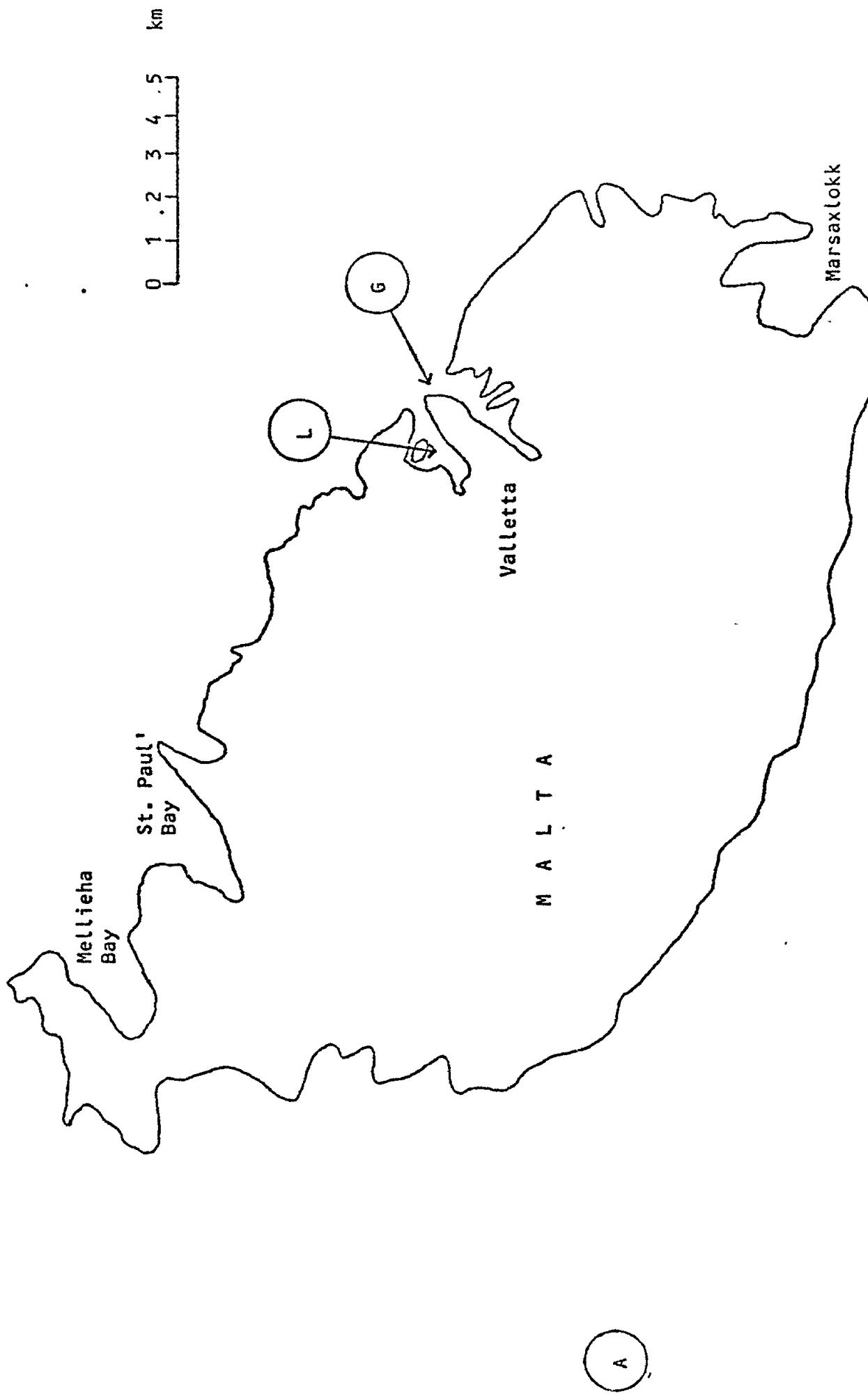


Fig. 1. Sampling sites in Malta

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

Chercheur principal : H. IDRISI

Période couverte par le rapport : Octobre 1977 - Mars 1980

INTRODUCTION

Aucune étude ayant un rapport avec le projet MED POL n'avait été faite dans le passé par l'ISPM. L'analyse des échantillons, recueillis depuis Octobre 1977, a commencé en février 1980.

CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces :

Mytilus galloprovincialis, Mullus surmuletus, Thunnus thynnus thynnus,
Pagellus acarne.

Polluants analysés :

Mercure total, cadmium et cuivre.

Zones étudiées :

Littoral atlantique marocain et Méditerranée occidentale. Sur le littoral atlantique les stations d'échantillonnage des moules sont situées à Larache et à Moulay Bou Selham; les poissons sont prélevés essentiellement dans deux zones situées, la première au large d'Agadir, dans le sud, et la seconde en face de la côte marocaine septentrionale. Dans la Méditerranée les stations d'échantillonnage des moules sont près de Nador, à Al Hoceima et, au niveau de Gibraltar, à Tanger. Les poissons sont recueillis près des stations des moules (Fig. 1).

METHODOLOGIE

L'échantillonnage des moules est fait manuellement, tandis que les poissons sont prélevés par les navires de l'ISPM. Tous les échantillons sont traités suivant les indications de FAO, Document technique sur les pêches n°. 158 (1977). Pour les analyses on a utilisé le muscle des poissons et les parties molles des moules. La décomposition des matériaux biologiques est faite par voie humide, sous pression (bombe teflon) et les analyses ont été réalisées par spectrophotométrie d'absorption atomique (mercure : vapeur froide; cadmium et cuivre : atomisation électrothermique).

Programme d'intercalibration :

L'échantillon "Copepod" (MA-A-1) envoyé par le Laboratoire de Monaco de l'IAEA a été analysé pour Hg, Cd et Cu.

RESULTATS

Métaux lourds dans Mytilus galloprovincialis :

Mercure : les moules méditerranéennes présentent une teneur moyenne de 246 µg/kg P.F. (n=7; gamme 200-273), tandis que celles de la côte atlantique montrent une teneur moyenne de 156 µg/kg P.F. (2; 22-290).

Les résultats ultérieurs permettront, probablement, de mettre mieux en évidence les différences entre ces deux zones.

Cadmium : Tous les échantillons de moules contiennent du cadmium. Les valeurs moyennes sont de 269 µg/kg P.F. (7; 148-520) pour les échantillons collectés en Méditerranée et de 160 µg/kg P.F. (2; 150-170) pour ceux collectés en Atlantique.

Cuivre : Les quatre valeurs suivantes en µg/kg P.F. ont été obtenues : 1100 et 1200 (Méditerranée), 1000 et 1800 (Atlantique).

Métaux lourds dans Mullus surmuletus :

Tous les échantillons traités jusqu'à maintenant proviennent du littoral atlantique. La première série a été collectée au large d'Agadir, dans le sud, et la seconde au large de Casablanca, au nord.

Mercure : Le taux moyen obtenu au Maroc assez proche de la Méditerranée est de 305 µg/kg P.F. (5; 147-418), nettement supérieur à celui obtenu au sud qui est de 147 µg/kg P.F. (5; 15-380), nonobstant la taille bien plus petite des animaux.

Cadmium : Tous les 10 échantillons analysés jusqu'à présent ont donné des résultats au-dessous du seuil de détection de la méthode employée (10 µg/kg).

Cuivre : Il est présent dans tous les spécimens analysés. La moyenne obtenue pour les échantillons traités est de 318 µg/kg P.F. (5; 250-400).

Métaux lourds dans les autres organismes marins :

Un seul spécimen de Thunnus thynnus thynnus a été analysé.

Il s'agit d'un thon de l'Atlantique de 22 kg., qui présente une teneur en mercure de 550 µg/kg P.F., une teneur en cuivre de 250 µg/kg P.F. et le cadmium est inférieur à 10 µg/kg P.F.

Deux spécimens de Pagellus acarne, provenant de l'Atlantique, au large d'Agadir, ont aussi été analysés. Les concentrations, exprimées en µg/kg P.F., sont les suivantes : mercure 200-260; cuivre 260-280; cadmium moins de 10 (seuil de détection).

DISCUSSION DES RESULTATS

Les résultats obtenus jusqu'à présent ne permettent pas une discussion valable, étant encore en trop petit nombre.

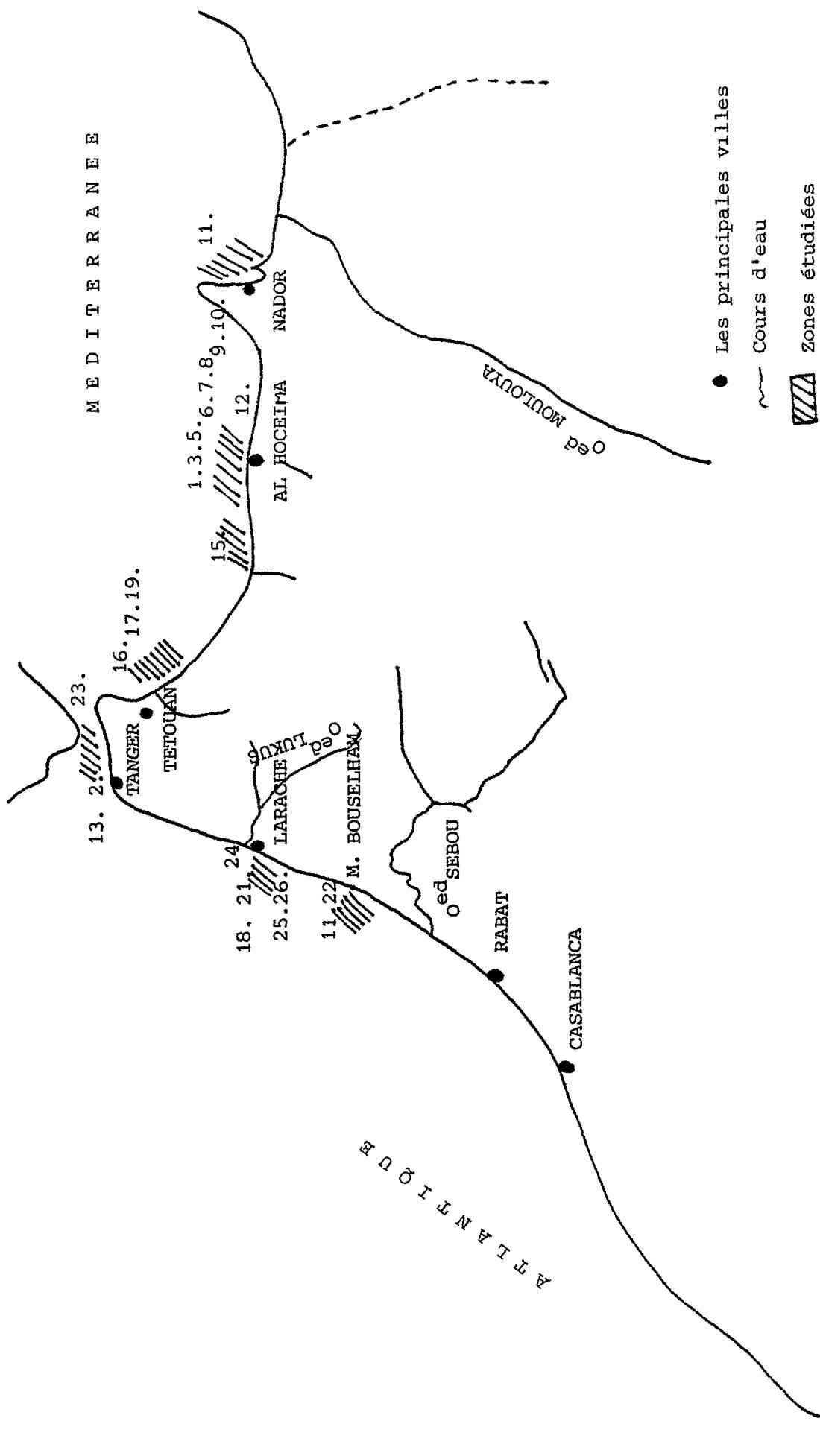


Figure 1. ZONES DE PRELEVEMENTS DES ÉCHANTILLONS

1.2.23. Numéro de l'échantillon

Centro de investigación: Instituto de Investigaciones Pesqueras
BARCELONA
España

Investigador principal: A. BALLESTER

El informe final no fué enviado por el Instituto. Sin embargo los resultados referentes al periodo desde junio 1975 hasta mayo de 1978 fueron presentados en la Reunión Intergubernamental de los Estados ribereños del Mar Mediterráneo para el Plan de Acción para el Mediterráneo (Barcelona 11-13 de febrero de 1980) y publicado en el "Summary Reports on the Scientific Results of MED POL" (UNEP/IG.18/INF.3, Part I, pp. 169-171; Barcelona, 6 February 1980).

Centro de Investigación: Laboratorio Oceanográfico del Mar Menor -
Instituto Español de Oceanografía,
San Pedro del Pinatar (Murcia)
España

Investigador principal: J. GUERRERO PEREZ

El informe final no fué enviado por el Instituto. Se dispone solamente de 3 formularios los cuales contienen datos sobre las concentraciones de Cd y Pb en Mytilus edulis, Mullus barbatus, Penaeus kerathurus, Nephrops norvegicus y Aristeus antennatus muestrados durante el período del 15 de agosto de 1978 hasta el 10 de octubre de 1979.

Centro de investigación

Instituto Químico de Sarriá
Barcelona
España

Investigador principal:

J. OBIOLS-SALVAT

Período:

octubre 1979 - marzo 1981

INTRODUCCION

La participación del Instituto Químico de Sarriá en el Programa MED POL se inició en octubre de 1979 en base a más de 10 años de experiencia en la determinación de metales por absorción atómica, y un contrato de colaboración con el Instituto Español de Oceanografía, especialmente para el muestreo. La actividad del Instituto se orienta fundamentalmente a la puesta a punto y aplicación de las metodicas analíticas.

CONSIDERACIONES METODOLOGICAS

Se han analizado muestras de Mullus barbatus y de Penaeus kerathurus procedentes de puntos de la Costa de Levante y de la Bahía de Palma de Mallorca. Igualmente se han analizado muestras de Mytilus galloprovincialis obtenidas de diferentes puntos de la Costa de Cataluña.

Un grupo de muestras tomadas en 1980 corresponden a la zona de influencia del núcleo urbano de Barcelona, y las demás a otros puntos relativamente cercanos como Sitges, Arenys, Vilanova y Ampolla.

Tratamiento de las muestras. Mineralización ácida a presión según FAO Fisheries Technical Paper No. 158 apartado 6.3.2.1.

Los análisis de mejillones y de langostino se han realizado sobre un homogeneizado de todo el cuerpo. Los análisis sobre salmonetes lo han sido sobre filetes obtenidos según FAO Fisheries Technical Paper No. 158 apartado 5.1.4. Las mediciones se realizan por absorción atómica. El mercurio se determinó por la técnica de vapor frío según el apartado 6.4.1.1.2 del mismo FAO Fisheries Technical Paper No. 158. El hierro y el cinc se determinaron por atomización con llama (mezcla de aire y gas acetileno) y los demás elementos mediante cámara de grafito.

Los resultados de las muestras se han obtenido interpolando las medidas obtenidas con absorción atómica sobre las correspondientes rectas de calibrado calculadas con patrones acuosos preparados a partir de nitratos de metal en calidad reactivo para el análisis.

Ejercicio de intercalibración:

Se ha realizado el ejercicio de intercalibración sobre muestras de copépodo (MA-A1 No. 295) y pescado (MA-A2 No. 251) en las que se han determinado concentraciones de Hg, Cd, Pb, Fe, Mn, Ni, Cr y Cu.

Estas muestras se han utilizado como referencia, repitiendo su análisis paralelamente a cada serie de muestras.

RESULTADOS OBTENIDOS

Los resultados se resumen en las tablas I, II, III y IV, según la zona de procedencia de las muestras, señalándose la población en donde se han obtenido (ver plano).

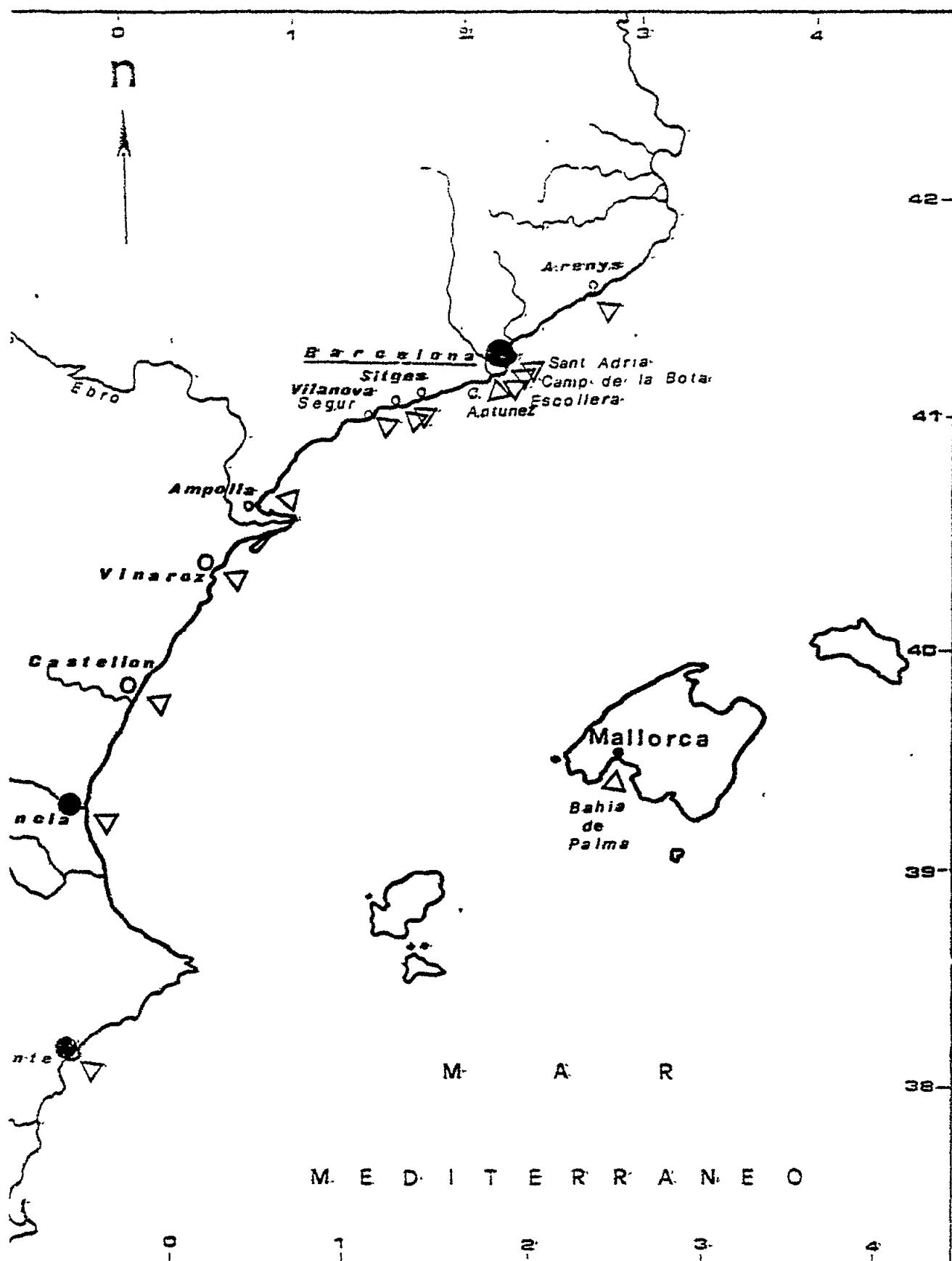
Los valores corresponden al valor de dos o tres análisis sobre partes alícuotas de la misma muestra.

DISCUSION DE RESULTADOS

- Excepto la zona de Barcelona, los resultados obtenidos no indican una contaminación importante con respecto a otros datos del Mediterráneo.
- No se dispone de suficientes datos para establecer correlaciones en el tiempo y en el espacio.
- La zona de Barcelona, como era de esperar, se revela como un importante foco de contaminación urbana, pues los resultados son muy elevados y además variables. Hay que tener en cuenta que los puntos de Sant Adriá y Camp de la Bota están junto a los principales emisarios del área Metropolitana.

PUBLICACIONES

OBIOLS, J. et al. Study of pollutants on Mytilus sp. and Mugil sp. in the 1980 Barcelona coast area. Presentado a la Fifth Workshop on pollution of the Mediterranean (ICSEM/UNEP), Calgliari, 9-13 October 1980.



PUNTOS DE MUESTRAS

Tabla I - Zona de Levante

	No. de piezas	Long. mm	Peso g	Hg(t) µg/kg	Cd sobre peso	Cu fresco
Alicante <u>Mullus barbatus</u>	6	130	24	46	inf. a 38	295
Valencia <u>Mullus barbatus</u>	6	150	57	79	161	889
		50	11	25	124	1133
		60	9	24	171	889
Castellón <u>Mullus barbatus</u>	6	130	32	62	inf. a 20	335
Vinaroz <u>Mullus barbatus</u>	6	130	34	156	inf. a 38	340
	6	120	12	78	71	2754

Tabla II - Bahía de Palma de Mallorca

Resultados de 6 piezas de Mullus barbatus

Long mm	Peso g	Hg(t)	Cd µg/kg	Cu sobre peso	Fe	Mn	Zn	Pb
120	39	887	16	1470	12000	111	5600	225
120	37	145	36	1250	12000	212	7800	210
120	30	147	77	1200	8000	126	6700	128
110	28	144	53	2450	9000	98	6200	172
110	26	163	47	800	7000	95	6600	112
100	23	143	24	630	6000	86	7000	168

Tabla III - Zona de Barcelona Ciudad

Mejillones de cuatro puntos muestreados en Mayo y en Agosto

	No. de piez.	Long. mm	Peso g	Hg(t)	Cd μg/kg sobre peso fresco	Cu	Pb	Mn	Se	Ag
Sant Adriá	20	55	4	1300	305	11500	94000	2500	480	160
	15	45	3	460	200	2700	16200	1450	-	-
Camp de la Bota	30	48	2	2860	260	20200	19500	2000	220	90
	15	40	2	880	1200	10800	15500	3050	-	-
Escollera	25	53	3	1480	440	12400	30250	7250	190	130
	12	50	3	380	1400	6600	8150	2050	-	-
Casa Antunez	40	24	1	250	340	77700	7600	2100	30	100

Tabla IV - Costa de Cataluña

Mejillones

	No. de piezas	Long. mm	Peso g	Hg(t)	Cd μg/kg sobre peso fresco	Cu	Pb	Mn
Arenys	22	34	1	100	240	1100	1030	1250
	20	41	3	140	160	2500	400	1180
Sitges	16	52	3	140	210	2700	3100	1000
	25	40	1	150	290	1600	7100	1400
	42	47	2	160	130	1510	1960	1020
Vilanova	20	42	2	90	1800	3900	5300	500
Segur	21	29	1	125	230	990	1240	1230
Ampolla	15	69	5	108	109	1130	1120	960
	20	40	2	61	480	3320	1480	1820

Centre de Recherche : Institut National Scientifique et
Technique d'Océanographie et de Pêche-
(INSTOP)
SALAMBO
Tunisie

Chercheur principal : Salem Hadj ALI

Période couverte par le rapport : novembre 1978. - octobre 1979

INTRODUCTION

Jusqu'à la participation au projet pilote MED POL, les activités analytiques spécifiques de l'I.N.S.T.O.P. étaient très réduites. En effet, la quasi-totalité des recherches de l'Institut intéressait directement la pêche. De ce fait, le sujet de recherche du projet MED POL en question est le premier de son genre à être abordé par l'I.N.S.T.O.P.

CONSIDERATIONS METHODOLOGIQUES

Sélection des espèces :

Nous nous étions limités aux espèces suivantes : Mullus barbatus et Mytilus galloprovincialis.

Polluants analysés : Seul le mercure a été analysé.

Zone étudiée :

Le Golfe de Tunis : Le Golfe de Tunis est situé à la limite nord-est de l'Afrique du Nord. Il s'étend entre 10°10' et 11°5' de longitude est, et entre 36°38' et 37°10' de latitude nord. Il se présente comme une grande baie largement ouverte vers la mer au nord et étranglée au sud (Fig. 1). La température dans l'ensemble du golfe correspond aux températures moyennes du bassin occidental de la Méditerranée et varie entre les valeurs 13°C et 28°C. La salinité de l'eau varie autour de 37°/oo. Au niveau des deux stations d'échantillonnage de Mullus barbatus, le fond est sablo-vaseux et riche en débris coquillers et en algues.

METHODOLOGIE

Mullus barbatus est pêché au chalut et les échantillons sont conservés dans des sachets en plastique. Les moules sont prélevées au moyen d'une drague et ramenées au laboratoire dans des sachets en plastique. Après mensuration, les filets de Mullus barbatus destinés à l'analyse sont prélevés, broyés, homogénéisés et congelés dans des flacons en plastique.

Après nettoyage de la coquille, les moules sont ouvertes et la chair est prélevée, homogénéisée et congelée dans des flacons en plastique. Environ 1 g (poids frais) est minéralisé par 4 ml de HNO₃ concentré dans des creusets en teflon fermés. Les minéralisats sont étendus à 50 ml dont 20 ml sont utilisés pour l'analyse du Hg par absorption atomique (FAO : Fish. Tech. Pap. 158).

Etant donné l'acquisition récente par l'I.N.S.T.O.P. d'un lyophilisateur, les échantillons seront dorénavant lyophilisés et l'analyse sera faite sur des échantillons secs.

Pour les échantillons lyophilisés la modification suivante est utilisée : environ 0,2 g (poids lyophilisé) est minéralisé par 2 ml HNO₃ concentré dans des creusets en teflon fermés. Les minéralisats sont ramenés à 10 ml avec de l'eau distillée. 5 ml seulement sont utilisés pour l'analyse du Hg. L'appareil utilisé est un spectrophotomètre AA 1250 Varian équipé du système d'analyse du mercure.

Seule la cellule de mesure du système Varian est conservée - une pompe d'aquarium et un simple tube à essais viennent compléter la cellule de mesure Varian pour former le système d'analyse - La manipulation est ainsi rendue plus facile et surtout plus rapide.

Programme d'intercalibration :

L'Institut a participé seulement aux exercices touchant le mercure.

RESULTATS

Mercure dans Mytilus galloprovincialis :

Les valeurs étant pratiquement les mêmes pour les 3 stations (Radès, Gammart et Canal de navigation), les moyennes et écarts saisonniers sont donnés pour les trois stations.

Hg µg/kg (P.F.)	Automne 1978	Hiver 78-79	Printemps 79	Eté 1979
	34,6	21,2	38,5	19,4
Domaine de variation	(26,6-46,4)	(0,0-40,9)	(30,5-46,5)	(17,3-21,4)

Mercure dans Mullus barbatus :

Les valeurs étant pratiquement les mêmes pour les deux stations (Gammart et Korbous), les moyennes et écarts saisonniers sont donnés pour les deux stations.

Hg µg/kg (P.F.)	Hiver 78-79	Printemps 79	Eté 1979	Automne 1979
	128,3	122,7	57,5	91,1
Domaine de variation	(123,9-132,6)	(82,8-162,1)	-	-

DISCUSSION DES RESULTATS

Mercure dans Mytilus galloprovincialis :

Les valeurs enregistrées sont toutes très basses. Compte tenu de l'erreur estimée à 50% sur les analyses on constate qu'il n'y a pratiquement pas d'écart saisonnier du taux de mercure trouvé.

Mercure dans Mullus barbatus :

Les concentrations de mercure sont très faibles et il semble que ces taux soient plus élevés en hiver et au printemps et passent par un minimum en été. Etant donné le nombre réduit d'échantillons analysés, ce résultat reste à confirmer.

CONCLUSION GENERALE

Les taux de mercure présents dans Mullus barbatus et Mytilus galloprovincialis du Golfe de Tunis correspondent le plus souvent au taux minimum enregistré sur les côtes européennes de la Méditerranée.

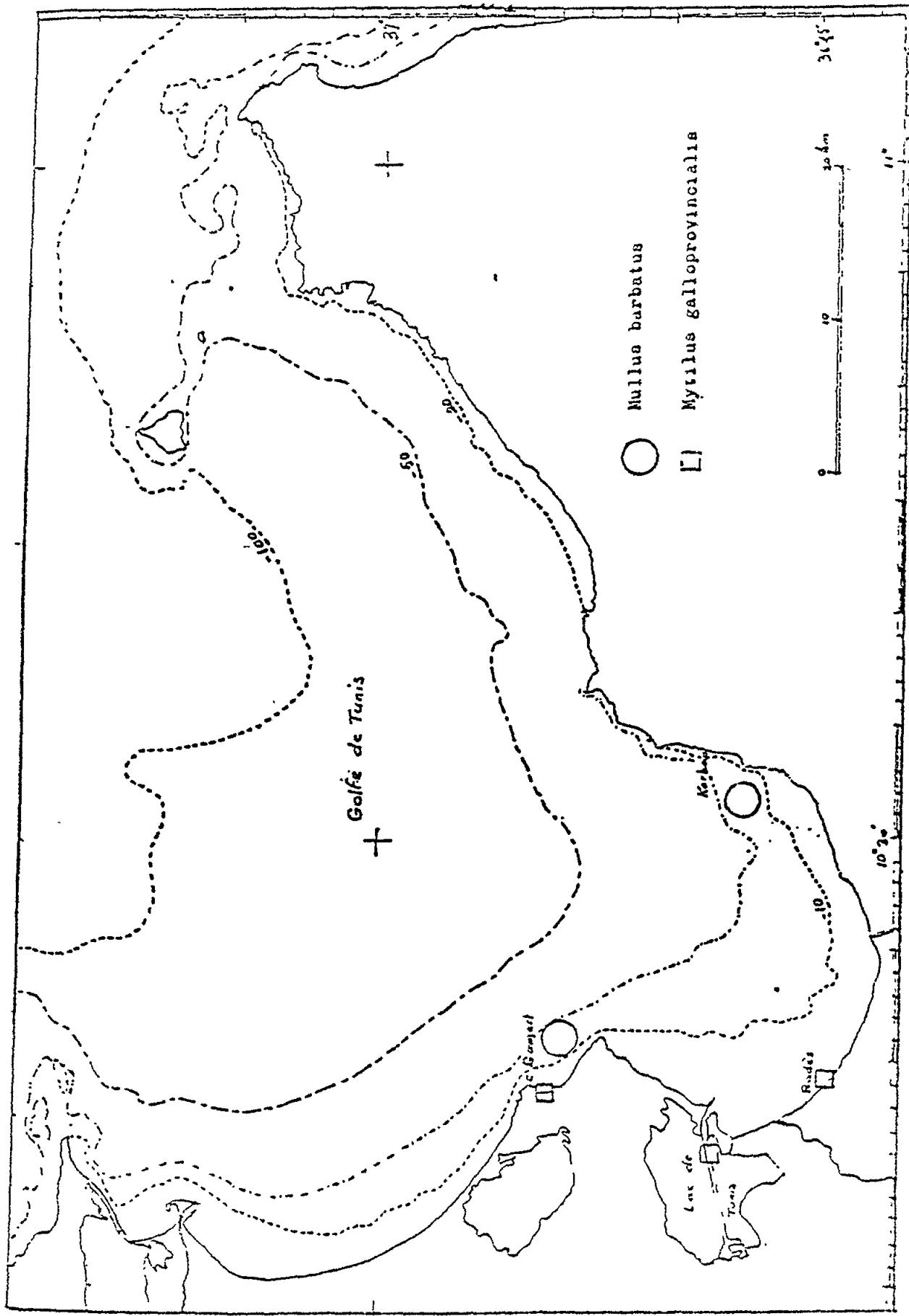


Fig. 1. Stations d'échantillonnage

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
ERDEMЛИ, İgel
Turkey

Principal Investigator: T.I. BALKAS

Period of reporting: September 1976 to May 1981

INTRODUCTION

The Department of Marine Science, M.E.T.U., began active participation in the MED POL II pilot project in Ankara, Sept. 1976. First samples, which were not identified exactly, were used primarily for the development and testing of analytical methods. With the transfer of the Department to Erdemli in June 1977, the activities related to MED POL II were expanded. An active sampling and analysis programme was initiated.

The determination of trace metals in edible marine organisms of considerable commercial importance from Turkish coastal waters, not previously extensively investigated, could give us an idea:

- (a) of the input of trace metals in the human diet, by fishery products; and
 - (b) of the level of environmental pollution, when concentration of contaminants in materials analysed is related to the environmental concentration.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The species selected for the study were not limited to those specified in the MED POL project. A wide range of species was analysed, particularly those of local importance. Mullus barbatus, Mullus surmuletus, Upeneus moluccensis, Mugil cephalus, Mugil chelo, Mugil capito, Mugil saliens, Mugil auratus, Boops salpa, Pomatomus saltator, Sardinella maderensis, Pagellus acarne, Pegusa lascaris, Penaeus kerathurus, Portunus pelagicus, Patella coerulea, Lithophaga lithophaga, Mytilus galloprovincialis and Saurida undosquamis are the analysed samples. Thunnus thynnus and Xiphias gladius were not available.

Pollutants analysed:

The metals Hg, Zn, Cu, Ni, Cr, Fe, Mn, Pb, and Cd, were analysed in the samples. Some metals, such as Cd, Pb, Ni, Cr and Mn, could not be determined in some stages of the project due to operational problems with the carbon rod atomizer (Varian, Model CRA-90).

Area studied:

Figure 1 shows the area studied (except Izmir and Gemlik) with the co-ordinates of the sampling locations which are located in the North Levantine part of the Mediterranean Sea.

Geologically the area is in the Cilician Basin, where the boundaries of the basin are the Toros Mts. in the north and the Cyprus (Kyrenia) Mts. in the south.

The sea-water temperature in the Eastern Mediterranean varies between 16.5°C and 29°C, and the salinity is relatively high (min. 37.8‰ & max. 39.2‰). Thermal stratification generally begins in March and water starts to become well mixed in October where the thermocline during stratification, on an average, is at 60 metres. The wind system, and the current system of the area are rather complicated. The currents have two main components. One is the high frequency 24 h component which is due to land breeze/sea breeze, and the second one is the low frequency component which varies between 3 to 10 days, and is possibly related to cyclonic disturbances.

Nutrient content, thus productivity of the area, is relatively low.

Mersin area (Fig. 1) and Izmir (27°08'E, 38°26'N) can be considered as hot points, since many industrial complexes, e.g. petrochemical, etc. and big busy harbours are located in these areas. Izmir area receives mercury via streams and atmospheric transport due to mercury mines present in the inland mountains. In Gemlik Bay (29°05'E, 40°26'N) there is no heavy harbour traffic. However, some factories manufacturing fertilizers and textiles are located near the bay. Inland agriculture is developed and large quantities of insecticides and pesticides are consumed.

METHODOLOGY

The samples collected by net were immediately taken to the laboratory where they were identified (1) and measured. They were then placed in plastic bags, marked and frozen at -30°C in a freezer. The trawl samples were immediately placed in plastic bags after collection and kept cold in an ice chest until delivery to the laboratory. At the laboratory they were treated in the same manner as those collected by net. The muscle tissues or soft parts were removed from each specimen (2). A small amount of tissue (approx. 1 g) was digested with HNO₃ in the high-pressure decomposition vessels. The digested solutions were then analysed by atomic absorption spectrophotometry.

Mercury analyses were performed by a cold-vapour technique using the system of our design. Flame AA measurements were made with the standard air-acetylene flame using standard techniques, except in a few cases where a pulse nebulization standard technique developed in our laboratory was used. Flameless measurements were carried out with the CRA-90 carbon rod atomizer supplied by FAO/UNEP and also with a Perkin-Elmer Model HGA-74 graphite furnace at the beginning of the project.

Intercalibration Exercise:

All samples supplied by IAEA were analysed and the analytical results of the intercalibration samples are comparable with the statistical test results of IAEA (3-5).

RESULTS

Heavy metals in Mytilus galloprovincialis:

The metal concentrations from the Gemlik and Izmir areas are tabulated in Table I with total length, weight and sampling periods. There are not enough data to compare the concentrations from these areas. However, increase in copper and cadmium concentrations (collected near Gemlik) with size (and thus age) is shown, although more data are needed to be conclusive.

Heavy metals in Mullus barbatus:

The results can be seen in Table I sampled from two locations. No difference by area, size or season was observed.

Other organisms:

The organisms, which have comparative metal results, were included in Table I. No regional differences in metal concentration were observed.

The preliminary results on zinc in Mugil auratus from the Campus area show that zinc decreases with increase in size during the summer and starts to increase from autumn to winter. The spawning time of Mugil auratus lies between November and December. Zinc in Mullus surmuletus tissue decreases with increase in size of samples taken during winter from the Campus area.

DISCUSSION OF RESULTS

The approximate current levels of trace metals in fish tissue and soft parts of shellfish are given in Table II.

The mercury levels in the marine organisms are low, and no significant local difference was found, as can be seen from Table I. The mercury levels in various organisms from the Mediterranean are compiled by Bernhard (10).

In general, the obtained mercury values in M. barbatus, Mullus surmuletus and Mugil auratus are comparatively lower than those from other areas, and there is no significant difference in mercury concentrations from the Atlantic (6) and Australia (7). Upeneus moluccensis has the significant ability to concentrate mercury in its tissue (approx 200 ug/kg, F.W.) compared to other organisms. But total mercury levels of Upeneus moluccensis in that table are given notwithstanding the difference in age and the sampling date of the fish.

Therefore, as can be seen, the standard deviations are very high. The reasons for this are (i) the total mercury content of fish increases with an increase in size (age), and (ii) there are seasonal variations (not included in Table I). The total mercury levels of Saurida undosquamis are lower than those found by Hornung, et al. (11), in samples obtained from the Israeli coast (approx. 166 ug/kg, F.W.).

Trace metal concentrations of Mugil species, Upeneus moluccensis, Mullus barbatus and Mullus surmuletus were compared with published results from different locations. Fish issues from Israeli coastal waters contain higher zinc, copper and cadmium levels (8). However, the average results obtained of Cd, Cu and Zn are similar to tentative "typical" metal concentrations in Mullus barbatus given by Bernhard (10). Zn and cd average levels in Mugil auratus from the Adriatic coast are lower than the results from Turkey. Trace metal concentrations in Mytilus galloprovincialis are lower than the results reported from other Mediterranean locations (10). The levels of trace metals

in Mugil species show no significant differences from Australia (7), the N.W. Atlantic (9) and the Atlantic coast of Spain (6).

As a conclusion, the absence of abnormally high concentrations of trace metals in fish and the different levels in different areas do not necessarily indicate that areas with low levels are free from local pollution; it may be that localized coastal pollution is not reflected in the trace metal levels of the edible muscle tissue of fish in a short period of time. However, the coastal area of the north-eastern Mediterranean sea under study has not been highly contaminated (with the exception of point squares).

The data given in Table I may be useful as a tentative "baseline" with which future changes within the study area can be correlated.

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SUNAY, M., BALKAS, T.I., SALIHOGLU, I. and RAMELOW, G. Determination and Distribution of Organochlorine Residues and Heavy Metals in Tar Balls. XXVI Cong. & Plenary Assembly of CIESM Antalya, 1978.

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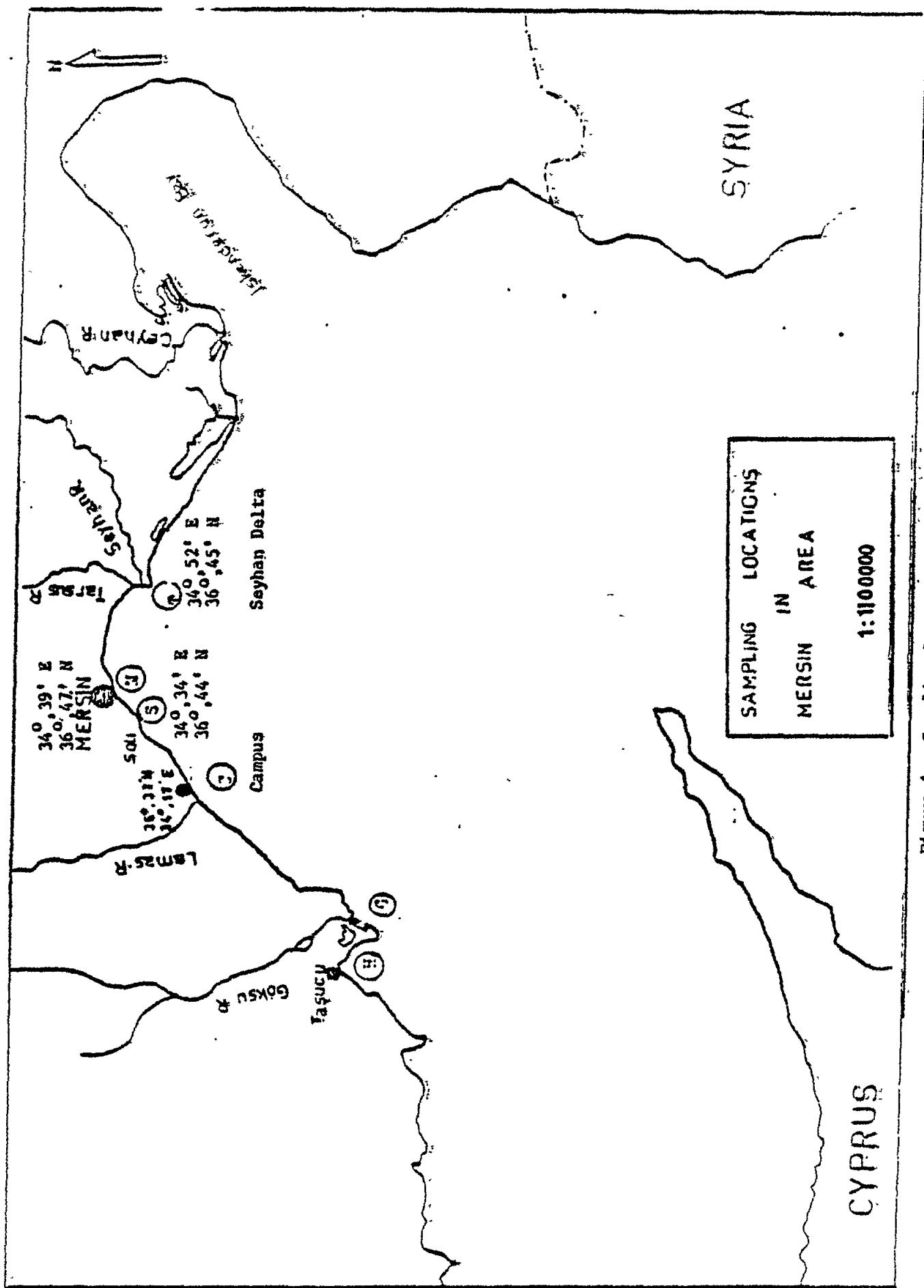


Figure 1. Sampling locations in Mersin Area

Table I. Trace metals in various Marine Organisms from the
Coastal Water of Turkey

Organism (n)*	length (mm)	location, sampling period	F.wt. ^t D.wt.	Hg	Zn	Cu	Ni	Cr	Fe	Mn	Pb	Cd	Sr
<i>Mytilus gallopro- vincialis</i> (6)	40-87 100-164	Gemlik Aug.76	-	20-50 40±10 (4)*	-	750-2650 1390±750 (4)	-	-	-	480-610 550±50 (4)	70-400 24±130 (3)	-	
<i>Mytilus gallopro- vincialis</i> (3)	56-160 6-17	Izmir Jan.77	-	-	9200-23700 14570±6500 (3)	1200-1800 1570-260 (3)	-	-	-	-	-	-	
<i>Mollus barbatus</i> (3)	180-160 43-76	Mersin Jan.77	-	60-90 80±12 (3)	6100-7400 6900 (2)	200-680 440 (1)	6190 (1)	140 (1)	700 (1)	220 (1)	120 (1)	20 (1)	
<i>Mollus barbatus</i> (21)	109-188 20-107	METU campus Jan.78-Sept.79	4.35 (17)	2-88 49±27 (13)	3660-6400 4900±700 (17)	220-690 480-170 (6)	-	-	1300-4700 2600±1070 (6)	<200 (6)	<100 (4)	20-40 30±8 (4)	
<i>Mollus barbatus</i> (9)	120-180 22-84	METU campus Sep.80-March.81	4.78 (9)	24-122 53±29 (9)	-	-	-	-	-	-	-	-	
<i>Mollus barbatus</i> (14)	140-227 47-188	Goksu Feb.80- Jan.81	4.42 (14)	19-232 71±54 (14)	-	-	-	-	-	-	-	-	
<i>Mollus barbatus</i> (5)	130-190 42-112	Seyben delta March 81	4.69 (5)	41-369 115±127 (5)	-	-	-	-	-	-	-	-	
<i>Mallus surmuletus</i> (2)	120-125 20-22	Seyhan delta Aug.77	5.74 (2)	16 3485 (1)	3070-3900 3485 (2)	323-428 375 (2)	-	-	4330-6590 4560 (2)	<200-330 (2)	-	7-12 10 (2)	
<i>Mallus surmuletus</i> (19)	110-192 22-137	NETU campus Jan.78- Sep.79	4.34 (16)	4-78 37±20 (8)	2660-5200 4150±800 (12)	540-110 115±475 (4)	690-1800 75±50 (5)	-	<200 (2)	<100 (3)	<10 (6)	-	

Table I continued

Organism (n)*	length (mm)	location, F.W.T. sampling D.M.C. period	Hg	Zn	Cu	Ni	Cr	Fe	Mn	Pb	Ca	Sn
Mugil auratus (3)	190-241 67-136	Mersin Aug.77	5.33 (3)	25 (1)	4070-9680 6950±2340 (3)	470 (1)	-	-	12900 (1)	460 (1)	-	60 (1)
Mugil auratus (52)	149-395 30-696	METU CAMPUS July 77- Sep.79	4.56 (32)	1-120 25±17 (42)	2700-8200 4270±1300 (40)	290-5700 710±950 (31)	60-540 120±150 (7)	10-850 120±200 (15)	1400-12600 4360±2040 (38)	160-840 140±260 (7)	100-790 (7)	10-60 (7)
Upeneus moluccensis (11)	145 39	Seyhan Delta Aug.77	4.40	110	2600	723	-	-	<200	-	-	40
Upeneus moluccensis (11)	117-164 21-68	METU CAMPUS Feb.78	4.47 (11)	110-430 210±120 (6)	2200-2950 2550±200 (11)	366-104 380±15 (3)	-	-	-	<100	<10-20	-
Upeneus moluccensis (65)	75-170 5-77	METU CAMPUS May 80- March 81	4.50 (65)	7-779 109±129 (65)	1600-8100 3570±1310. (23)	-	-	-	1000-4900 2480±115 (23)	-	-	24-193 97±63 (7)
Upeneus moluccensis (64)	80-170 8-86	Goksu May 80- March 81	4.60 (56)	11-766 98±109 (64)	1900-5700 3400±1060 (14)	-	-	-	915-10600 3510±2385 (13)	-	100 <(6)	61-1770 635±800 (3)
Upeneus moluccensis (23)	90-140 10-42	Seyhan Delta Nov.-80- March 81	4.34 (23)	6-154 45±45 (23)	2930-5250 3660±560 (14)	-	-	-	860-2400 1310±535 (13)	-	-	-
Sardinella maderensis (4)	144-165 30-41.	Seyhan Delta Aug.77	3.95 (4)	49 (1)	4420-8110 6010±1550 (3)	350 (1)	-	-	<200 (2)	-	-	4 (1)
Sardinella maderensis (3)	157-230 42-180	METU CAMPUS Sep.- Dec.77	3.93 (3)	22 (1)	14200-14400 14320 (2)	435-1690 854±590 (3)	-	-	<200 (2)	-	-	-

Table 1 continue.

Cat. No. *	length (mm)	length total	wt. (gr)	sampling period	F.wt. D.wt.	Hg	Zn	Cu	Ni	Cr	Fe	Mn	Pb	Cd	Sn
<i>Protororulus</i> <i>sulcator</i> (2)	67.5-130.0			Mersin Nov. 77	3.56	-	5850 (2)	685 (2)	-	-	-	585 (2)	56 (2)	-	
<i>Panaceus</i> <i>kerathurus</i> (11)	10-29			METU CAMPUS Nov. 77- Sep. 79	3.98 (11)	17-18 28±13 (3)	9250-18800 14600±2560 (8)	2950-11400 6650±2200 (8)	910-1000 85±5 (3)	70-80 85±5 (3)	<200 (8)	-	10-30 20±10 (3)	-	
<i>Patella</i> ** <i>coerulea</i>	-			METU CAMPUS	-	-	8400	1730	-	-	-	-	-	4160	-
<i>Lithophaga</i> *** <i>lithophaga</i>	-			METU CAMPUS March 78	-	-	-	-	-	-	-	-	-	-	1170
Boobs Salpa (10)	103-140 100-164			METU CAMPUS Aug. 77- March 78	4.67 (9)	3-17 8±7 (3)	16620-7800 6550±1160 (9)	272-353 310 (2)	-	-	-	-	-	-	-
Saurida <i>uniosquamis</i> (35)	155-319 29-297			METU CAMPUS Oct. 80- March 81	4.92 (35)	25-297 68±58 (33)	2390-3500 3000±330 (6)	-	-	-	-	-	-	-	
Saurida <i>uniosquamis</i> (37)	11.0-230 20-119			Goksu Oct. 80- March 81	10-107 48±21 (37)	2890-4200 3250±490 (5)	-	-	-	-	-	-	-	-	
Saurida <i>uniosquamis</i> (21)	130-215 19-87			Seyhan delta Dec. 80- March 81	5.05 (21)	14-127 55±28 (21)	-	-	-	-	-	-	48 (2)	-	

† : Fresh weight/Dry weight

** : Composite sample

* : Number of specimens

Table II. Trace Metal levels in Fish Tissue etc. East part of Shellfish from the Coastal Seawater, Turkey. (pe/KE-ret)

Table II continued

Organ**	Fork length(mm) total weight(gr)	F.wt. [†] D.wt.	Hg	Zn	Cu	Ni	Cr	Fe	Mn	Pb	Ca	Su
<i>Panaeus kerathurus</i>	155-170 20-33	3.77-4.75 4.06 (13)	8-48 20 (7)	9200-18800 13550 (12)	1770-11400 5250 (12)	910-2920 1610 (3)	70-330 140 (4)	1600-11500 6170 (3)	0.2-350 247 (11)	10-67 340 (1)	26 (6)	-
<i>Mytilus galloprovincialis</i>	40-87* 6-68	- 38 (4)	20-50 38 (3)	9200-23700 14570 (7)	750-2650 1470 (7)	- -	- -	15100-21000 20130 (3)	- -	480-610 550 (4)	70-400 240 (3)	-
<i>Saurida undosquamis</i>	110-319 19-297	4.22-6.43 4.98 (93)	10-297 57 (91)	2390-4200 3110 (11)	- -	- -	- -	- -	- -	- -	48 (2)	-

[†] : Fresh weight/Dry weight ratio

* : Total length

** : Composite sample

Research Centre:

Department of Biological Oceanography
and Institute of Hydrobiology
Faculty of Science
Ege University
IZMIR
Turkey

Principal Investigator:

H. UYSAL

Period of Reporting:

April 1977 to March 1980

INTRODUCTION

The Research Centre has been working continuously on this subject since 1970, especially in the Bay of Izmir. We started the work related to the MED POL pilot project in April 1977. Before this pilot project started the Department had completed a few projects with IAEA. The work connected with the MED POL II pilot project has been extended until March 1981.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The following organisms were selected: Mytilus galloprovincialis, Penaeus kerathurus, Mullus barbatus, Mullus surmuletus, Mugil spp., Thunnus thynnus thynnus, Carcinus mediterraneus.

The sampling was performed seasonally.

Mugil spp. and Mullus spp. are most abundant along the coasts of the Aegean Sea. M. galloprovincialis is not found in the south part of Izmir Bay and all the southern part of Turkey. P. kerathurus is found in relatively normal amounts along the Aegean costs; but in some localities it is very rare. Carcinus mediterraneus is found in normal amounts along the coasts; but rare in Bodrum (F.5).

Pollutants analysed:

The following metals were determined: Hg, Cd, Cu, Co, Cr, Pb, Fe, Zn, Mn.

Areas studied:

The sampling areas included the Bay of Izmir and the Aegean coast (Turkey). The sites are indicated on the map (Fig.1). The sampling station codes, names, geographical co-ordinates and the organisms sampled during 1977-1980 are indicated in Table I.

METHODOLOGY

Mussels and crabs were collected by hand from the sea-shore (intertidal zone), but fishes and shrimps were caught using fishermen's nets, from indicated areas on the map.

Samples were taken and transported daily to the laboratory and were kept in thermoisolated boxes (with ice in them) in plastic materials. Samples were kept in a deep-freeze (-21°C) until analysis.

Sample preparation for the analyses of metals was performed following the FAO Fisheries Technical Paper No.158. Decomposition vessels were used for the sample preparation. These consist of a closed teflon crucible in a steel block and a hot plate with thermostatic control for digestion of samples. Wet-digested samples were diluted with distilled water and assayed using a Varian Techtron Model 1250 Atomic Absorption Flame Spectrophotometer. The determination of the total mercury (Hgt) in biological samples using the AAS followed the Flameless Hg determination in open system (PARKER 1972). Cold Vapour Technique and Varian Techtron Model 64 As/Se/Hg Analysis kit were also used.

Intercalibration exercise:

The following intercalibration samples have been analysed: sea plant (SP-M-1), copepod (MA-A-1) and fish (MA-A-2).

RESULTS

The results of the analyses of the previously mentioned organisms were reported only in LOG-FORMS.

DISCUSSION OF RESULTS

According to the present results the heavy metal concentrations in C. mediterraneus were higher than in other species and mercury concentrations of Thunnus thynnus thynnus and Mullus barbatus were higher than in other mentioned species. The concentrations of analysed elements vary according to species, locality and the season.

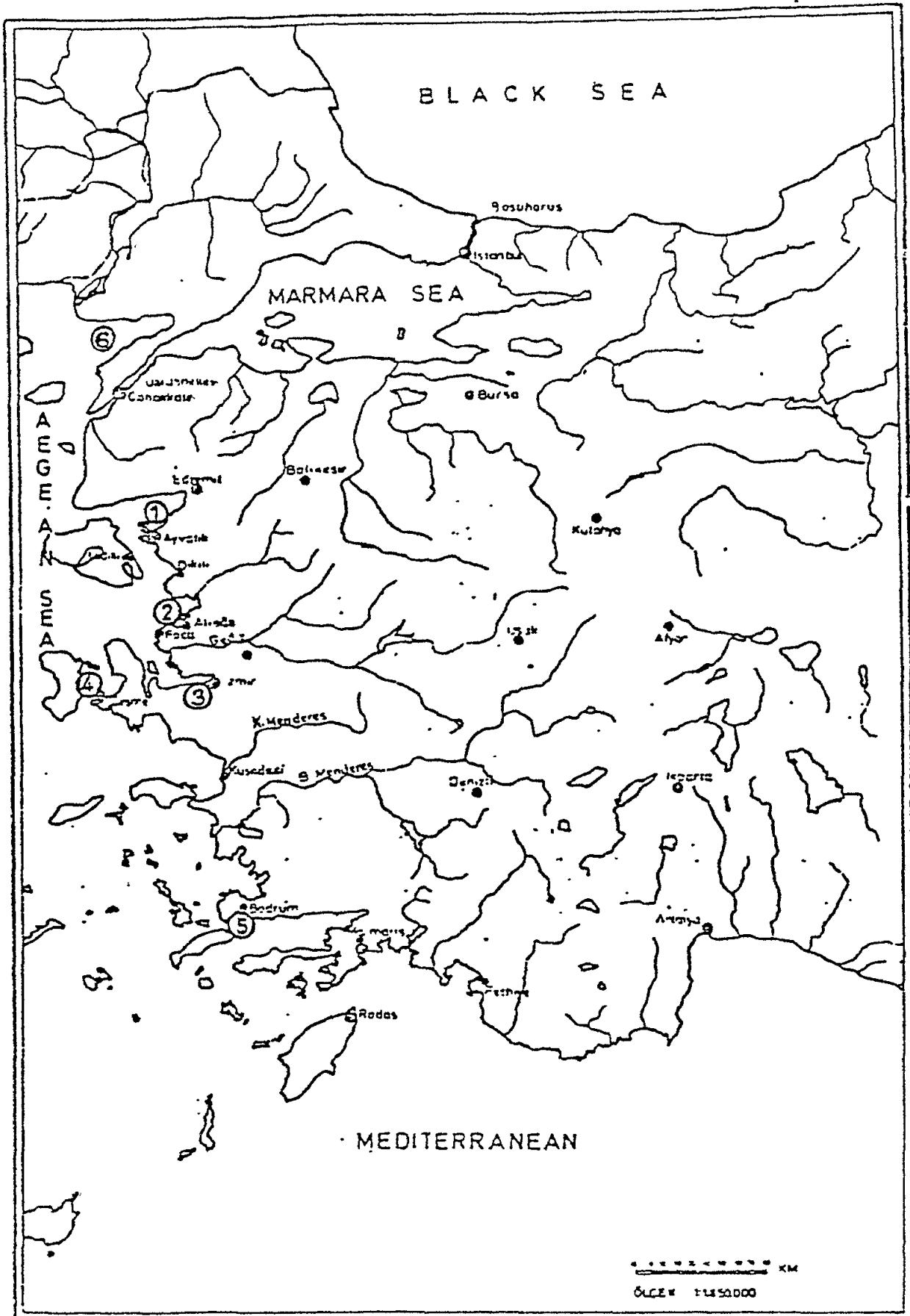


Fig. 1. Sampling stations

Table I

Sampling stations and corresponding organisms collected during 1979

Sample Code	Sample Stations	Scientific Names	Date of Collection
F.1	AYVALIK 26°41'00"E 39°19'00"N	1. <u>Mugil spp.</u> 2. <u>Mullus barbatus</u> 3. <u>Mytilus galloprovincialis</u> 4. <u>Carcinus mediterraneus</u>	1977-1980
F.2	ALJAGA. 26°58'00"E 38°48'00"N	1. <u>Mugil spp.</u> 2. <u>Mullus barbatus</u> 3. <u>Carcinus mediterraneus</u> 4. <u>Mytilus galloprovincialis</u> 5. <u>Palaemon adspersus</u>	1977-1980
F.3	IZMIR 27°09'00"E 38°27'00"N	1. <u>Mugil spp.</u> 2. <u>Mullus barbatus</u> 3. <u>Carcinus mediterraneus</u> 4. <u>Penaeus kerathurus</u> 5. <u>Mytilus galloprovincialis</u>	1977-1980
F.4	CESME 26°18'00"E 38°20'00"N	1. <u>Mugil spp.</u> 2. <u>Mullus surmuletus</u> 3. <u>Carcinus mediterraneus</u>	1977-1980
F.5	BODRUM 27°26'00"E 37°02'00"N	1. <u>Mugil spp.</u> 2. <u>Mullus barbatus</u> 3. <u>Penaeus kerathurus</u>	1977-1980
F.6	SAROZ BAY 26°40'00"E 40°35'00"N	1. <u>Thunnus thynnus thynnus</u>	1977-1980

Research Centre: Center for Marine Research
"Rudjer Boskovic" Institute
ROVINJ - ZAGREB
Yugoslavia

Principal Investigator: M. BRANICA

Period of Reporting: September 1976 to March 1981

INTRODUCTION

During a period of more than 20 years, laboratories of the research Centre gained experience in the development and application of electroanalytical techniques and neutron activation analysis (NAA) on trace and sub-trace element determination in the aquatic system, sea-water, sediments and organisms. From 1973 a large-scale monitoring of heavy metals in the Adriatic Sea began. It was part of the environmental study of the Adriatic Sea in which analysis of sea-water was carried out over the whole area, particularly in the northern part and Rijeka Bay.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The following obligatory species were sampled and analysed: Mytilus galloprovincialis and Mullus barbatus. The rest of the obligatory species, Thunnus thynnus, thynnus and Xiphias gladius could not be analysed since they are very rare in this area. For these mandatory species some alternative should be found.

The following non-obligatory species were analysed: Sardina pilchardus and Sepia officinalis.

Analysis of the sea-water and the particulate matter taken at the site where Mytilus galloprovincialis was sampled in Limski kanal, was carried out as well.

Pollutants analysed:

The following obligatory metals were determined, i.e. Hg, Cd, Cu, Pb, Se and Zn.

Non-obligatory elements determined were: Fe, Co, Cr, Ni, As, Br, Rb, Zr, Sc, Eu, Ag, Sb, Cs, Ba, La, Ce, Tb, Ta, Au, Th, Hf, U.

Areas studied: There were nine sampling stations in Rijeka Bay (10b, 10a, 9a, 8a, 7, 6, 2, Krk and Rabac) and two on the West Istria (Rovinj and Limski kanal). The sampling stations are indicated on the enclosed map (Fig. 1).

METHODOLOGY

Sampling and sample storage were performed according to the procedures proposed by FAO Fisheries Technical Paper No. 158. Three different analytical techniques and methods were used for the determination of the concentration of trace metals in marine organisms and two for sea-water samples.

The techniques applied were the following:

- electroanalytical (polarographic and voltammetric);
- neutron activation analysis (NAA); and
- atomic absorption spectroscopy (AAS).

The voltammetric technique was applied using anodic stripping voltammetry with the linear change of the potential (ASV) and with the pulse mode (DPASV) on the following electrodes placed in order of increasing sensitivity:

- hanging drop mercury electrode (HMDE);
- rotating glassy carbon thin film mercury electrode (RGCE);
- glassy carbon thin film mercury electrode with the efficient mixing system of the electrolyte (TMFE-Mix).

For the electroanalytical determination of the concentration of mercury in the dissolved phase, a special type of electrode, the rotating gold electrode, was developed.

The organic matter in the species to be analysed with the electroanalytical technique was decomposed by using the "wet procedure". The samples analysed by the NAA technique were dried, without destroying the organic matter.

The species analysed by applying the AAS technique, were treated with concentrated nitric acid and decomposed under increased pressure at about 160°C.

For complete mineralization, the samples were treated with a mixture of concentrated nitric, sulphuric and perchloric acid.

Intercalibration exercise:

In the frame of the intercalibration exercise organized by IAEA, Monaco, the following samples were analysed:

Sea plant (SP-M-1); Copepod (MA-A-1); Fish flesh (MA-A-2); Oyster (MA-M-1); NBS Standard Reference Material ("Orchard leaves").

The analyses were performed using three independent measuring procedures and techniques. The concentrations of Cd, Cu, Pb and Zn in the previously mentioned biological samples were determined.

RESULTS

During the period of the pilot-phase from 1976 up to now, heavy metals in the soft part of Mytilus galloprovincialis and the fillet of Mullus barbatus, Sepia officinalis and Sardina pilchardus have been determined. Results are reported in Tables I to XII as the range of concentrations, the average concentrations with the standard deviations. Sampling seasons and the areas are indicated, too.

In the clean area of the Limski kanal, which is already known as the traditional place for growing of mussels, Mytilus galloprovincialis was carefully sampled each month from June to December 1979 and analysed on the heavy metal concentrations. Beside the metal concentrations in the whole edible part of the mussel (see Table IV) the distribution of metals in its various organs was measured too (see Tables IV and V). The results of analysis of dissolved concentration of trace metals in the surrounding sea-water and the particulate matter are presented in Table VI. The concentration ratio of Cd, Pb, Cu and Zn in various organs of Mytilus galloprovincialis with respect to their concentration in sea water and particulate matter was expressed in the form of the concentration factor (see Table VII).

The concentration of dissolved trace metals, Cd, Cu, Pb and Zn, in sea water from the whole Adriatic Sea and its northern part are reported in Tables XIIa and XIIb. Beside those, the complexing capacity of the same samples of sea-water is reported indicating the bioavailability of heavy metals to the organisms.

Heavy metals in Mytilus galloprovincialis:

On the basis of the results presented in Tables I and II, where the concentrations of heavy metals Cd, Cu, Pb and Zn were determined in the soft part of Mytilus galloprovincialis according to the seasons, there is no evidence of seasonal variation of the heavy metal concentrations in those species. The results indicate that of the four investigated metals zinc is the most abundant in Mytilus galloprovincialis, while cadmium is the least abundant one.

The results of the analysis of the edible part of Mytilus galloprovincialis sampled in Limski kanal are represented in Table IV. Comparing these results with the one on heavy metal concentrations in Mytilus galloprovincialis sampled in Rijeka Bay it might be concluded that in spite of different surroundings in which the mussels were grown, i.e., the area of industrial pollution (Rijeka Bay) and the clean, isolated area of Limski kanal, the observed concentrations of heavy metals (except for Pb) are very similar. The distribution of trace heavy metals in different organs of the mussel Mytilus galloprovincialis are presented in Tables IV and V. The results indicate that the highest accumulation of Pb and Cu occurs in byssus, while of Cd in kidney. These results could indicate that the speciation of trace heavy metals plays an important role in the process of their accumulation and that in sea-water the speciation of each investigated metal is different.

If the concentrations of Cd, Cu, Pb and Zn in different organs of Mytilus galloprovincialis are divided with the average concentrations of the same metals in the dissolved state and the particulate matter, the factor of concentration of that metal in the particular part of the mussel is obtained. From Table VII, where the results are summarized, it follows that the concentration factors for Cd, Cu, Pb and Zn calculated with respect to the concentration in particulate matter are higher than with respect to the dissolved concentration.

Heavy metals in Mullus barbatus:

The results of the analysis of Mullus barbatus which were sampled seasonally from March 1977 till June 1978 are presented in Table VIII. The samples from

March 1977 were analysed by two independent methods, by electrochemical and by NAA. In the latter case, metals other than Cd, Cu, Pb and Zn were determined (see Table IX). In Table VIII samples were taken at two geographically separated areas, i.e. in Rabac, which belongs to Rijeka Bay and in Rovinj, which belongs to the West Istrian coast. Each value in Table VIII refers to only one determination.

As in the case of Mytilus galloprovincialis, the analyses for the concentrations of Cd, Cu, Pb and Zn in the fillet of Mullus barbatus do not indicate seasonal variations. From Table VIII it is possible to notice that Zn is again the most abundant metal in comparison with Cd, Cu and Pb, while Cd is the least abundant one.

Heavy metals in Thunnus thynnus thynnus (and/or Xiphias gladius):

The obligatory species Thunnus thynnus thynnus and/or Xiphias gladius were not analysed as they are very rare in the Adriatic Sea.

Heavy metals in other marine organisms:

In Table X the results of multi-element analysis of Sepia officinalis done by NAA are presented. The concentrations of obligatory and nonobligatory metals are given as the range between the minimum and maximum concentrations determined.

In Table XI the concentrations of Cd, Cu, Pb and Zn determined in the fillet of Sardina pilchardus according to the seasons are presented. The samples refer to two geographically separated areas, i.e., to Rovinj, which belongs to the West Istrian coast and to Rabac, which belongs to Rijeka Bay. Each value in the Table refers to only one determination.

Sepia officinalis was sampled only once, therefore it is not possible to draw any conclusions about the variation of trace metals according to the season, sampling area, size etc.

From Table XI it is possible to see that the concentration of determined trace heavy metals decreases (especially Pb one) from March 1977 toward June 1978, which might be an indication of the existing contamination of the samples in the starting measurements.

Heavy metals in sea-water:

In Tables XIIa and XIIb the concentrations of dissolved trace heavy metals in sea-water and its complexing capacity are presented. The results in Table XIIa are presented as the average concentrations of dissolved trace metals in the whole Adriatic Sea. The values, which decrease in the period from 1974 to 1980, indicate the improvement in the procedure of sampling, sample storage and the analysis. The results presented in Table XIIb refer to the sampling performed in the northern Adriatic on November 2, 7, 8, and December 6, 1979, on the transect Rovinj - estuary of the river Po.

CONCLUSIONS

In the study of marine pollution, the most essential problem is to recognize the natural biochemical cycle of the element and the real anthropogenic

influence on it. In the case of trace heavy metals, the mistake is very often made in considering all heavy metals as belonging to a single group. The efficiency of each metal fixation into the marine organism is influenced by its physico-chemical state and reactivity in sea-water. Consequently, additional information on the concentration of metal ions in sea-water and the formation of different ionic and redox species is also needed. The release of heavy metals into the marine environment is not always followed by their rapid concentration in the marine organisms. This comparative monitoring does not indicate any significant difference in trace metal concentrations of Mytilus galloprovincialis sampled in the environment with the significant industrial pollution (Rijeka Bay) and without it (Limski kanal). It is possible to conclude that Mytilus galloprovincialis in particular, and the living organisms in general, would not be suitable indicators of the marine pollution with the heavy metals. This statement is also proved by the broad and detailed discussion at the VI^{es} International Symposium "The Chemistry of the Mediterranean", Rovinj, May 1980, dealing with biological availability of different heavy metal species to bivalves.

Our measurements of the dissolved concentration of trace metals in sea-water clearly indicate that if the additional contamination of the sample, (through sampling, sample storage and analysis) is excluded, the investigated metals are present in sea-water of trace and sub-trace levels. There is no proportional relationship between the dissolved concentration of metals and the accumulated one. If the increased input concentrations of heavy metal are reduced through the absorption, precipitation and sedimentation processes, it seems more reasonable to consider and monitor the marine sediments as the indicators of marine pollution at the given area.

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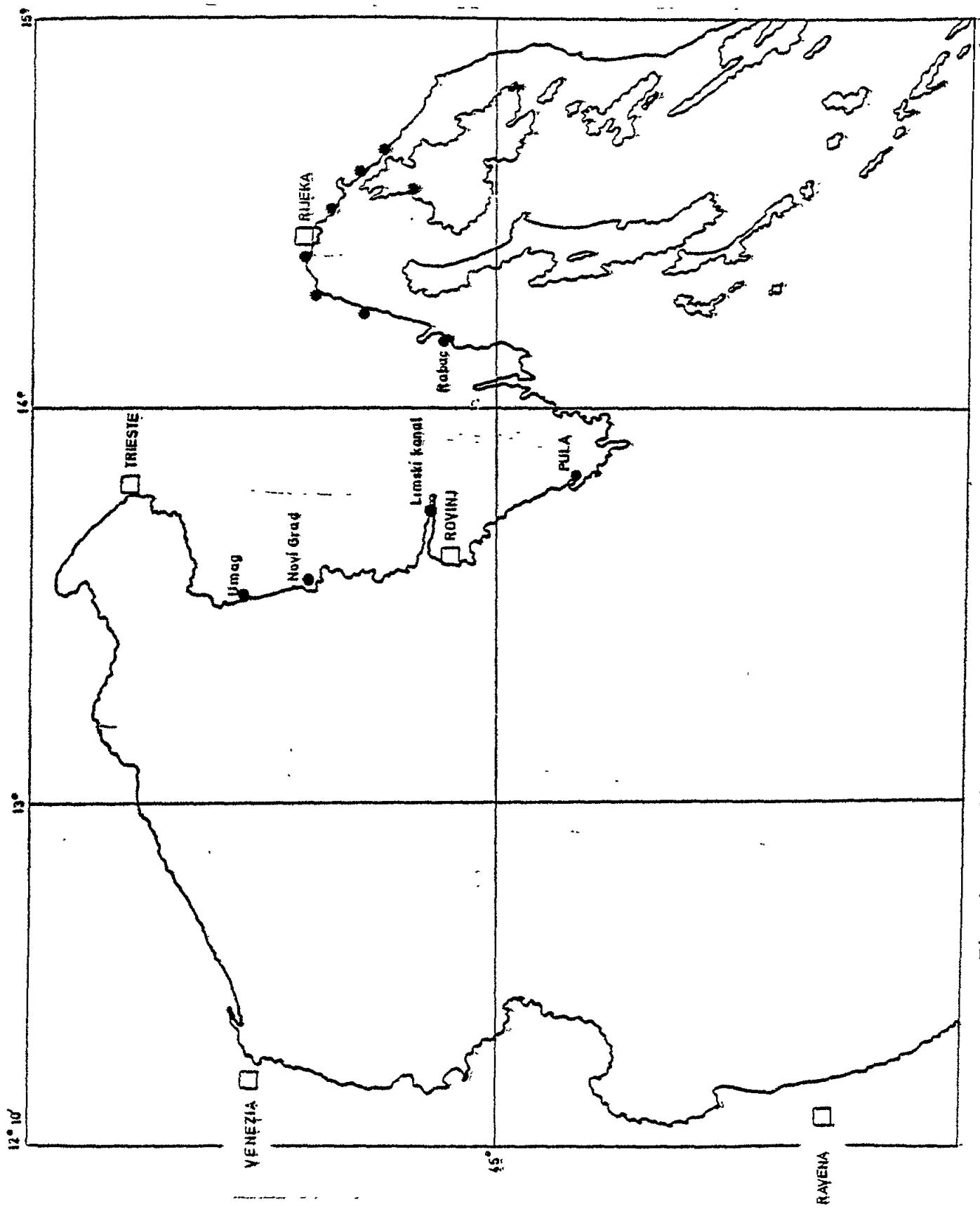


Fig. 1. Sampling stations in Rijeka Bay and along West Istrian Coast

Table I

Seasonal observations of heavy metal concentrations in soft part of Mytilus galloprovincialis sampled in the Rijeka Bay. The results were determined by electrochemical technique.

Year	Month	Concentration ($\mu\text{g/g. FW}$)				
		Cd	Cu	Pb	Zn	
1977	March	Range 87.5-100 Average 93.8	622.5- 912.5 787.5	1312.5-7825 4568.8	15625-22500 19063	
	June	Range 37.5-212.5 Average 111.1 ± 51.3	500 -1387.5 1267 ± 1212	412.5-2437.5 1115 1791	6750-64250 1875 ± 17724	
	Sept.	Range 62.5-475 Average 153 ± 132	438 -1638 1129 ± 430	350 -1925 1192 ± 573	5625-37625 18565-12606	
	Dec.	Range 63 -475 Average 157 ± 130	350 -1613 1018 ± 439	438 -3500 1295 ± 936	5630-37625 17274-13300	
1978	March	Range 63 -325 Average 163 ± 74	263 - 975 522 ± 209	63 - 725 432 ± 203	2500-18125 7931 ± 5677	
	June	Range 63 -150 Average 99 ± 28	288 - 463 367 ± 63	138 -1075 460 ± 381	3375- 2800 12306 ± 9283	
	Dec.	Range 56 -106 Average 81 ± 35	190 - 540 365 ± 247	690 -1870 1280 ± 834	6900-13800 10350 ± 4879	
	March	Range 175 -363 Average 272 ± 63	1000 -4400 2447 ± 1097	738 -4875 2073 ± 1474	19500-42500 30064 ± 9480	
1981	March	Range 75 -238 Average 153 ± 76	688 -3850 1515 ± 1324	550 -8200 2630 ± 3177	12350-42775 21870 ± 11988	

Table II

Seasonal observations of heavy metal concentrations in soft part of Mytilus galloprovincialis sampled at the West Irian Coast. The results were determined by electrochemical technique.

Year	Month	Concentration ($\mu\text{g/kg. FW}$)				
		Cd	Cu	Pb	Zn	
1977	March	Range 38- 63 Average 51 ± 18	525- 850 688 ± 230	75- 375 225 ± 212	12750-18250 15500 ± 3889	
	June	Range 50-288 Average 169 ± 168	413-1513 963 ± 778	600-1575 1088 ± 689	18875-29750 24313 ± 7690	
	Sept.	Range 400 Average	1763 1155 ± 141	908 488 ± 71	29625 18250 ± 7601	
	Dec.	Range 25- 74 Average 50 ± 35	1050-1250 282 ± 168	438- 538 113 ± 18	12875-23625 6938 ± 1503	
1978	March	Range 50- 75 Average 63 ± 18	163- 400 282 ± 168	100- 125 113 ± 18	5875- 8000 6938 ± 1503	
	June	Range 75-125 Average 100 ± 35	225- 263 244 ± 27	100- 225 163 ± 88	5750-10125 7938 ± 3094	
	Dec.	Range 38- 88 Average 63	250- 440 345	525-1440 982.5	8750-12500 10625	

Table III

The range of concentrations of metals others than Cd, Cu, Pb and Zn determined by NAA in soft part of Mytilus galloprovincialis. Sampling performed at Limski kanal, Rovinj, Rabac and Omisalj in March and June 1977.

Metal	Concentration ($\mu\text{g}/\text{kg. FW}$)	
	minimum	maximum
Hg _T	10.6	37.5
Se	1300	2160
Co	43	1870
Fe	8000	82000
Cr	150	462
Ni	30	340
As	2700	7700
Br	27000	95000
Rb	320	6500
Zr	450	1200
Ag	8	4300
Sb	12	31
Cs	15	73
Ba	1600	3200
La	26	97
Ce	35	187
Eu	0.8	1.9
Tb	1.2	2.6
Ta	2.6	6.3
Au	1.8	25.8
Th	9	52
Hf	3.3	10.3

Table IV

Concentrations of trace metals ($\mu\text{g}/\text{kg}$ FW) in *M. galloprovincialis*, sampled in Limpi Canal
from June to December 1979.

Sampling month	Average length(cm)	Total weight(g of FW)	Cd	Cu	Pb	Zn
June	6.02	16.42	edible part shell kidney	137(5) 40(2) 312(10-775(30)	1586(16) 4465(77) 3000(150-6300(310)	191(41) 1172(4) 1005(32)-3352(112)
July	5.50	17.20	edible part shell kidney	111(13) 9(0.2) 153(15)-367(20)	1624(74) 1118(32) 1223(40)-2502(80)	207(18) 853(40) 668(10)-1225(42)
August	5.68	14.22	edible part shell kidney	114(3) 310(4) 363(15)-710(15)	1021(28) 712(212) 1216(40)-2222(100)	156(181) 1112(225) 547(8)-3409(90)
September	-	-	-	-	-	-
October	6.18	22.03	edible part shell kidney	103(14) 30(8) -	1080(80) 951(20)	195(2) 118(27) 523(8)
November	6.38	29.77	edible part shell kidney	74(5) 4(0.7) 284(6)-645(10)	1126(56) 1229(16) 1190(35)-1285(51)	239(5) 77(60) 180(75)-3305(150)
December	6.12	13.13	edible part shell kidney	..102(1) 5(1) 474(32)-517(30)	599(76) 1352(100) 1083(31)-1303(30)	266(9) 804(81) 1387(43)-2782(110)

Note - The values in the brackets indicate the standard deviations

Table V

Distribution of Cd, Cu, Pb and Zn in the organs of *Mytilus galloprovincialis* sampled in June 1979 in Limski kanal. The concentrations of trace heavy metals are presented as the average (A) and as the range (R). The analysis were performed using AAS.

Organs	Concentration ($\mu\text{g}/\text{kg. FW}$)			
	Cd	Cu	Pb	Zn
Mantle without gonads:	A: 273 R: 202-344	1140 910-1370	581 446-716	21590- 17380-25790
Mantle with gonads:	A: 95 R: 94-96	1180 1010-1350	243 193-293	25900- 21870-29920
Gills:	A: 212 R: 183-241	1940- 1510-2370	568- 427-708	43750- 35130-32370
Lobial palps:	A: 250 R: 227-273	1620 1440-1790	366- 305-427	29760- 27500-32020
Foot:	A: 307 R: 281-333	1640 1580-1690	292 258-326	36320- 32000-40650
Adductor muscle:	A: 175 R: 164-185	830 800-890	149 146-152	25990- 25360-26610
Bivalve retractor muscle and foot retractor muscle:	A: 157 R: 142-172	910 890-930	162 152-172	32080- 31590-32570
Digestive gland with stomach and hepatopancreas:	A: 295 R: 288-303	2590 2440-2730	902 885-919	36570- 36320-36900
Liver (Hepatopancreas):	A: 371 R: 368-373	3390 3290-3490	915 907-923	51080- 49420-52730
Kidney:	A: 544 R: 312-775	4700 3000-6390	2209 1065-3352	45680- 45350-86000
Shell:	A: 40 R: 39-41	4400 4350-4460	1170 1166-1176	1650 1640-1670
Byssus:	A: 485 R: 395-610	14540 14450-14630	11040 10494-11583	81910- 68970-94840

Table VI

The average concentrations and standard deviations of Cd, Cu, Pb and Zn ($\mu\text{g}/\text{kg}$) in filtered sea water and the particulate matter, sampled in Limski Kanal in June 1979.

	Cd	Cu	Pb	Zn
Filtered sea water, pH 8:	<0.003	0.20 ± 0.07	0.03 ± 0.008	1.21 ± 0.33
pH 2:	0.015 ± 0.004	0.40 ± 0.22	0.13 ± 0.02	2.19 ± 0.76
Particulate matter	0.0023 ± 0.0022	0.115 ± 0.035	0.103 ± 0.025	0.110 ± 0.066

Table VII

Concentration factors of Cd, Cu, Pb and Zn in various organs of Mytilus galloprovincialis sampled in June 1979, with respect to their concentrations in dissolved and particulate form.

Organ:	Concentration-factors of							
	Zn-	Cd-	Cu-	Pb-	dissolved	particulate	dissolved	particulate
Mantle without gonads	9860	196270	18200	118700	2850	9910	4470	5640
Mantle with gonads	11830	235450	6330	41300	2950	10260	1870	2360
Gills	20000	398000	14130	92170	4850	16870	4370	5510
Lobial palps	13600	270550	16670	108700	4050	14090	2820	3550
Foot	16580	330180	20470	133480	4100	14260	2250	2830
Adductor muscle	11870	236270	11670	76090	2130	7400	1146	1450
Bivalve retractor muscle and foot retractor muscle	14650	291640	10470	68260	2275	7910	1250	1570
Digestive gland with stomach	16700	332450	1960	128260	6475	22520	6940	8760
Liver (Hepatopankreas)	23320	464360	24730	161300	8475	29480	7040	8880
Kidney	29990	597090	36270	236520	11750	40870	16990	21450
Shell	750	15000	2670	17390	11000	38260	9000	11360
Byssus	37400	744640	32340	210870	36350	126430	84920	107190

Table VIII

Seasonal observations of Cd, Cu, Pb and Zn concentrations in Mullus barbatus sampled at Rovinj (West Istrian coast) and Rabac (the Rijeka Bay). The results were determined by electrochemical technique.

Year	Month	Concentration ($\mu\text{g}/\text{kg FW}$)				
		Cd	Cu	Pb	Zn	
1977	March	Rovinj 100	525	1275	5250	
		Rabac 75	2550	2525	5500	
	June	Rovinj 225	1250	2500	16250	
		Rabac 175	750	1125	17500	
	Sept.	Rovinj 75	1300	17500	5500	
		Rabac 200	2250	1500	9500	
	Dec.	Rovinj 8	200	3000	3000	
		Rabac 75	175	1275	2500	
1978	March	Rovinj 25	250	2350	2750	
		Rabac 8	200	1150	2250	
	June	Rovinj 75	250	3200	3250	
		Rabac 8	150	2275	3250	
Rijeka Bay						
1978	June	Range	0.8-5	150-325	25-75	2000-5000
		Average	2.2 \pm 2.4	225 \pm 90	50 \pm 25	3083 \pm 1665

Table IX

The range of concentrations of metals others than Cd, Cu, Pb and Zn determined by NAA in Mullus barbatus. Sampling sites Rovinj and Rabac in March 1977.

Metal	Concentration ($\mu\text{g}/\text{kg FW}$)	
	minimum	maximum
Hg _T	~ 79	110
Se	610	5150
Fe	14000	59000
Ca	9.7	35
Br	14300	47000
Rb	635	2000
Ag	18	81
Sb	11.5	20.4
Ca	56	224
Br	1700	2740
Sc	1.8	7.8
Eu	0.6	0.9
Tb	0.9	2.0
Au	0.6	12.9
Th	4.7	7.5
U	590	730

Table X

The range of metal concentrations determined by NAA in fillet of Sepia officinalis. The sampling was performed in March 1977 in Rabac and Rovinj.

Metal	Concentration ($\mu\text{g}/\text{kg FW}$)	
	minimum	maximum
Hg _T	160	200
Cd	650	
Zn	23000	29000
Se	1800	5000
Fe	300	4000
Ca	150	51200
As	3000	50000
Br	30000	33000
Rb	1300	1400
Ag	650	1000
Cs	12	23
Au	2.1	

Table XI

Seasonal observations of Cd, Cu, Pb and Zn concentrations in fillet of Sardina pilchardus sampled at Rovinj (West Istrian coast) and Rabac (Rijeka Bay). The results were determined by electrochemical techniques.

Year	Month		Concentration (µg/kg FW)			
			Cd	Cu	Pb	Zn
1977	March	Rovinj	125	3650	1550	6500
		Rabac	250	1500	4450	22250
	June	Rovinj	213	1375	450	20000
		Rabac	200	875	525	22500
1978	Sept.	Rovinj	125	1375	488	12500
		Rabac	175	1000	500	10000
	Dec.	Rovinj	23	375	25	10500
		Rabac	50	700	10	9000
	March	Rovinj	8	475	50	6250
		Rabac	50	675	25	3250
	June	Rovinj	50	1100	25	3500
		Rabac	50	925	75	3250

Table XIIa

Average concentrations of Cd, Cu, Pb and Zn ($\mu\text{g} \cdot \text{dm}^{-3}$) in filtered sea water sample of the Adriatic Sea in different sampling periods (Cruises of RV "Andrija Mohorovičić"). The results were determined by electrochemical techniques.

Sampling period		Cd	Cu	Pb	Zn
September	1974	0.08	1.2	0.44	9.7
May	1975	0.07	0.70	0.50	9.7
February	1976	0.09	0.90	0.60	8.0
January	1980	(pH 8) 0.004 (pH 2) 0.007	0.090 0.240	0.046 0.071	1.8 3.7

The complexing capacity of the opened sea water samples is between 0.67 and 2.5×10^{-8} mol eq. $\text{Cu}^{2+} \cdot \text{dm}^{-3}$.

Table XIIb

The average concentration and the standard deviation of Cd, Cu, Pb and Zn in filtered sea water sample of North Adria at pH 8.2 and 2.3. The results were determined by electrochemical technique.

pH	Concentration ($\mu\text{g} \cdot \text{dm}^{-3}$)			
	Cd	Cu	Pb	Zn
8.2	0.002 ± 0.001	0.03 ± 0.05	0.029 ± 0.024	2.0 ± 0.9
2.3	0.001 ± 0.001	0.195 ± 0.114	0.117 ± 0.122	3.9 ± 1.6

The average complexing capacity of the same surface samples of sea water equals to 2.9×10^{-8} M Cu^{2+}/l .

Research Centre: Marine Biological Station
 Institute of Biology
 University of Ljubljana
 PORTOROZ
 Yugoslavia.

Principal Investigator: S. GOMISCEK (1976-1979), P. STEGNAR
 (from 1980)

Period of Reporting: From 1976 until March 1980

INTRODUCTION

The Marine Biological Station has been occupied with the monitoring of the distribution of potentially toxic elements in sea-water, sediments, plankton and selected larger biota (fish, mussels) from 1973 onwards, but the analyses have been performed by collaborating laboratories of the University of Ljubljana, the Chemical Institute "Boris Kidric", and the Nuclear Institute "Jozef Stefan". 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 have already been partly published (Kosta, et al., 1978, Stirn, et al. 1974).

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

Obligatory species: The mussel Mytilus galloprovincialis was available at all sampling sites regularly, the red mullet Mullus barbatus only occasionally. These two species were systematically monitored for the basic purpose of MED POL II. A number of non-obligatory species were also sampled and analysed in order to obtain an overview on the concentration of metals in various taxa, regardless of whether they play a role in human nutrition or not.

Pollutants analysed:

The obligatory metals Hg, Cd, Cu, Pb, Mn, Se and Zn were determined, as well as As, Sb, Ni and Cr.

Area studied:

The sampling area is presented in Fig. 1 and the geographical co-ordinates of particular sampling stations are given in Table I.

Some of the sampling sites were located in the S.R. Slovenia coastal waters. The Bay of Strunjan served as a reference area free of local pollution sources.

The Bay of Koper is heavily polluted by sewage discharges, partly by some industrial wastes, and influenced by the river Rizana. In addition, sampling of fish was performed in open waters off the Bay of Piran, serving as a reference area, while the mercury-laden fish were sampled off Grado, as they were influenced by mercury discharges carried into the marine environment by the river Soca (Isonzo).

The mussels were collected all along the northern Adriatic coast and at the "super-clean" locations (Jabuka Island in the middle Adriatic). Biological material, mainly mesopelagic fish and bathyal invertebrates, bred far from pollution sources, were collected in mesopelagic nekton (100-400 m depth) and offshore bathyal benthos (100-300 m depth) in the middle and southern Adriatic.

An experimental area was located in the Lagoon of Strunjan formed by two basins with natural communities. One of them received 300 l of sewage daily, experimentally discharged, while the other was kept clean for comparison of conditions.

METHODOLOGY

Samples were analysed mainly by AAS, partly at the Chemical Institute "B. Kidric" using Perkin-Elmer systems, and partly at the MBS at Portoroz using Varian systems. Preparation of samples, decomposition and analytical methods were carried out according to the instructions of FAO Fisheries Technical Paper No.158. Many samples were checked for Hg concentrations and many selected samples were also analysed for Se, As, Cu, Zn, Mn, and Sb by NAA at the Nuclear Institute "J. Stefan" by the methods described in Kosta L., et al., 1978.

Intercalibration exercise:

The analyses of oyster (MA-M-1), fish (MA-A-2), copepod (MA-A-1), sea plant (SP-M-1) and sediment (SD-M-1) were performed using NAA and AAS techniques. The concentrations of Hg, Cd, Ni, Cr and Pb were determined.

RESULTS

Metals in Mytilus galloprovincialis:

The results of the metal concentration in Mytilus galloprovincialis, which was sampled in "clean" and polluted areas of the Adriatic sea, are presented in range, mean and standard deviation in Table II.

In Table III the mean concentrations of metals (taken from Table II) in Mytilus galloprovincialis, which was sampled in "clean" and polluted areas of the Adriatic Sea, are summarized. Note the significant accumulation of Hg, Zn, Cr and Ni but not of Cd, Pb, etc.

Metals in Mullus barbatus:

Table IV summarizes the results of metal concentration determination in Mullus barbatus, which was sampled in unpolluted and polluted areas of the Adriatic Sea. In single samples the concentration of metals was determined in internal organs (liver and kidney).

Metals in other marine organisms:

Results concerning metal concentrations in non-obligatory species of fish, invertebrates and plants mainly from clean (C) and sewage-polluted (P) coastal waters along S.R. Slovenia, clean offshore waters of the middle and southern Adriatic (M and S) and western offshore waters of the northern Adriatic (NW) contaminated by industrial-river discharges, are summarized in Table V.

Results on the accumulation of metals in sediments and selected biota as a consequence of artificial sewage discharges into an experimental lagoonal ecosystem are given in Table VI. With some exceptions (significantly increased concentrations of Pb, Fe and Cr in sea-grass and Mn in oysters and a slight increase of Pb, Zn, Cr, Ni and Fe in oysters and partly in shrimp (*Upogebia*) only the accumulation of Hg, Cd, Pb, Zn, Cu and Fe in sediments is of any importance.

PUBLICATIONS.

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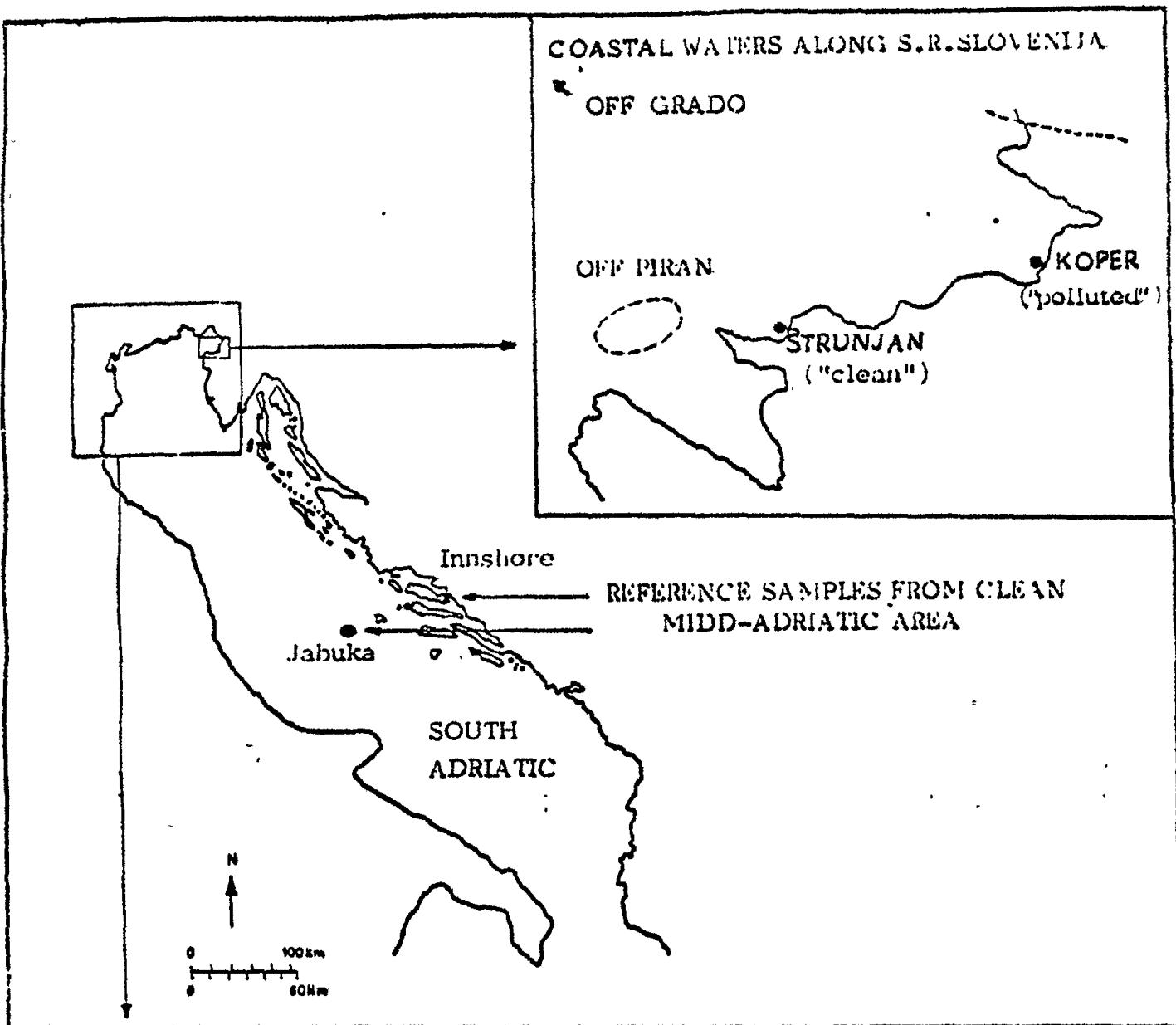


Figure 1. Sampling area

Table I

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'

Table II

Concentrations of metals ($\mu\text{g}/\text{kg FW}$) in *Mytilus galloprovincialis*Middle Adriatic Offshore "Clean" Area (Island Jabuka)

Hg	26	-	45	34	9.8
As	6,530	-	11,340	8,935	3,401.2
Cn	600	-	1,070	835	332.3
Zn	8,130	-	9,390	8,760	890.9
Sb	12	-	49	30	26.2
Cr	240	-	384	321	67.6
Ni	606	-	1,278	924	341.8
Pb	366	-	650	510	131.5

Middle Adriatic Inshore Area Industrially Heavily Polluted

Hg	2,320	-	7,000	5,209	2,077.1
Cd	159	-	186	172	19.1
Se	900	-	1,750	525	530.3

Northeastern Adriatic Inshore "Clean" Area (Istrian coast)

Hg	40	-	175	72	43.9
Cd	122	-	427	241	100.8
Se	123	-	910	517	556.5
As	4,600	(single sample)	-	-	-
Cu	1,340	-"	-	-	-
Zn	65,200	-"	-	-	-
Sb	23	-"	-	-	-
Ni	154	-	294	219	53.0
Cr	82	-	223	129	54.6
Pb	128	-	315	201	77.6

Table II(continued)

<u>Northwestern Adriatic Inshore Polluted by Hg-discharges</u>					
<u>from River Soča (Isonzo) and Industry</u>					
Hg	240	-	1,640	588	282.0
Cd	177	-	402	212	30.0
Se	590	-	1,120	802	164.3
As	2,100	-	5,300	3,240	1,348.3
Cu	790	-	1,260	1,036	205.0
Zn	10,600	-	40,000	23,400	11,822.6
Sb	4	-	30	12	10.6
Mn	520	-	1,070	770	232.5
Cr	142	-	711	341	181.9
Ni	167	-	1,020	571	278.8
Pb	62	-	262	161	69.8
<u>Northeastern Adriatic Inshore Polluted by Mixed Port-effluents</u>					
<u>and Sewage (Bay of Koper)</u>					
Hg	40	-	198	124	56.3
Cd	120	-	372	208	118.6
Se	330	-	940	579	324.7
As	2,800	(single sample)	-	-	-
Cu	1,550	--"	-	-	-
Zn	30,700	--"	-	-	-
Sb	18	--"	-	-	-
Cr	256	-	651	358	120.7
Ni	160	-	335	219	60.4
Pb	201	-	419	284	91.5

Table III

Summarized table of mean concentrations of metals found in
Mytilus galloprovincialis from some areas of the Adriatic Sea(1976-1980)

ELEMENTS p.p.m. FW	A R E A S				
	CLEAN OFFSHORE SOUTH	CLEAN INSHORE NORTH	POLLUTED SEWAGE NORTH	POLLUTED RIVER NORTH	POLLUTED INDUSTRY SOUTH
	0.034	0.072	0.124	0.588	5.209
Cd	-	0.241	0.208	0.212	0.172
Se	-	0.517	0.579	0.802	0.525
As	8.900	4.600	2.800	3.240	-
Cu	0.835	1.340	1.550	1.036	-
Zn	8.760	65.200	30.700	23.400	-
Sb	0.030	0.023	0.018	0.012	-
Cr	0.321	0.129	0.358	0.341	-
Ni	0.924	0.219	0.219	0.571	-
Pb	0.510	0.201	0.284	0.161	-

Significant concentrations of Hg,Zn,Cr and Ni, but not of Cd,Pb and others, were found.

Table IV Metals in Mullus barbatus

Eastern Offshore-waters of North Adriatic

(Not contaminated by metals)

FLESH

Hg	98	-	100	99	1.4
Cd	234	(single sample)	-	-	-
As	14,450	-	16,600	15,525	1,520.3
Se	390	-	420	405	21.2
Cu	140	-	160	150	14.1
Zn	2,900	-	3,230	3,065	233.3
Sb	1.3	-	1.5	1.4	0.1

INT. ORGANS

(single samples)

	Hg	Se	As	Zn	Cu	Sb
LIVER	260	3,160	12,100	26,300	2,520	1.4
KIDNEY	220	5,470	-	-	-	-

Western Offshore-waters of North Adriatic

(River-industry contaminated, particularly by Hg.).

FLESH

Hg	222	-	228	227	0.7
Cd	266	(single sample)	-	-	-
As	12,140	-	13,140	12,780	905.1
Se	260	-	270	265	7.1
Cu	400	-	700	550	212.1
Zn	3,510	-	3,590	3,550	56.6
Sb	1	-	1.3	1.3	1

INT. ORGANS

(single samples)

	Hg	Se	As	Zn	Cu	Sb
LIVER	460	1,720	7,700	13,700	1,800	1.3
KIDNEY	410	1,560	-	-	-	-

Table V

Metal concentrations (ppm) in non-obligatory specimens sampled in clean (C) and sewage-polluted (P) coastal waters along S.R.Slovenia, clean offshore waters of the middle and southern Adriatic (M and S) and western offshore waters of the northern Adriatic (NW)

	Species.	Hg	Cd	Se	As	Cu	Zn
	<u>Fucus</u> (C)						
A	<u>virsoides</u>	0.01	0.15	-	10.0	1.71	8.0
L	<u>F.virsoides</u> (P)	-	0.05	-	9.50	0.72	26.5
G							
A	<u>Ulva</u>						
E	<u>rigida</u> (C)	0.02	0.01	-	0.68	0.66	1.32
	<u>U.rigida</u> (P)	0.01	0.02	-	0.59	0.50	0.53
S	<u>Tethya</u> (C)						
P	<u>aurantium</u>	0.014	0.35	0.18	3.56	0.92	13.20
O							
N	<u>Verongia</u> (C)						
G	<u>aerophoba</u>	0.140	0.09	2.63	21.38	5.14	6.42
E	<u>Halichondria</u>						
S	<u>paniacea</u> (C)	0.019	0.14	0.12	1.85	0.64	1.90
	<u>Ostrea</u> (C)						
M	<u>edulis</u>	0.04	-	0.37	3.4	26.8	248.0
O	<u>O.edulis</u> (P)	0.04	-	0.32	2.5	55.8	453.0
L							
L.	<u>Octopus</u> (C)						
	<u>vulgaris</u>	0.07	-	0.34	-	-	-
	<u>Upogebia</u> (NW)						
	<u>littoralis</u>	0.34	-	0.52	-	-	-
D	<u>U.littoralis</u> (P)	0.05	0.01	-	1.7	15.7	18.2
E	<u>U.littoralis</u> (C)	0.05	0.03	-	3.2	14.7	21.1
C	<u>Pagurus</u> sp. (P)	0.04	-	0.59	-	-	-
A	<u>Pagurus</u> sp. (C)	0.11	0.22	0.93	24.0	50.0	27.2
P	<u>Pilumnus</u> sp. (P)	0.02	-	0.19	4.6	21.0	23.9
O	<u>Pilumnus</u> sp. (C)	0.06	-	0.81	-	-	-
D							
A	<u>Portunus</u>						
	<u>depurator</u> (M)	0.86	-	1.77	80.7	13.9	19.6
	<u>P.depurator</u> (P)	0.03	-	0.26	3.7	24.4	22.6
	<u>P.depurator</u> (C)	-	0.02	-	3.3	11.0	13.0
	<u>Nephrops</u>						
	<u>norvegicus</u> (M)	1.67	-	1.43	-	-	-

Table V. (continued)

	Species	Hg	Cd	Se	As	Cu	Zn
E	<u>Sphaerech.</u> (C)						
C	<u>granularis</u> (gonad)	0.30	-	1.77	27.6	3.9	86.7
H	<u>Ophiotrix</u> (C)						
I	<u>fragilis</u>	0.15	0.26	0.84	1.3	0.9	29.8
N.	<u>Spatangus</u> sp. (M)	0.30	0.08	2.01	6.5	-	-
T	<u>Ascidia</u> sp. (M)	0.05	-	0.67	141.7	5.9	19.6
U	<u>Ascidia</u> sp. (C)	-	0.02	-	2.8	4.5	17.5
I	<u>Microcosmus</u> (C)						
C.	<u>sulcatus</u>	-	0.05	-	4.5	0.9	15.0
	<u>Torpedo marm.</u> (M)	0.65	-	0.26	-	1.56	6.9
	<u>Raja clavata</u> (M)	0.67	-	0.45	-	-	-
	<u>Mustellus</u> sp. (M)	1.84	-	0.46	-	-	-
F	<u>Clupea pilch.</u> (C)	0.10	-	-	-	-	-
I	<u>Boops boops</u> (M)	0.37	-	0.63	3.9	0.20	4.0
H	<u>Pagellus erythr.</u> (M)	0.66	-	0.56	5.9	0.25	3.1
	Mesopelagic (M) fish (mean)	0.04	-	1.12	4.6	1.15	17.1
	Mesopelagic (S) fish (mean)	0.06	-	1.36	3.2	1.27	18.2

Note: These results were partly published by Kosta et al. (1978) and Stegnar et al. (1978)

Table VI

Data on metal accumulations in selected biota and sediments from artificially sewage-polluted (P) and blank "clean" lagoon (C) of Strunjan. Concentration in p.p.m. fresh weight (sediments dry weight)

S P E C I E S	E L E M E N T S										
	Hg	Cd	Pb	Zn	Cr	Ni	Cu	Fe	As	Mn	Sb
Sediment	(C) AAS (P)	(0.010) 0.632	0.16 0.27	18.38 20.98	131.2 167.7	0.04 0.04	0.05 0.05	23.5 26.5	22x10 ³ 24x10 ³	5.03 2.78	- -
<i>Ulva rigida</i>	(C) NAA (P)	0.016 0.005	0.01 0.02	- -	1.3 0.5	- -	- 0.5	0.7 0.5	- -	0.68 0.59	17.5 6.7
<i>Cymodocea nodosa</i>	(C) AAS (P)	0.083 0.096	0.12 0.15	0.95 1.48	20.3 19.7	0.96 1.91	2.14 2.67	2.6 2.6	339.9 772.9	0.34 0.45	- -
<i>Crassostrea gig.</i>	(C) AAS (P)	0.096 0.088	0.23 0.23	0.27 0.69	385.1 342.3	0.30 0.51	0.53 0.90	17.1 16.6	117.9 172.8	2.32 1.68	- -
<i>Crassostea gig.</i>	(C) NAA (P)	- -	0.11 0.07	- -	123.0 225.0	- -	- 16.0	24.0 -	- -	6.53 3.80	2.8 11.5
<i>Mytilus gallopr.</i>	(C) AAS (P)	0.066 0.045	0.25 0.21	0.04 0.04	32.4 36.6	0.41 0.35	1.18 0.64	1.3 1.1	82.8 77.2	1.82 1.44	- -
<i>Mytilus gallopr.</i>	(C) NAA (P)	- -	0.15 0.15	- -	19.0 20.0	- -	- 1.0	1.3 1.0	- -	7.40 2.10	2.2 1.9
<i>Upogebia litt.</i>	(C) AAS (P)	0.051 0.054	0.03 0.01	0.81 0.76	21.1 18.2	0.39 0.47	0.65 0.57	14.7 15.7	161.0 209.8	3.22 1.66	- -

Research Centre: Institute of Oceanography and Fisheries
SPLIT
Yugoslavia

Principal Investigator: L. STOJANOSKI

Period of Reporting: From 1978 to 1979

INTRODUCTION

The analyses of heavy metals in marine organisms should contribute to a better understanding of the level of pollution.

METHODOLOGICAL CONSIDERATIONS

Selection of the species:

The obligatory species, *Mytilus galloprovincialis* and *Mullus barbatus* were selected for the analysis.

Pollutants analysed:

Mercury and cadmium were analysed.

Area studied:

The sampling stations were located in the middle and southern Adriatic. No map of the sampling area was attached to the report.

METHODOLOGY

Fish samples were obtained with research trawler m/b "Bios". Shellfish were collected manually. Methods used are those described in FAO Fisheries Technical Paper No. 158.

Intercalibration exercise:

This was not performed.

RESULTS

Some preliminary results of the analyses were reported in LOG-Forms.

DISCUSSION OF RESULTS

These are the first results of heavy metal analyses performed at the laboratory. Not enough analyses were performed for any scientific comment.

Research Centre:

Laboratory for Trace Element Analyses
Department of Physics and Mathematics
Faculty of Industrial Pedagogy
University of Rijeka
RIJEKA
Yugoslavia

Principal Investigators:

V. VALKOVIC and A. LJUBICIC

No final report was submitted by the Laboratory. The results for 1977 and 1978 were presented during the Intergovernmental Review Meeting of Mediterranean Coastal States on the Mediterranean Action Plan (Barcelona, 11-13 February 1980) and published in the Summary Reports on the Scientific Results of MED POL (UNEP/IG-18/ INF.3; Part I, pp. 189-191; Barcelona, 6 February 1980).

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Leoforos Vassileos Konstantinou, 48
116 35 Athènes
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