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Meeting of Experts to Evaluate the
Pilot Phase of MED POL and to Develop
a Long-Term Monitoring and Research
Programme for the Mediterranean
Action Plan

Geneva, 12-16 January 1981

CO-ORDINATED MEDITERRANEAN POLLUTION MONITORING AND
RESEARCH PROGRAMME (MED POL)
PART I : SUMMARY SCIENTIFIC REPORT
FEBRUARY 1975 - JUNE 1980



FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS



WORLD HEALTH ORGANIZATION



WORLD METEOROLOGICAL ORGANIZATION



INTERNATIONAL ATOMIC ENERGY AGENCY



INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION

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MED POL I : BASELINE STUDIES AND MONITORING OF OIL AND PETROLEUM

HYDROCARBONS IN MARINE WATERS (Prepared by IOC)

I. INTRODUCTION

This report is based on the following material:

- a) A compilation of the individual reports of the Principal Investigators of MED POL I (UNEP/IG.18/INF.3) presented to the UNEP Intergovernmental Review Meeting of Mediterranean Coastal States on the Mediterranean Action Plan (Barcelona, 11-13 February 1980).
- b) An ad hoc IOC document entitled "Summary report on the scientific data of the Pilot Project Baseline Studies and Monitoring of Oil and Petroleum Hydrocarbons in Marine Waters - MED POL I."
- c) The final reports from the Principal Investigators in the following countries: Cyprus, Egypt, France (Montpellier), Greece (Athens, Demokritos and Thessaloniki), Malta, Spain (Cadiz), Turkey and Yugoslavia (Zagreb), covering the period up to March 1980.

II. AREAS STUDIED

Most of the areas covered so far by the participating Research Centres are rather limited; indeed, some of them are very local. The reasons for this are mainly logistical; e.g., availability of suitable ships and adequate manpower to carry out the MED POL projects. Nevertheless, the Israel Oceanographic and Limnological Research Co. Ltd., in Haifa, conducted several cruises covering most of the Levantine Basin, and the Demokritos Nuclear Research Institute in Athens was able to sample regularly various sites in the Aegean Sea and, at a later stage, a part of the Ionian Sea as well.

Although UV fluorescence data are now available from 10 institutes the southern coast is still insufficiently covered. Several important coastal regions with fisheries, tourism and industrial activities are covered by the Pilot Project. When more results and experience have been gained from MED POL VI (coastal transport of pollutants) the results from these areas may become valid for parts of the coast not yet included in the studies.

III. MATERIAL AND METHODS

Oil Slicks: The procedure recommended in the IOC Manuals and Guides No.7 was generally followed by participants in MED POL I.

Floating tar balls: The Manual leaves considerable freedom to the participating institutes as far as choice of equipment and frequency of observations are concerned.

Tar on beaches: Various techniques had been favoured by the Principal Investigators, although the Manual calls for sampling of a few 1m-wide strips on each beach and with a frequency of at least every two weeks. All Principal Investigators used strip sampling in one way or the other. One of them also used sampling of 1-m² quadrats for complementary information (with an accompanying uncertainty in the reporting as to which data came from the use of which method). Some of the reports reflected sampling every 15 days, and some others, sampling apparently every 9th and 10th day. One institute reported a variant of this with sampling every 9th and 10th day in each month.

Dissolved/dispersed hydrocarbons: Most of the Principal Investigators' reports indicated that they adhered to the Manual. Most reports contain data for the 1m depth and the sampling seems to have been carried out according to the Manual in most cases. However, most investigators seem to take one sample at each occasion and only few practiced multiple sampling or reported data from multiple samples.

Two different analytical techniques have been employed: infra-red spectrophotometry and ultraviolet fluorescence spectrophotometry. Most of the Principal Investigators seem to have followed the procedure in the Manual or at least something rather similar.

One of the Principal Investigators reported data from sediment analysis.

So far several of the participating Research Centres have not participated in the intercomparison exercise which was only partly successful. The shape of the chrysene emission spectrum, and the fact that, for some of the samples, the emission maxima appeared at wrong wavelengths, suggest that the intercomparison exercise did not show the true comparability between the participating laboratories.

IV. RESULTS

Oil Slicks: The data reported within MED POL I are very few. The observations are only qualitative or at best semi-quantitative.

Floating tar balls: This component of MED POL I provide a simple quantitative method of monitoring one of the results of petroleum hydrocarbon pollution: the quantity of weathered oil in the form of tar balls. Since tar balls come mainly from tanker operations, other shipping and accidental spills, monitoring of tar-ball concentrations over a reasonable time period should provide information on the effectiveness of measures that have been introduced to reduce oil pollution from these sources.

Data are reported from only a few of the Research Centres, making a temporal and spatial evaluation of the floating tar balls premature.

Tar on beaches: It is apparent from the differences in values obtained at different beaches that some are strongly susceptible to contamination by tar balls whereas others are almost completely free. The concentration of tar balls appears to depend upon the exposure of the beach to prevailing onshore winds (and sometimes currents) with a fairly long stretch of open water. Examples from Cyprus and Malta illustrate this point. A beach on the south-western coast of Cyprus exposed to the onshore prevailing wind has a far higher concentration than a beach on the south coast sheltered from the prevailing winds by a headland. Similarly a beach on the western coast of Malta exposed to the prevailing westerly winds has a higher concentration than one on the eastern coast that is effectively free from tar.

Information from Greece shows that a beach in Patraikos Gulf, which is exposed to the westerly winds, has some tar, whereas a beach in Messiniakos Gulf, which opens to the south, is clean, as are the beaches monitored on the islands of Lesbos and Crete. The seasonal variation also seems to depend on the strength and direction of the prevailing winds. On the coast of Cyprus, concentrations are higher in winter than summer, correlating with wind strength and direction. A similar seasonal variation is apparent for the western coast of Malta, whereas a beach in a bay on the south coast of Malta showed some contamination during the period of the sirocco in 1977. Similar correlation between tar concentration and wind strength and duration was reported from Egypt.

Apart from these general conclusions, the interpretation of the data is difficult. Where values have been determined on the 9th and 10th days, the concentration after the first day is usually far higher than the value after 9 days divided by 9, but not equal to the value after 9 days. In other words the beach sorts itself out fairly quickly but needs more than one day to reach equilibrium. Thus the concentration should not be considered as an accumulation but should be regarded as an instantaneous value of the mean tar concentration on the beach.

The concentration recorded on any one beach will also depend on the character of the beach, including its slope and tidal range; consequently, any regional assessment is extremely difficult.

Dissolved/dispersed hydrocarbons: The data for dissolved/dispersed petroleum hydrocarbons may be divided into two groups depending on the analytical techniques used:

Aromatic hydrocarbons

The technique adopted for MED PQL I, UV spectrofluorimetry, is sensitive (but not specific) to those aromatic hydrocarbons that are considered to be the more hazardous components of petroleum oils in the marine environment. If the type of oil is known and samples are available (as may be the case in a tanker accident), then it is possible to use this technique to

determine the concentration of the oil in the seawater samples. However, in a monitoring programme, the type of oil is not usually known and comparison against some standard is necessary. The standard chosen for MED POL I was chrysene, but not all the results were reported in concentrations referred to chrysene. The gravimetric concentration of the pollutant oil may be from 2 to 20 times the value in chrysene units, depending upon the type of oil and the proportion of aromatic hydrocarbons it contains. The oil is often not strictly dissolved in the sea-water, some of the hydrocarbons being associated with particulate matter; hence the sea-water cannot be considered homogeneous. In sampling such a heterogeneous medium the concentration in the sample may depart considerably from the mean concentration in the sea-water. The concentration also varies with depth.

Total extractable organics

Some institutes where U.V. spectrofluorimeters were not available have submitted data obtained by infra-red spectrometry. The methods used, although not identical, are sufficiently similar for a comparison to be made. The methods are sensitive to the organic compounds in the sea-water sample that are extracted by the solvent used (normally CCl_4) and so the value presented may be regarded as the concentration of total extractable organics, which, however, is well below the concentration of all organic material in the water. The values are useful inasmuch as the petroleum hydrocarbon content cannot exceed the total extractable organics.

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

1. INTRODUCTION

The evaluation contained in this document is based on the final scientific reports submitted by the participating research centres, as well as on data provided on LOG FORMS for computer treatment. As at 1 July 1980, 25 of the 32 participating research centres had submitted their final reports. Of the remaining seven centres five had submitted the latest scientific report during 1979 as part of the normal reporting routine of the pilot project.

During the first half of the pilot phase the number of analyses reported was rather limited; this made possible the evaluation of results from all participants without the use of computer facilities. A preliminary evaluation on a Mediterranean basis was also presented and discussed at the Mid-term Expert Consultation, Dubrovnik, 2 - 13 May 1977. As the participating centres improved their analytical capabilities during the second half of the pilot phase, the number of analyses performed increased considerably. It was, therefore, apparent that, for the preparation of the final report, the use of computer facilities for data treatment would be necessary.

The LOG FORMS, which serve as the basis for entering the data into a computer system, were completed and provided in a usable form by 29 centres. A total of more than 13,000 data lines, each giving one analytical value, as well as information on location and biological parameters, was reported.

A common system for analysis, storage and presentation of all MED POL data is envisaged but is, at the time of preparation of this report, only at the early stage of implementation. FAO therefore made use of an existing computer system designed essentially for the Fisheries Commodities Data Base, with supplementary print programmes to generate tables in order to meet the requirements of the pilot project.

The results presented in this report are mainly based on tables giving concentrations by species and elements for different sampling stations and MED POL areas, which were produced by the FAO Fisheries Information Data and Statistics Service. It is, however, envisaged that the data will be transferred to, and utilized by, the Mediterranean data processing system in Geneva, as and when operational.

2. METHODOLOGICAL CONSIDERATIONS

2.1 Selection of the species

The marine organisms selected in the Operational Document as mandatory species are *Mytilus galloprovincialis* (Mediterranean mussel) and/or *M. edulis*, *Mullus barbatus* (striped mullet), *Thunnus thynnus thynnus* (bluefin tuna) and/or *Xiphias gladius* (broadbill swordfish). These species were selected as being representatives of different ecotypes. They are also of considerable economic importance and are common almost everywhere in the Mediterranean.

Results on *Mytilus galloprovincialis* and *Mullus barbatus* were reported by the 22 and 27 centres participating in the pilot project.

Mullus barbatus was sampled by all institutes with two exceptions; the Centre de Recherches océanographiques et des Pêches in Algiers and the Institut scientifique des Pêches maritimes in Casablanca. These two centres had selected another member of the Mullidae family, *Mullus surmuletus* (red mullet), as an alternative species. It can therefore be concluded that *Mullus barbatus*, as far as availability is concerned, is a very useful organism for monitoring purposes.

Mytilus galloprovincialis has been reported as being unavailable in some areas of the Eastern Mediterranean, e.g. Israel and Cyprus. No information regarding its availability was received from the other centres that did not sample *Mytilus*. It can nevertheless be concluded that *Mytilus galloprovincialis* is sufficiently common in the Mediterranean coastal areas to make it, from this point of view, a suitable organism for a monitoring exercise.

Thunnus thynnus thynnus was sampled only by 11 centres. As *Thunnus* migrates over great distances it is not so much the number of sampling areas as the number of samples that is determinant for the evaluation of results. The same also applies to *Xiphias gladius* which, being the alternative to *Thunnus*, was sampled by six centres.

The total number of additional species that were sampled is close to 70, but the number of samples and the frequency of sampling, though variable, are generally low. Table 1 and 2 shows all the additional species and the number of centres that have collected samples.

Only species for which the full scientific names were given have been included in the list. Most of the species have only been sampled by one centre. Some, however, have been used more frequently and the following species have been sampled by three or more centres: *Engraulis encrasicolus*, *Mullus surmuletus*, *Trachurus mediterraneus*, *Merluccius merluccius*, *Boops boops*, *Pagellus acarne*, *Pagellus erythrinus*, *Carcinus mediterraneus* and *Penaeus kerathurus*.

Some of the additional species are also sampled for analysis of chlorinated hydrocarbons (MED POL III) but not necessarily by the same research centre.

Table 1. Species sampled and metals analysed

Research Centre	Species					Metals							
	<i>Mytilus galloprovincialis</i>	<i>Mytilus barbatus</i>	<i>Thynnus thynnus</i>	<i>Xiphias gladius</i>	Other	Hg	Cd	Cu	Pb	Mn	Se	Zn	Other
	X				X	X	X					X	
Centre de Recherches océanographique et des pêches, Alger	X	X		X				X				X	
Fisheries Department, Nicosia		X			X							X	
Institute of Oceanography and Fisheries, Alexandria		X				X							
Centre for Post-graduate Studies and Research, Alexandria	X	X			X	X						X	
Laboratoire Central d'Hygiène alimentaire, Paris	X	X				X	X	X	X				
Laboratoire de Chimie analytique et Toxicologie, Montpellier	X	X			X	X	X			X			
Institute scientifique et technique des pêches maritimes, Sète	X	X			X	X	X		X				
Institute of Oceanographic and Fisheries Research, Athens	X	X			X		X	X	X	X		X	X
Nuclear Research Centre "Demokritos", Athens	X	X			X			X			X	X	X
General Chemical State Laboratory, Athens	X	X			X	X							
Department of Food Hygiene, University of Thessaloniki	X	X			X	X							

continued

Table 1. Species sampled and metals analysed (continued -2)

Research Centre	Species					Metals							
	<i>Mytilus galloprovincialis</i>	<i>Mytilus barbatus</i>	<i>Thynnus thynnus</i>	<i>Xiphias gladius</i>	Other	Hg	Ca	Ce	Pb	Mn	Se	Zn	Other
Laboratory of Analytical Chemistry, University of Thessaloniki	X	X	X	X		X	X		X				
Israel Oceanographic and Limnological Research Ltd., Haifa		X			X	X	X	X	X			X	X
Laboratory of Hydrobiology and Fish Culture, Siena	X	X	X	X	X	X	X	X	X	X	X	X	
Marine Contamination Laboratory - CNEN, Fiascherino	X	X	X	X	X	X	X						
Centre for Radiochemistry and Activation Analyses - CNR, Pavia													
Group for Oceanographic Research, University of Genova	X	X			X	X	X	X	X	X		X	X
Station for Marine Biology, University of Messina	X	X	X		X	X	X		X				
Centre de Recherche marine, Beyrouth													
The University of Malta, Msida		X			X	X	X	X	X	X		X	
Institut scientifique des Pêches maritimes, Casablanca	X		X		X	X	X	X					
Instituto de Investigaciones Pesqueras, Barcelona	X	X	X		X	X	X	X				X	X

continued

Table 1. Species sampled and metals analysed (continued -3)

Research Centre	Final report	Species						Metals							
		<i>Mytilus galloprovincialis</i>	<i>Mytilus barbatus</i>	<i>Thynnus thynnus</i>	<i>Xiphias gladius</i>	Other		Hg	Cd	Cu	Pb	Mn	Se	Zn	Other
Laboratorio Oceanográfico del Mar Menor, San Pedro del Pinatar		X	X			X			X						
Instituto Químico de Sarria, Barcelona	X	X	X					X	X	X	X		X	X	
Institut national scientifique et technique d'océanographie et de Pêche, Salammbô	X	X	X					X							
Hydrobiological Research Institute, Istanbul		X	X					X							
Marine Science Department (METU), Erdemli-Içel	X	X	X					X	X	X	X		X	X	
Institute of Hydrobiology, Ege University, Izmir		X	X			X		X	X	X	X		X	X	
Laboratory for Trace Element Analyses, Rijeka															
Institute for Oceanography and Fisheries, Split	X	X	X					X	X						
"Rudjer Bošković" Institute, Zagreb	X	X	X					X	X	X	X		X	X	
Marine Biological Station, Portorož	X	X	X					X	X	X	X		X	X	

Table 2. Additional species sampled.

<u>Species sampled</u>	<u>Number of centres</u>	<u>Sampled also in MED III</u>
<u>Arca noae</u>	1	X
<u>Aristeus antennatus</u>	1	
<u>Belone belone</u>	1	X
<u>Boops boops</u>	4	X
<u>Carcinus mediterraneus</u>	3	X
<u>Clupea vilchardus</u>	1	
<u>Grenilabrus tinca</u>	1	
<u>Conger conger</u>	2	X
<u>Dentex filiosus</u>	1	
<u>Dentex macropthalmus</u>	1	X
<u>Diplodus annularis</u>	2	
<u>Engraulis encrasicolus</u>	3	X
<u>Ephinephelus guaza</u>	1	
<u>Lithophaga lithophaga</u>	2	X
<u>Loligo vulgaris</u>	1	X
<u>Maena maena</u>	1	X
<u>Maena smaris</u>	1	
<u>Merlangius merlangus</u>	2	X
<u>Merluccius merluccius</u>	4	X
<u>Microcosmus sulcatus</u>	1	
<u>Mugil auratus</u>	1	X
<u>Mugil capito</u>	1	X
<u>Mugil cephalus</u>	1	
<u>Mugil chelo</u>	1	
<u>Mugil saliens</u>	1	X

Table 2. Additional species sampled (continued-2)

<u>Species sampled</u>	<u>Number of centres</u>	<u>Sampled also in MED III</u>
<u>Mullus surmuletus</u>	8	X
<u>Nephrops norvegicus</u>	4	X
<u>Oblata melanura</u>	1	X
<u>Octopus vulgaris</u>	2	
<u>Ophiotrix fragilis</u>	1	
<u>Ostrea edulis</u>	1	X
<u>Pagellus acarne</u>	5	X
<u>Pagellus erythrinus</u>	4	X
<u>Pagrus ehrenbergii</u>	1	
<u>Parapenaeus longirostris</u>	4	X
<u>Patella coerulea</u>	2	X
<u>Pegusa lascaris</u>	1	
<u>Penaeus kerathurus</u>	5	X
<u>Perna perna</u>	1	
<u>Phycis blennoides</u>	1	
<u>Pomatomus saltator</u>	2	
<u>Portunus depurator</u>	1	
<u>Raja asterias</u>	1	
<u>Raja alaneta</u>	1	
<u>Sarda sarda</u>	1	
<u>Sardina pilchardus</u>	1	X
<u>Sardina vulgaris</u>	1	
<u>Sardinella maderensis</u>	1	
<u>Saurida undosquamis</u>	1	X
<u>Scomber japonicus</u>	1	
<u>Scomber scombrus</u>	1	X

Table 2. Additional species sampled (continued-3)

<u>Species sampled</u>	<u>Number of centres</u>	<u>Sampled also in MED III</u>
<u>Scorpaena porcus</u>	1	
<u>Scorpaena scrofa</u>	2	
<u>Sepia officinalis</u>	2	
<u>Serranus cabrilla</u>	1	
<u>Serranus scriba</u>	1	
<u>Solea vulgaris</u>	1	
<u>Squilla mantis</u>	1	
<u>Synodus saurus</u>	1	
<u>Torpedo marmorata</u>	1	
<u>Trachinus draco</u>	1	
<u>Trachurus mediterraneus</u>	4	X
<u>Trachurus trachurus</u>	1	X
<u>Ueneus molluccensis</u>	2	X
<u>Upogebia littoralis</u>	1	X
<u>Uranoscopus scaber</u>	1	

An evaluation, on a Mediterranean basis, of the levels of contamination in all the additional species is impossible because of the limited number of samples. The results can, however, be useful for the assessment of local pollution and to provide baseline information. Furthermore, many of the species sampled are of local commercial importance. For some migratory species the data may also give an indication of body burdens in the Mediterranean.

In a few cases, results of analyses of zooplankton, sediments and water have also been reported.

2.2 Pollutants analysed

Results on mercury were reported by 25 centres and on cadmium by 21 centres. Analysis of cadmium was apparently rather difficult, requiring the use of graphite furnace techniques together with the atomic absorption spectrophotometer. It was clear, therefore, that several of the centres that did not report results on cadmium had only recently begun analysis of heavy metals, and it may be assumed that, when their analytical capability is further improved, cadmium will be one of the elements to be analysed.

Among the additional elements in the Operational Document, copper and zinc received most attention, both being reported on by 15 centres.

An appreciable number of results were also received for lead and manganese, while selenium was only reported on by four centres.

The interrelation between mercury and selenium concentrations in organisms makes this latter element especially interesting. Methyl-mercury, the most common organic form of mercury in organisms, was, unfortunately, only reported on by one centre.

Besides these mandatory and additional elements, many others were also monitored but only by a limited number of centres. Among them special mention should be made of arsenic, antimony, cobalt, chromium, iron, nickel and silver.

2.3 Areas studied

The baseline studies and monitoring were to be carried out primarily in coastal waters. Furthermore, the sampling stations were to be selected by the participating research centres so that the results obtained could be used to characterize the level of pollutants in certain areas. The sampling frequency was to be seasonal.

The number of sampling stations selected by the different centres varies considerably, from two stations to over 30. In the latter case, the samples were, however, collected only occasionally, which makes statistical treatment of the data from one particular station impossible. In fact very few centres have strictly followed the agreed sampling frequency with regard to seasonal sampling. Figure I shows the different areas that have

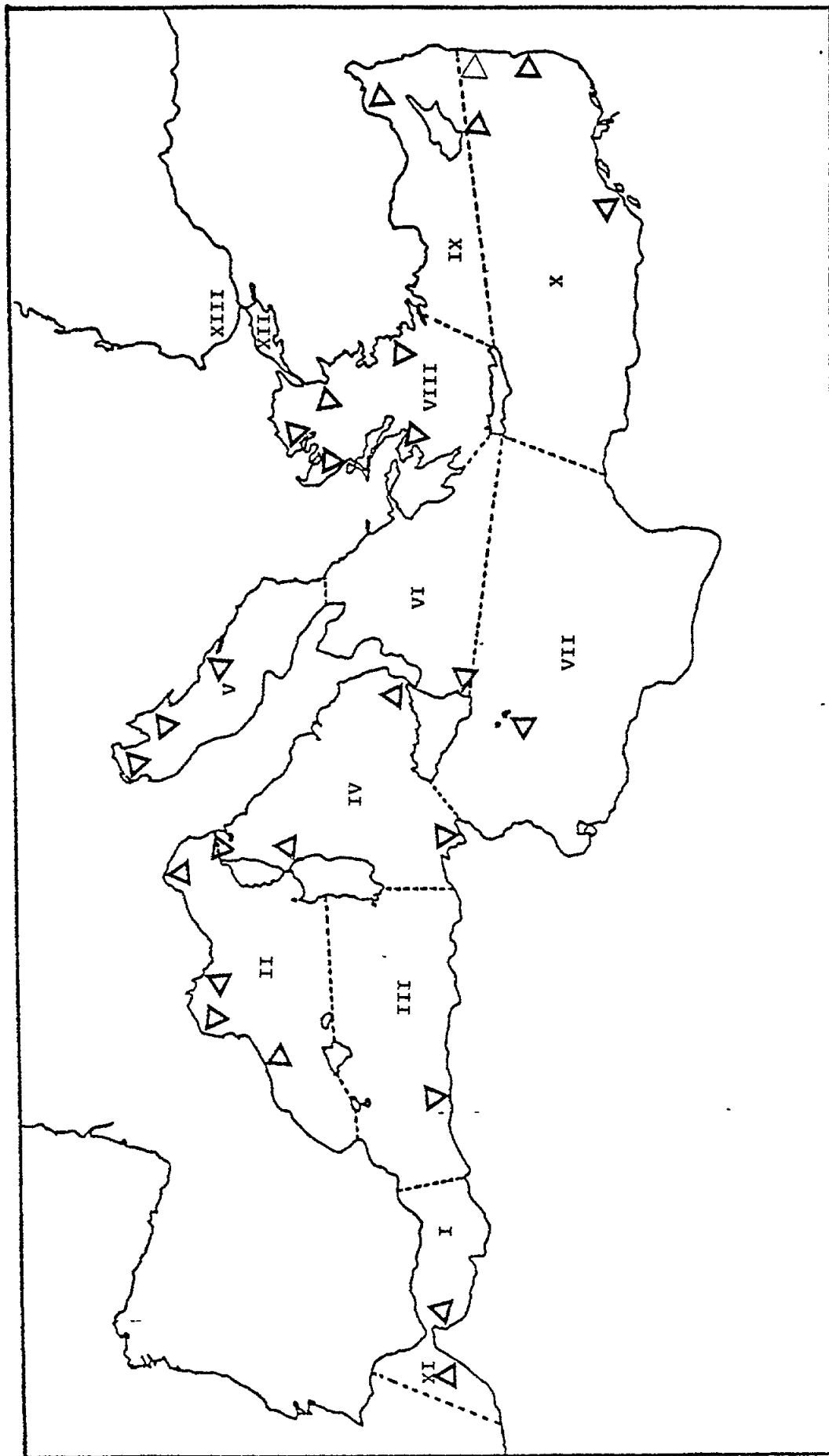


Figure 1 Sampling areas for MED I-I

- | | | | |
|--------------------|--------------|---------------------|-----------------|
| I. Alboran | V. Adriatic | IX. N. Levantin | XIII. Black Sea |
| II. North-Western | VI. Ionian | X. S. Levantin | |
| III. South-Western | VII. Central | XI. Atlantic | |
| IV. Tyrrhenian | VIII. Aegean | XII. Sea of Marmara | |
| △ Data reported | | | |
| | | △ No data reported | |

been monitored or where monitoring is planned but data have not been reported. The whole Mediterranean is quite well covered by sampling areas and in all MED POL areas there is at least one centre that has reported results. The number of sampling stations is more than 300, but as previously mentioned, many of them have only been sampled once or twice for perhaps one species. This makes the number of stations for which time-trends could possibly be calculated about 100. Table 3 shows for each MED POL area the number of research centres that have reported results.

Table 3 - Number of research centres by MED POL areas

MED POL AREA	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Research centres	1	9	1	4	4	1	1	7	2	3	1	1

2.4 Methodology

Sampling and sample preparation were generally carried out in accordance with the recommendations given in the Manual of Methods in Aquatic Environment Research, Part 3 - Sampling and Analysis of Biological Material; FAO Fisheries Technical Paper No. 158. In some cases, however, the samples were obtained from the market. But as this was generally done only for tuna or swordfish an appropriate subsampling should prevent the risks of contamination.

For destruction of the organic material, wet combustion was generally used. The pressure decomposition vessels, which many centres were provided with through the project, constituted the equipment most commonly used. In some cases low temperature ashing was utilized.

For the analysis, atomic absorption spectrophotometers (AAS) were employed. The determination of mercury was carried out by the cold vapour technique, while the other metals were generally determined by air acetylene flame at higher concentrations, or graphite furnace at lower concentrations. With the comparatively low concentrations of cadmium, in particular, graphite furnace techniques had to be used. This technique apparently causes initial difficulties for those centres that are just embarking on metal analysis with AAS.

Other methods that were used were: neutron activation analysis (NAA), electroanalytical techniques (polarographic and voltametric) and X-ray fluorescence.

3. INTERCALIBRATION EXERCISE

An extensive evaluation of the intercalibration exercise (MED POL XI) is

presented in document UNEP/WG/46/3 Part II.

The following evaluation is restricted only to questions directly related to treatment of the monitoring data.

The participating centres were provided with three or four different intercalibration samples depending on the stage of the pilot project at which they commenced the analyses. Results for three or four samples were reported by 26 centres, while two centres analysed only one sample. The remaining centres did not participate in the intercalibration, although two of them reported monitoring results (table 4). However, as these two centres were just recently in a position to perform the analysis, it can be expected that they will carry out the intercalibration, this being an obligatory part of the pilot project.

The intercalibration exercise is a world-wide one with not only Mediterranean research centres reporting results. For each sample and compound, the arithmetic mean and standard deviation (SD) of the results reported by the participating centres have been calculated.

In order to exclude "outliers", Dixon's test was used. As a basis for estimating the reliability of the data and their fitness for inclusion in the evaluation of the monitoring exercise, the following criteria were used:

- (i) results within one standard deviation from the mean (after Dixon's test) to be considered as "good";
- (ii) results within two standard deviations to be considered as "acceptable";
- (iii) results deviating more than two standard deviations from the mean to be considered as "not acceptable".

For the overall evaluation of three intercalibration samples, the average of two "good" or "acceptable" results and one "not acceptable" was considered as acceptable. With two "not acceptable" and one "good" or "acceptable" the average was considered as "not acceptable". In the cases where four samples were reported on and two results were "not acceptable", the judgement was based on how much the values deviated from the mean.

When considering these principles for accepting the data for evaluation of the monitoring results it was revealed that, in general, only data from a limited number of centres would have to be deleted. One centre for mercury, and two for cadmium would have to be eliminated. In the case of copper one, and for zinc, two centres did not have acceptable intercalibration results. For lead the situation was somewhat different as five of the 14 centres that reported results for this metal would have to be excluded.

It can, hence, be concluded that, with the exception of lead, an evaluation of the baseline studies and monitoring without rejecting data could be made

Table 4. Participation in intercalibration of samples MA-M-1 (oyster), SP-M-1 (sea plant), MA-A-1 (copepod) and MA-A-2 (fish)

Research Centre	Data reported	MA-M-1	SP-M-1	MA-A-1	MA-A-2
Centre de Recherches océanographiques et des pêches, Alger	X	X	X	X	X
Fisheries Department, Nicosia	X	*	X	X	X
Institute of Oceanography and Fisheries, Alexandria	X				
Centre for Post-graduate Studies and Research, Alexandria	X	*	*	X	X
Laboratoire Central d'Hygiène alimentaire, Paris	X	*	X	X	X
Laboratoire de Chimie analytique et Toxicologie, Montpellier	X				
Institute scientifique et technique des pêches maritimes, Sète	X	X	X	X	X
Institute of Oceanographic and Fisheries Research, Athens	X	X	X	X	X
Nuclear Research Centre "Demokritos", Athens	X	X	X	X	X
General Chemical State Laboratory, Athens	X	X	X	X	X
Department of Food Hygiene, University of Thessaloniki	X	X	X	X	X
Laboratory of Analytical Chemistry, University of Thessaloniki	X	X	X	X	X
Israel Oceanographic and Limnological Research Ltd., Haifa	X	X	X	X	X
Laboratory of Hydrobiology and Fish Culture, Siena	X	X	X	X	X
Marine Contamination Laboratory - CNEN, Fiascherino	X	X	X	X	X
Centre for Radiochemistry and Activation Analyses - CNR, Pavia		X	X	X	
Group for Oceanographic Research, University of Genova	X	X	X	X	X
Station for Marine Biology, University of Messina	X	X	X	X	X
Centre de Recherche marine, Beyrouth					
The University of Malta, Msida	X	*	X	X	X
Institut scientifique des Pêches maritimes, Casablanca	X	*		X	
Instituto de Investigaciones Pesqueras, Barcelona	X	X	X	X	X
Laboratorio Oceanográfico del Mar Menor, San Pedro del Pinatar	X	X	X	X	
Instituto Químico de Sarria, Barcelona	X	*	X	X	X
Institut national scientifique et technique d'océanographie et de Pêche, Salammbô	X	*	X	X	X
Hydrobiological Research Institute, Istanbul	X	*	X	X	X
Marine Science Department (METU), Erdemli-Içel	X	X	X	X	
Institute of Hydrobiology, Ege University, Izmir	X	*	X	X	X
Laboratory for Trace Element Analyses, Rijeka		X	X	X	X
Institute for Oceanography and Fisheries, Split	X	X	X	X	X
"Rudjer Bosković" Institute, Zagreb	X	X	X	X	X
Marine Biological Station, Portorož	X	X	X	X	X

* sample not sent.

without introducing unacceptable errors. However, consideration has, in this case, to be given to the variation related to the analytical performance. Nevertheless, for the evaluation, data from those centres with "not acceptable" values or with no intercalibration performed, have been deleted in order to improve the comparability of the results.

For the other metals analysed an evaluation of the performance of the individual laboratories was not possible due to the limited number of results reported.

A comparison of the results in this intercalibration exercise with those that have been reported in the International Council for the Exploration of the Sea (ICES), North Sea and North Atlantic baseline studies, shows that the coefficient of variation between the laboratories is larger in the Mediterranean than in the ICES area, ICES (1978). This is, however, expected as all laboratories in the ICES study are well established, while many centres in the Mediterranean have recently started with analysis of heavy metals. As was pointed out for the ICES studies, a regular repetition of the exercise will certainly further improve the quality of the data.

4. RESULTS OF THE BASELINE STUDIES AND MONITORING

4.1 Introduction

The levels of contamination presented in this section are based only on data reported on LOG FORMS received before 15 June 1980. Data from the very first phase of the pilot project, before the LOG FORMS were developed, have not been key-entered unless these data have been transferred to LOG FORMS by the reporting research centre.

Data presented for the different pollutants and organisms are mean values of all results reported for the various stations in the relevant MED POL area, with due consideration given to the intercalibration results. They do not take into account the differences between the conditions prevailing at the individual sampling stations (i.e. levels of pollution). Bearing in mind the wide extent of heterogeneous conditions within each MED POL area, it is obvious that the overall averages of the levels reported should not be interpreted as mean values for an area. References to (author, final

References to (author, final) report) refer to the individual summary reports prepared by the principal investigators and presented in document UNEP/WG.46/Inf.6.

4.2 Mercury

Levels of total mercury in the obligatory species, by area, are reported in figure 2.

4.2.1 Mytilus galloprovincialis

The highest levels are reported in samples from area V (Adriatic),

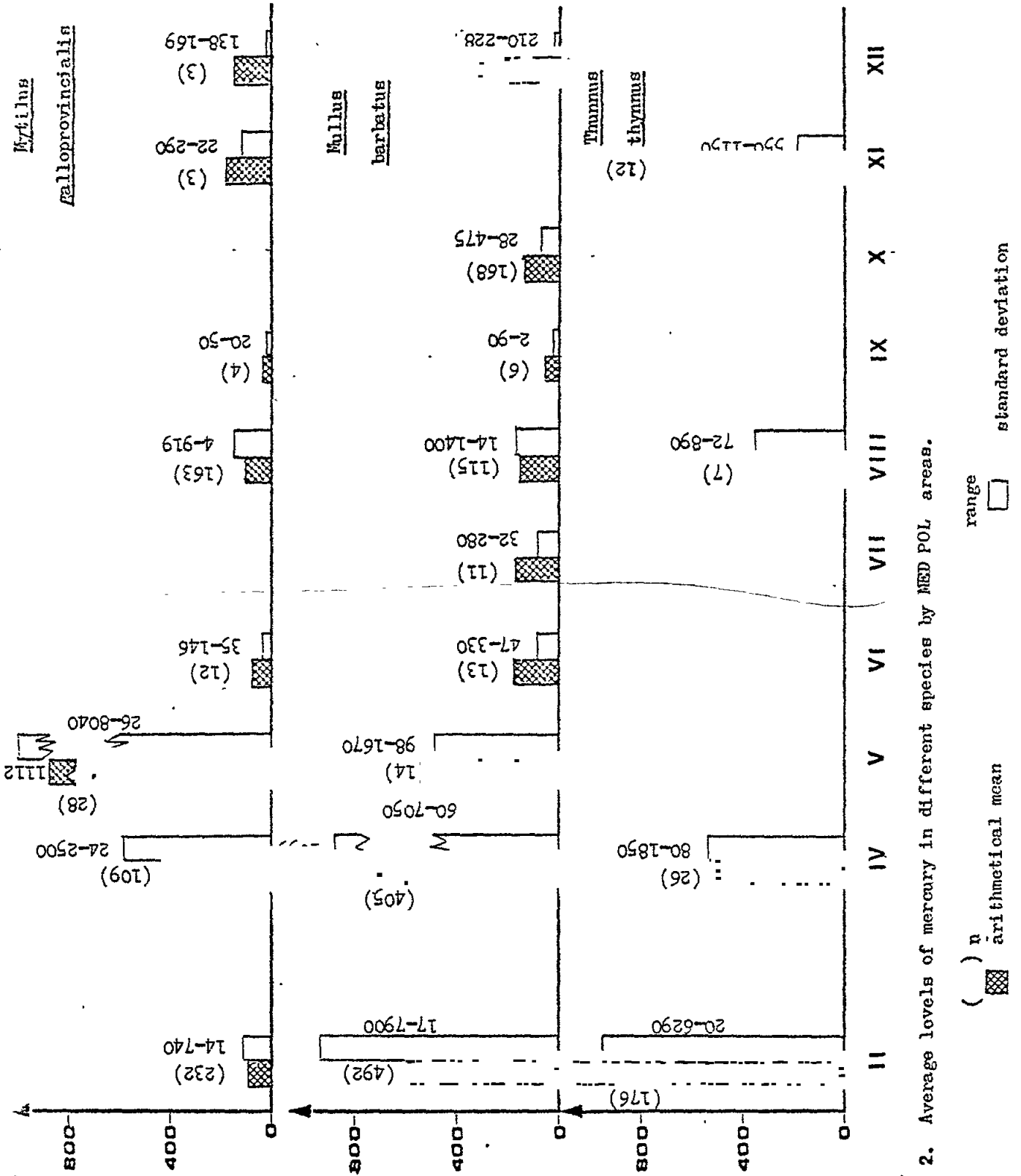


Fig. 2. Average levels of mercury in different species by MED POL areas.

range
 arithmetic mean
 standard deviation

collected in rather polluted sites (Gomiscek and Stegnar, final report) (table 5). Also values from area IV (Tyrrhenian) are rather high with an average concentration of 524 ug/kg.

Table 5 - Average levels of mercury in *Mytilus galloprovincialis*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)
II	4	232	94	108	9 - 740	47 (226)
IV	2	109	524	602	24 - 2500	38 (106)
V	2	28	1112	2329	26 - 8040	51 (28)
VI	1	12	77	37	35 - 146	49 (12)
VIII	5	163	102	158	4 - 919	35 (98)
IX	1	4	37	13	20 - 50	63 (4)
XI	1	3	191	120	22 - 290	-
XII	1	3	158	14	138 - 169	72 (3)

*Number of specimens in brackets

All other results are below 200 ug/kg FW. The variation between the individual samples are considerable as can be seen from the standard deviation (SD) which in many cases is more than 100 per cent of the mean.

The highest values reported were in several cases in areas IV and V above 1000 ug/kg. A statistical comparison of the average concentrations in areas II, IV and VIII, which are based on a sufficient number of samples, shows significantly higher concentrations in area II.

The lower averages are similar to the levels reported for *Mytilus edulis* in the North Sea by ICES as part of the baseline survey of 1972 (ICES, 1974). Levels reported from the Canadian coast in the ICES North Atlantic baseline study are however lower with concentrations between 10 and 100 ug/kg with an overall average of 50 ug/kg, ICES (1980).

4.2.2 Mullus barbatus

The concentrations of mercury in *Mullus barbatus* are generally around 200 ug/kg or less. In areas II, IV and V however, samples from the Tyrrhenian Sea and Adriatic have elevated averages (table 6).

Table 6 - Average levels of mercury in *Mullus barbatus*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)	average* weight (g)
II	4	492	595	944	17 - 7900	133 (478)	45 (487)
IV	3	405	1304	1059	60 - 7050	140 (405)	46 (405)
V	2	14	513	486	98 - 1670	154 (14)	38 (14)
VI	1	13	188	82	47 - 330	129 (13)	23 (13)
VII	1	11	166	86	32 - 280	135 (11)	39 (11)
VIII	5	115	155	169	14 - 1400	134 (99)	-
IX	1	6	55	28	2 - 90	163 (6)	64 (6)
X	2	168	141	73	28 - 475	148 (168)	34 (168)
XII	1	3	217	8	210 - 228	148 (3)	41 (3)

*Number of specimens in brackets

Along the Italian coast in area IV is the Mount Amiata region with cinnabar-rich bedrock and mercury-extracting industries. Bacci *et al.* (1980) have reported an increase in levels of mercury in *Mullus barbatus* from this region with increasing depth and distance from the coast. The average of data reported from sampling stations in area IV were 1,304 ug/kg with a range of 60-7,050 ug/kg. The average concentration in this area is significantly higher than in areas II and VIII.

4.2.3 Thunnus thynnus thynnus

The levels of mercury in *Thunnus thynnus thynnus* are generally high, especially in specimens of large size. The average concentration in 176 specimens caught in area II was 1,096 ug/kg with a range of 20-6,290 (table 7).

Table 7 - Average levels of mercury in *Thunnus thynnus thynnus*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)	average* weight (g)
II	1	176	1096	937	20 - 6290	1219 (89)	-
IV	1	26	497	545	80 - 1850	-	-
V	1	2	1485	625	860 - 2110	650 (2)	-
VIII	2	6	300	331	50 - 890	634 (6)	-
XI	2	12	715	181	550 - 1150	-	-

* Number of specimens in brackets

Cumont et al. (1972 and 1975) and Renzoni et al. (1979) have shown that levels of mercury in tuna from the Mediterranean are higher than levels in tuna from the Atlantic. As tuna migrates over great distances the values reported are not only valid for one area but can be considered as Mediterranean levels.

4.2.4 Other species

Several additional species have also been analysed for mercury, although most of them only in one or two areas. The average concentrations based on three or more samples for each species are shown in table 8. *Nephrops norvegicus* have higher values in areas II and IV with average concentrations of 967 and 962 ug/kg respectively.

The correlation between mercury concentration, body weight and sex has been discussed in the final report of Renzoni. The levels in *Sarda sarda* are also somewhat higher in area II with an average concentration of 1,002 ug/kg. For *Merluccius merluccius* the levels are higher in samples from area XII (Sea of Marmara) but the small number of samples makes the results quite uncertain.

In the ICES baseline study in the North Atlantic, the mean concentrations in samples of *Merluccius* were between 30 and 130 ug/kg, (ICES, 1977b).

Average levels in *Trachurus mediterraneus*, which are between 93 and 345 ug/kg, are similar to the mean values between 170 and 330 ug/kg reported for *Trachurus trachurus* in the North Sea ICES (1977). The anchovy *Engraulis encrasicolus*, a plankton feeder, generally shows levels below or near 150 ug/kg.

Table 8. Overall averages of levels of mercury in samples of non-obligatory species.

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
II	<u>Boops boops</u>	8	127	70	23-250
	<u>Engraulis encrasicolus</u>	114	179	107	21-425
	<u>Maena smaris</u>	5	188	55	150-280
	<u>Mullus surmuletus</u>	9	211	148	60-510
	<u>Nephrops norvegicus</u>	345	967	850	350-3000
	<u>Sarda sarda</u>	14	1002	641	290-2300
	<u>Sardina pilchardus</u>	46	247	70	150-390
	<u>Scomber scombrus</u>	16	335	121	125-510
	<u>Scorpaena scrofa</u>	5	90	42	40-160
	<u>Solea vulgaris</u>	11	65	64	20-220
	<u>Scuilla mantis</u>	20	151	86	65-455
	<u>Trachurus trachurus</u>	3	705	397	330-1255
	<u>Trisopterus minutus capelanus</u>	5	308	304	60-840
	III	<u>Mullus surmuletus</u>	210	90	43
<u>Perna perna</u>		192	76	50	20-370
IV	<u>Engraulis encrasicolus</u>	98	162	64	64-380
	<u>Nephrops norvegicus</u>	189	961	507	59-2900
	<u>Thunnus alalunga</u>	8	215	85	90-336
VI	<u>Engraulis encrasicolus</u>	11	144	74	53-270
	<u>Nephrops norvegicus</u>	7	291	52	190-360
	<u>Thunnus alalunga</u>	8	276	124	60-399
VII	<u>Lithophaga lithophaga</u>	5	163	76	79-290
	<u>Trachurus mediterraneus</u>	5	345	317	80-955
VIII	<u>Merluccius merluccius</u>	10	317	337	62-838
	<u>Pagellus erythrinus</u>	3	219	6	213-228
	<u>Parapenaens longirostris</u>	42	339	225	110-1195
	<u>Trachurus mediterraneus</u>	3	338	19	320-365
	<u>Xiphias gladius</u>	8	279	281	84-755

Table 8. (continued 2)

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
IX	<u>Boops salpa</u>	3	8	7	3-17
	<u>Mugil auratus</u>	39	170	881	1-5600
	<u>Mullus surmuletus</u>	13	35	23	1-78
	<u>Penaeus kerathurus</u>	7	20	12	8-48
	<u>Upeneus molluccensis</u>	7	199	118	110-430
X	<u>Boops boops</u>	5	134	149	40-432
	<u>Dentex dentex</u>	6	385	92	220-480
	<u>Dentex gibbosus</u>	12	139	19	99-178
	<u>Donax trunculatus</u>	42	209	220	35-909
	<u>Epinephelus aeneus</u>	4	252	120	99-397
	<u>Merluccius merluccius</u>	6	152	102	31-258
	<u>Parcellus acarne</u>	7	190	80	71-337
	<u>Parcellus erythrinus</u>	112	204	115	53-805
	<u>Saurida undosquaris</u>	143	137	93	42-649
	<u>Solaraena solaraena</u>	7	164	45	81-246
	<u>Trachurus mediterraneus</u>	48	93	107	8-417
	<u>Upeneus molluccensis</u>	120	439	292	38-1122
XI	<u>Mullus surmuletus</u>	5	147	129	15-380
XII	<u>Merluccius merluccius</u>	3	817	30	778-850
	<u>Parcellus erythrinus</u>	3	219	6	210-225
	<u>Parapenaeus longirostris</u>	3	299	38	269-352
	<u>Trachurus mediterraneus</u>	3	346	5	340-352

Concentrations of methyl-mercury are only reported for a small number of samples of *Sarda sarda* and *Nephrops norvegicus* (Capelli, final report).

4.3 Cadmium

Concentrations of cadmium in the obligatory species, by area, are reported in figure 3.

4.3.1 Mytilus galloprovincialis

Average levels in *Mytilus galloprovincialis* are approximately 100 to 250 ug/kg in all areas, except area VI (Ionian Sea) where the mean of the samples is below 50 ug/kg (table 9).

Table 9 - Average levels of cadmium in *Mytilus galloprovincialis*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	Average* length (mm)
II	4	148	169	111	40 - 1060	46(147)
IV	1	70	169	118	70 - 1000	33 (67)
V	2	72	157	100	38 - 475	50 (14)
VI	1	12	36	8	27 - 52	49 (12)
VIII	2	73	97	122	5 - 403	33 (71)
IX	1	3	237	135	70 - 400	72 (3)

* Number of specimens in brackets

The highest maximum values which were around 1000 ug/kg were reported from areas II and IV. In the ICES North Sea Baseline Study, 1972, mean values reported for *Mytilus edulis* ranged from 100 to 500 ug/kg, (ICES, 1974). In the subsequent monitoring exercises of 1974 and 1975, mean values were between 30 and 390 ug/kg, (ICES 1977a and 1977c). Values from the Canadian coast in the ICES North Atlantic baseline study were between 90 and 330 ug/kg, ICES (1980).

4.3.2 Mullus barbatus

The levels of cadmium in *Mullus barbatus* are lower than in *Mytilus*, with averages in samples from the different areas of between 17 and 69 ug/kg (table 10).

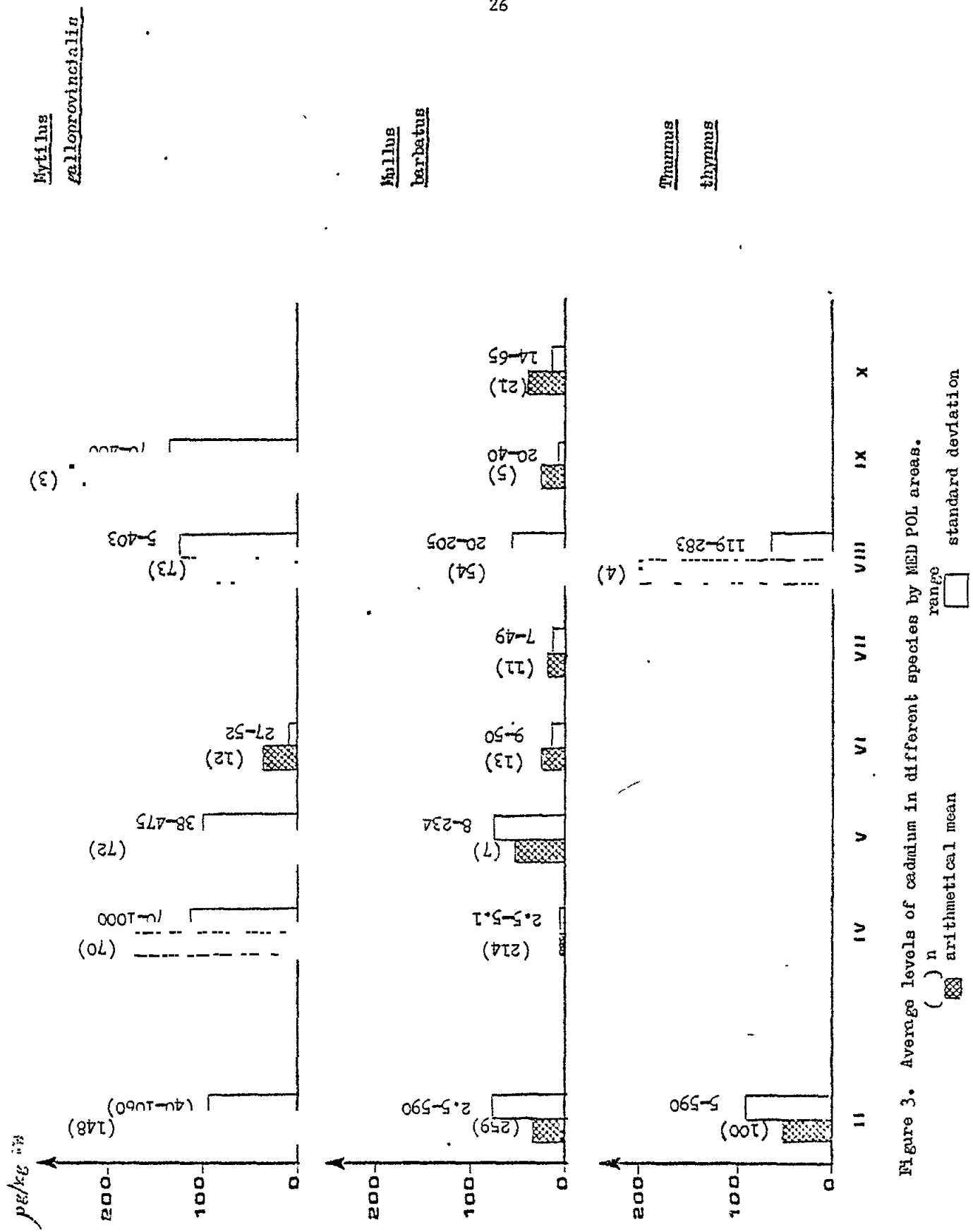


Figure 3. Average levels of cadmium in different species by MED POL areas.

Table 10 - Average levels of cadmium in *Mullus barbatus*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)	average* weight (g)
II	5	259	31	71	2.5-590	140 (247)	57 (254)
IV	2	214	4	5	2.5- 51	141 (214)	48 (214)
V	2	7	49	75	8-234	155 (7)	41 (7)
VI	1	13	25	14	9- 50	129 (13)	23 (13)
VII	1	11	17	15	7- 49	135 (11)	39 (11)
VIII	2	54	69	55	20-205	122 (54)	41 (41)
IX	1	5	26	8	20- 40	164 (4)	73 (4)
X	1	21	39	14	14- 65	140 (21)	33 (21)

* Number of specimens in brackets

From an analytical point of view, determinations at such low levels are very difficult, which may render the results somewhat uncertain. It is therefore advisable that the intercalibration exercises in the future should include samples with cadmium levels below 100 ug/kg. The analytical methodology may also have to be improved in order to enhance the reliability of the data. Nevertheless it can be concluded that the concentrations of cadmium in *Mullus barbatus* are generally low, with only a few high values reported in the range of about 200 to 500 ug/kg.

4.3.3 Thunnus thynnus thynnus

Data on cadmium in *Thunnus* are only available from three centres sampling in areas II, V and VIII (Aegean Sea). The levels are rather low as for *Mullus barbatus* (table 11).

Table 11 - Average levels of cadmium in *Thunnus thynnus thynnus*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)
II	1	100	53	88	5 - 590	1 225 (88)
VIII	1	4	196	61	119 - 283	772 (4)

* Number of specimens in brackets

The mean concentration of 100 samples in area II was 53 ug/kg with a range of 5-590 ug/kg.

4.3.4 Other species

The overall averages of levels of cadmium based on three or more samples of non-obligatory species are shown in table 12. Contrary to the results for mercury, the levels of cadmium in *Nephrops norvegicus* are very low with mean values of between 5 and 26 ug/kg. The molluscs *Mytilus edulis* and *Perna (Mytilus) perna* show about the same or slightly lower averages than *Mytilus galloprovincialis*. The mean concentration in another mollusc *Lithophaga lithophaga* sampled in area VII is over 600 ug/kg. This value is however based on only five samples which were actually collected in the harbour of Valetta in Malta. Average values of samples of fish are generally low (less than 50 ug/kg).

4.4 Copper and zinc

Levels of copper and zinc in *Mytilus galloprovincialis*, *Mullus barbatus* and *Mullus surmuletus* are reported in figures 4 and 5 respectively.

4.4.1 Mytilus galloprovincialis

Average values for copper in *Mytilus galloprovincialis* (see table 13) vary between 1002 to 1730 ug/kg with the highest concentrations in areas II, VIII and IV.

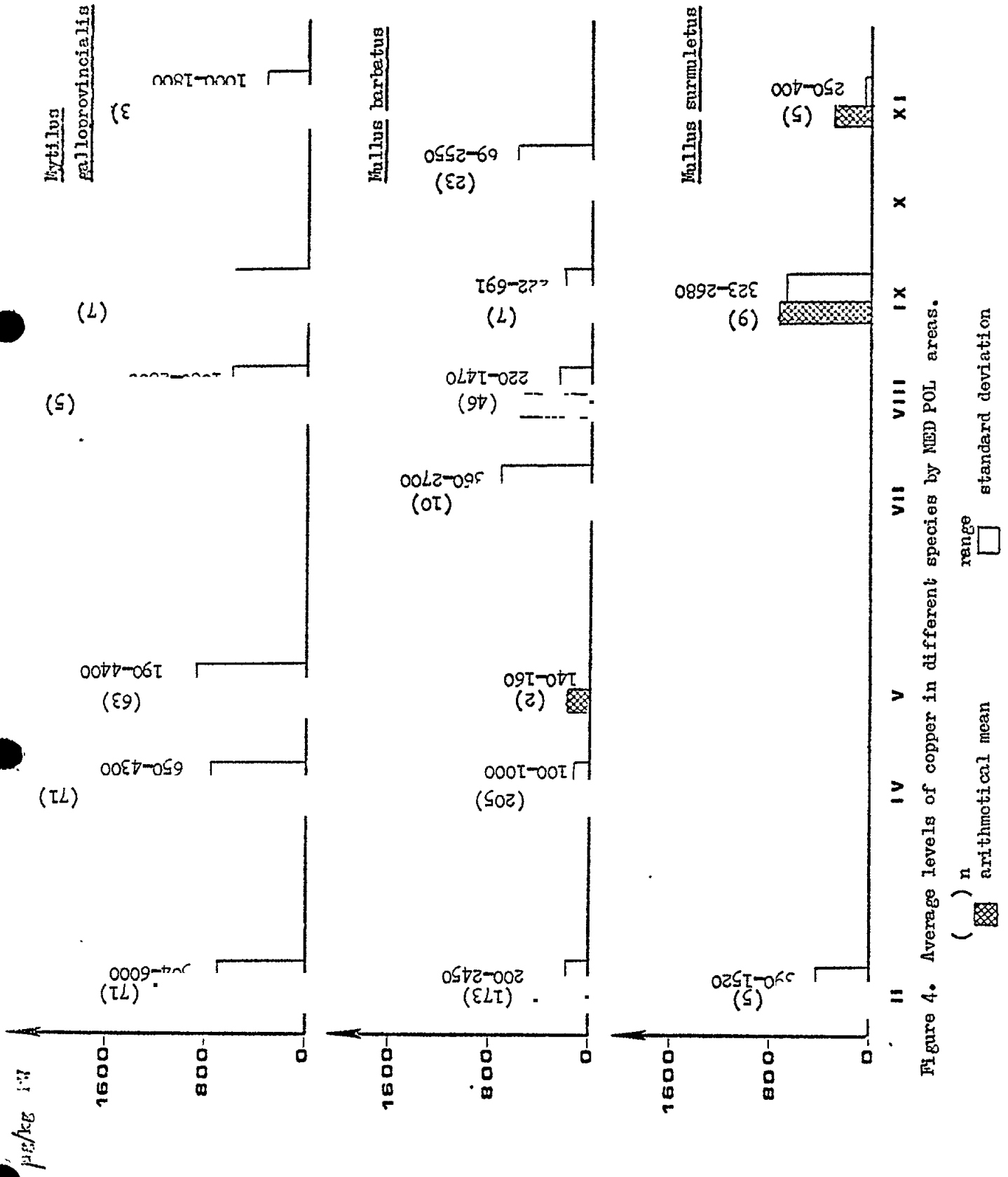


Figure 4. Average levels of copper in different species by MED POL areas.

range
 standard deviation
 arithmetical mean
 n

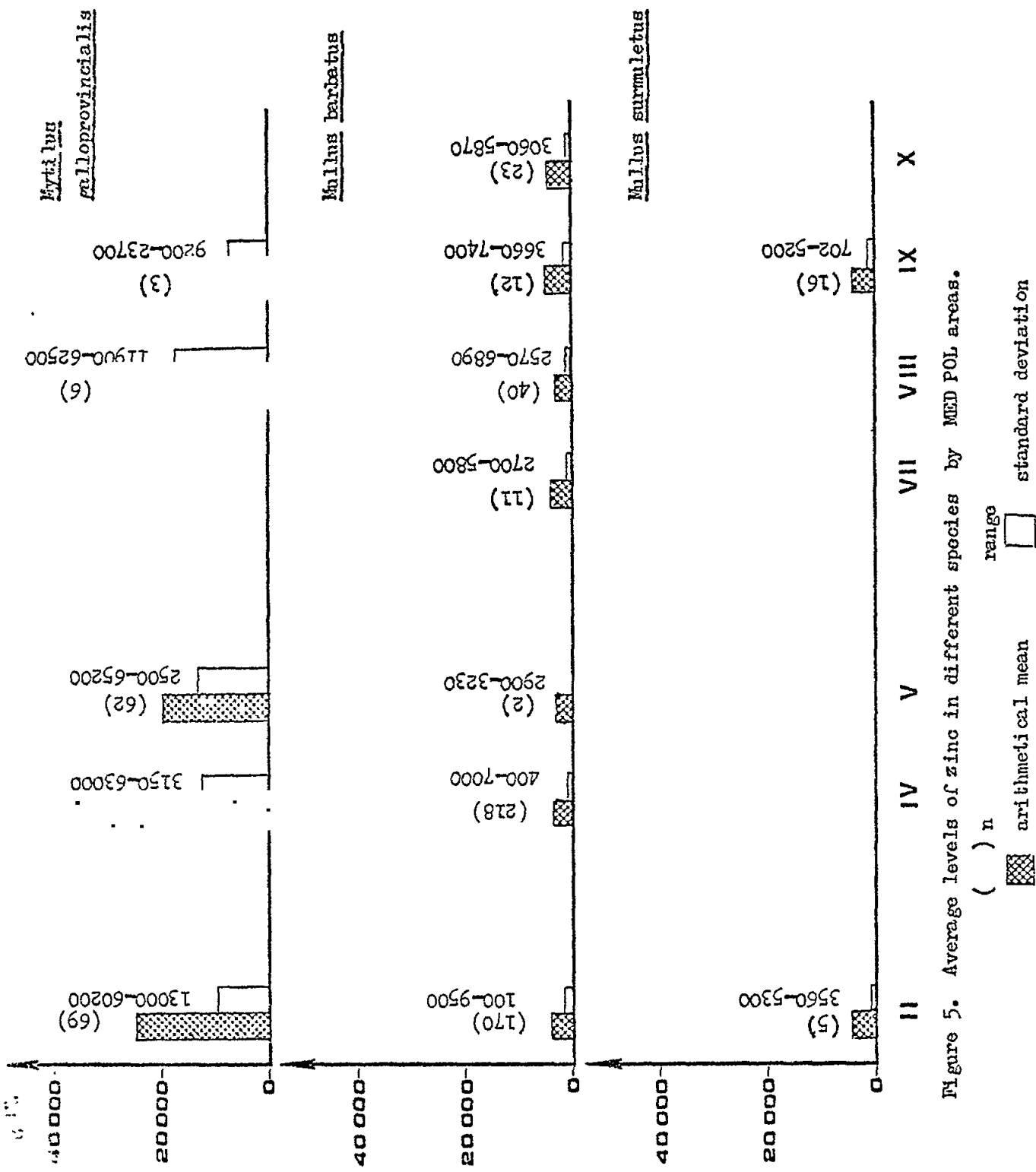


Figure 5. Average levels of zinc in different species by MED POL areas.

() n
 [hatched] arithmetic mean
 [white] range
 [dotted] standard deviation

Table 12. Overall averages of levels of cadmium in samples of non-obligatory species.

sampling area	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
II	<u>Boops boops</u>	7	11	3	10-20
	<u>Engraulis encrasicolus</u>	83	18	31	2.5-160
	<u>Maena smaris</u>	5	12	4	10-20
	<u>Mullus surmuletus</u>	5	40	-	-
	<u>Mytilus edulis</u>	10	85	36	40-140
	<u>Nephrops norvegicus</u>	249	11	27	2.5-200
	<u>Sarda sarda</u>	14	40	-	-
	<u>Scorpaena scrofa</u>	5	220	40	200-300
	<u>Solea vulgaris</u>	11	10	-	-
	<u>Trisopterus minutus capelanus</u>	4	12	4	10-20
III	<u>Mullus surmuletus</u>	203	151	79	30-320
	<u>Perna perna</u>	192	126	67	30-362
IV	<u>Engraulis encrasicolus</u>	91	5	7	2.5-40
	<u>Nephrops norvegicus</u>	117	5	12	2.5-111
	<u>Thunnus alalunga</u>	8	18	3	14-22
VI	<u>Engraulis encrasicolus</u>	11	20	7	13-39
	<u>Nephrops norvegicus</u>	7	26	14	13-48
	<u>Thunnus alalunga</u>	8	16	5	9-26
VII	<u>Lithophaga lithophaga</u>	5	666	481	311-1590
	<u>Trachurus mediterraneus</u>	5	46	57	7-160
VIII	<u>Parapenaeus longirostris</u>	14	26	12	20-50
	<u>Xiphias gladius</u>	2	112	-	75-148
IX	<u>Murex auratus</u>	10	47	85	5-200
	<u>Murex saliens</u>	3	17	16	5-40
	<u>Mullus surmuletus</u>	9	20	41	3-135
	<u>Peraeus kerathurus</u>	6	28	18	10-67
	<u>Uneneus molluccensis</u>	4	19	13	5-40
X	<u>Donax trunculatus</u>	16	80	26	41-138
	<u>Parcellus erythrinus</u>	3	30	17	12.5-53
	<u>Saurida undosquamis</u>	5	15	8	4-23
	<u>Trachurus mediterraneus</u>	3	49	9	40-62

Table 13 - Average levels of copper in *Mytilus galloprovincialis*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)
II	3	71	1730	1224	504-6000	42 (71)
IV	1	71	1659	773	650-4300	34 (68)
V	2	63	1002	855	190-4400	53 (5)
VIII	1	5	1686	596	1080-2800	49 (3)
IX	1	7	1466	600	750-2650	64 (7)
XI	1	3	1300	356	1000-1800	-

* Number of specimens in brackets

Taking into consideration the limited number of samples from each area and the relatively high standard deviations, it can nevertheless be concluded that these differences are not significant.

A "typical" concentration of copper in *Mytilus galloprovincialis* in the Mediterranean seems from these data to be about 1,200 to 1,400 ug/kg. The variations between the samples from the ICES North Sea and North Atlantic studies of *Mytilus edulis* are slightly higher. The concentrations seem also in many cases to be somewhat higher.

In the 1972 baseline study in the North Sea, the sample means reported varied between 1,600 and 13,000 ug/kg (ICES, 1974). In the subsequent monitoring exercises of 1974, 1975 and 1976 the values varied between 600 and 9,400 ug/kg, (ICES, 1977a and 1977c).

Also for zinc, the number of samples of *Mytilus galloprovincialis* is too limited to allow any conclusion about differences between areas (table 14).

Table 14 - Average levels of zinc in *Mytilus galloprovincialis*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	Average* length (mm)
II	2	69	27768	9528	13000-60200	41 (69)
IV	1	70	34032	11133	3150-63000	34 (67)
V	2	62	17752	13195	2500-65200	53 (5)
VIII	1	6	29300	16183	11900-62500	51 (5)
IX	1	3	14567	6491	9200-23700	62 (3)

* Number of specimens in brackets

The averages of samples from the different areas are between 14,567 (area IX, North Levantine) and 34032 (area IV). A "typical" value for the Mediterranean based on these samples seems to be around 20,000 to 30,000 ug/kg. The variation between individual samples is, however, considerable with a lowest concentration of 2,500 ug/kg and the highest 63,000 ug/kg. Zinc values from the North Sea baseline studies and monitoring show an equal scatter of data with concentrations of the same levels as in the Mediterranean, (ICES 1974, 1977a, 1977b and 1977c).

4.4.2 *Mullus barbatus* and *Mullus surmuletus*

The average concentration of copper in *Mullus barbatus* and *Mullus surmuletus* are all below 1,000 ug/kg varying between 150 and 926 ug/kg (table 15).

Table 15 - Average levels of copper in *Mullus barbatus* and *Mullus surmuletus*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)	average* weight (g)
<i>Mullus barbatus</i>							
II	3	173	436	259	200-2450	137 (173)	46 (173)
IV	1	205	384	126	100-1000	146 (205)	52 (205)
V	1	2	150	-	140- 160	148 (2)	45 (2)
VII	1	10	926	684	360-2700	134 (10)	38 (10)
VIII	2	46	548	250	220-1470	140 (45)	49 (33)
IX	1	7	453	198	222- 691	171 (5)	80 (5)
X	1	23	797	563	69-2550	141 (23)	33 (23)
<i>Mullus surmuletus</i>							
II	1	5	705	412	390-1520	164 (5)	67 (5)
IX	1	9	731	698	323-2680	139 (9)	55 (9)
XI	1	5	318	50	250- 400	216 (5)	240 (5)

* Number of specimens in brackets

A "typical" concentration of copper in these species is about 500 ug/kg. The variation is, however, quite high, which may not only reflect variations between specimens but also variations due to the analytical procedure.

The average levels of zinc in *Mullus barbatus* and *Mullus surmuletus* vary between 3,065 and 5,067 ug/kg (table 16).

Table 16 - Average levels of zinc in *Mullus barbatus* and *Mullus surmuletus*

sampling area	no. of centres sampling	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)	average* weight (g)
<i>Mullus barbatus</i>							
II	3	170	4248	1264	100-9500	137 (170)	46 (170)
IV	1	218	3869	988	400-7000	146 (218)	51 (218)
V	1	2	3065	-	2900-3230	148 (2)	45 (2)
VII	1	11	4332	864	2700-5800	135 (11)	39 (11)
VIII	1	40	3499	804	2570-6890	145 (39)	-
IX	1	12	5067	1042	3660-7400	167 (10)	74 (10)
X	1	23	4370	651	3060-5870	141 (23)	33 (23)
<i>Mullus surmuletus</i>							
II	1	5	4222	580	3560-5300	164 (5)	67 (5)
IX	1	16	3897	1101	702-5200	158 (16)	78 (16)

* Number of specimens in brackets

The averages from the different areas are very similar and the standard deviations are comparatively small. This indicates a rather uniform body burden which, however, may reflect the actual environmental concentrations.

4.4.3 Other species

Overall averages of levels of copper in non-obligatory species are shown in table 17 and for zinc in non-obligatory species in table 18. Only averages based on three or more samples are presented.

4.5 Other elements

As was discussed in section 3 (Intercalibration exercise), the results for lead highlighted the difficulties with the analyses of this metal in biological material. In fact, results from five of the 14 research centres had to be deleted on the basis of the intercalibration exercise.

Table 17. Overall averages of levels of copper in samples of non-obligatory species.

sampling area	species	no. of samples (n)	mean conc. ug/kg F.W.	standard deviation	range
II	<u>Engraulis encrasicolus</u>	65	884	495	150-1800
	<u>Nephros norvegicus</u>	209	6283	2816	1250-24400
	<u>Sarda sarda</u>	12	1347	877	370-3900
IV	<u>Engraulis encrasicolus</u>	32	1223	613	400-2200
	<u>Nephros norvegicus</u>	110	5867	1999	2150-11350
VII	<u>Lithothaera lithothaera</u>	5	3892	754	3140-5140
VIII	<u>Parapenaeus longirostris</u>	9	12508	10826	4570-35400
IX	<u>Musil auratus</u>	31	697	964	200-5700
	<u>Musil saliens</u>	3	483	245	150-730
	<u>Pagellus acarne</u>	3	450	42	390-480
	<u>Penaeus kerathurus</u>	12	5253	2727	1770-11400
	<u>Pomatomus saltator</u>	3	760	178	510-910
	<u>Sardinella maderensis</u>	4	728	557	350-1690
	<u>Upeneus molluccensis</u>	4	466	149	366-723
X	<u>Donax trunculatus</u>	19	3478	1810	1454-7742
	<u>Pagellus erythrinus</u>	4	835	179	570-1040
	<u>Saurida undosquamis</u>	6	452	136	310-670
	<u>Trachurus mediterraneus</u>	3	713	232	530-1040

Table 18. Overall averages of levels of zinc in samples of non-obligatory species.

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
II	<u>Engraulis encrasicolus</u>	63	17122	6213	6500-41650
	<u>Nephrops norvegicus</u>	217	15676	4460	6500-35600
	<u>Sarda sarda</u>	14	4793	1312	2600-7500
IV	<u>Engraulis encrasicolus</u>	36	20393	5580	9600-29400
	<u>Nephrops norvegicus</u>	110	14662	2057	10700-20700
VII	<u>Lithothauma lithothauma</u>	5	25070	36059	120-96000
VIII	<u>Merluccius merluccius</u>	4	2615	1001	1000-3740
	<u>Parapenaeus longirostris</u>	19	10834	3419	3810-16700
IX	<u>Boops salpa</u>	9	6559	1157	4620-8220
	<u>Muril auratus</u>	50	4780	1474	2700-9680
	<u>Muril saliens</u>	3	2833	249	2500-3100
	<u>Parcellus acarne</u>	3	4770	905	4100-6050
	<u>Penaeus kerathurus</u>	12	13546	2653	9250-18800
	<u>Poratomus saltator</u>	3	10400	6438	5600-19500
	<u>Sardinella maderensis</u>	5	9338	4241	4420-14440
	<u>Uneneus molluccensis</u>	12	2553	195	2200-2950
X	<u>Donax trunculatus</u>	17	21420	16697	9172-82144
	<u>Parcellus erythrinus</u>	4	5820	1324	3760-7300
	<u>Saurida undosquamis</u>	6	3910	700	2610-4900
	<u>Trachurus mediterraneus</u>	3	6027	682	5140-6800

Table 19. Overall averages of levels of lead in samples of obligatory and non-obligatory species.

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
II	<u>Boops boops</u>	7	314	485	100-1500
	<u>Engraulis encrasicolus</u>	59	50	-	-
	<u>Maena smaris</u>	5	360	355	100-1000
	<u>Mullus barbatus</u>	163	55	17	33-169
	<u>Mytilus galloprovincialis</u>	110	901	1050	50-6800
	<u>Nephrops norvegicus</u>	214	50	-	-
IV	<u>Engraulis encrasicolus</u>	91	74	66	50-391
	<u>Mullus barbatus</u>	214	56	26	50-200
	<u>Mytilus galloprovincialis</u>	71	1634	2606	50-16100
	<u>Nephrops norvegicus</u>	117	68	104	50-865
	<u>Thunnus alalunga</u>	8	195	79	45-256
V	<u>Mytilus galloprovincialis</u>	77	960	1340	50-7825
VI	<u>Engraulis encrasicolus</u>	11	149	75	43-236
	<u>Mullus barbatus</u>	13	135	67	30-233
	<u>Mytilus galloprovincialis</u>	12	503	237	165-960
	<u>Nephrops norvegicus</u>	7	604	253	186-900
	<u>Thunnus alalunga</u>	8	202	91	40-290
VIII	<u>Mullus barbatus</u>	29	286	189	41-861
	<u>Mytilus galloprovincialis</u>	83	1070	1492	55-8260
	<u>Parapenaeus longirostris</u>	3	300	-	-
	<u>Thunnus thynnus</u>	6	377	156	159-560
	<u>Xiphias gladius</u>	2	242	-	126-358
IX	<u>Murex auratus</u>	7	243	278	50-790
	<u>Murex saliens</u>	3	210	226	50-530
	<u>Mullus barbatus</u>	5	64	28	50-120
	<u>Mytilus galloprovincialis</u>	4	550	47	480-610
	<u>Upeneus molluccensis</u>	3	50	-	-
X	<u>Donax trunculatus</u>	19	1200	647	357-2957
	<u>Mullus barbatus</u>	22	371	121	144-610
	<u>Parcellus erythrinus</u>	4	393	158	166-590
	<u>Saurida undosouamis</u>	6	510	144	292-735
	<u>Trachurus mediterraneus</u>	3	401	113	290-556

The remaining results should also be considered with caution when interpreting the levels of lead. Overall averages for all species, where there are more than three samples have been collected in each area, are shown in table 19. The average levels in *Mytilus galloprovincialis* in areas II, IV, V and VIII are between 901 and 1634 ug/kg with a considerable variation between individual samples. Values from the Canadian coast in the ICES North Atlantic baseline study show a similar variation with an overall average of 330 ug/kg, ICES (1980).

Another additional element that was recommended in the Operational Document was selenium. The limited number of centres reporting and of samples analysed does not permit any evaluation of levels on a Mediterranean basis. The results, which should be considered only as indicative until more data are available, are presented in table 20.

Table 20 - Overall average of levels of selenium in samples of obligatory and non-obligatory species

sampling area	species	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range
II	<i>Mullus barbatus</i>	14	575	130	350- 850
	<i>Nephrops norvegicus</i>	16	634	254	310-1250
IV	<i>Mullus barbatus</i>	65	686	281	150-1500
	<i>Nephrops norvegicus</i>	16	1007	586	490-3050
V	<i>Mytilus galloprovincialis</i>	9	845	464	123-1750
VIII	<i>Merluccius merluccius</i>	4	261	94	171- 416
	<i>Mullus barbatus</i>	38	468	111	290- 723
	<i>Mytilus galloprovincialis</i>	6	331	137	101- 550
	<i>Parapenaeus longirostris</i>	19	1 247	556	525-2500

Among other elements that have been analysed are chromium, nickel, iron and manganese but the scarcity of data does not permit an evaluation even on an area basis. Results for chromium and nickel are however presented in table 21. Reference is also made to the final reports by the participating research centres presented in document UNEP/WG.46/Inf.6.

4.6 Discussion

The results presented in this evaluation and in the final reports of the

Table 21. Overall averages of levels of chromium and nickel in samples of obligatory and non-obligatory

sampling area	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
chromium					
V	<u>Mytilus galloprovincialis</u>	19	260	140	89-558
VIII	<u>Merluccius merluccius</u>	4	91	66	21-156
	<u>Mullus barbatus</u>	38	88	151	24-981
	<u>Mytilus galloprovincialis</u>	5	287	194	113-530
	<u>Parapenaeus longirostris</u>	18	111	64	64-300
IX	<u>Mugil auratus</u>	15	115	206	12-850
	<u>Mugil saliens</u>	3	346	77	250-440
	<u>Mullus surmuletus</u>	5	74	49	40-170
	<u>Penaeus kerathurus</u>	4	140	110	70-330
nickel					
V	<u>Mytilus galloprovincialis</u>	18	409	300	125-1216
IX	<u>Mugil auratus</u>	7	240	153	30-540
	<u>Mugil saliens</u>	3	263	57	190-330
	<u>Mullus surmuletus</u>	4	1147	474	690-1800
	<u>Penaeus kerathurus</u>	3	1610	927	910-2920
X	<u>Donax trunculatus</u>	4	641	80	560-766
	<u>Mullus barbatus</u>	17	246	76	122-455
	<u>Pagellus erythrinus</u>	4	209	22	177-231
	<u>Saurida undosquamis</u>	6	276	70	209-423

research centres should primarily be considered as baseline information on the levels of heavy metals in marine organisms in the Mediterranean. These results may be used to evaluate health hazards from the consumption of seafood and possible adverse effects on the marine ecosystem. It is for example clear that some migratory species such as *Thunnus thynnus thynnus* have high body burdens of mercury which often exceed the national standards. *Mytilus galloprovincialis* and *Mullus barbatus* show high average concentrations in samples from the Tyrrhenian Sea, the North-West Mediterranean and the Adriatic. Although the high levels of mercury in tuna were expected it is maybe more surprising that the crustacea *Nephrops norvegicus* sampled in the Tyrrhenian Sea and the North-West Mediterranean has the same average concentration (around 1000 ug/kg). For the other areas and species the average concentrations are generally lower and of the same size as those found in the ICES North Sea studies. The range and the standard deviation indicate however that organisms in certain areas also may have high body burdens.

For cadmium and the the other heavy metals studied the situation is somewhat different as there is no pronounced difference between the areas. *Mytilus galloprovincialis* and other molluscs seem to have higher average concentrations than teleosts.

The information is also an important basis for the planning of future long-term monitoring activities using marine organisms. It is certainly neither feasible nor desirable to include such a variety of organisms and pollutants, as has been studied in this pilot phase, in any long-term monitoring exercise. The following brief discussion of the combinations of species and pollutants used may therefore be useful for future activities.

4.6.1 Mercury

Mytilus galloprovincialis and/or *M. edulis* and *Perna* (*Mytilus*) *perna* have a wide distribution in the Mediterranean, being unavailable only in a few regions. They are able to accumulate and release mercury in proportion to the environmental levels. As they are sessile organisms feeding on plankton and particulate matter, the concentrations of pollutants should primarily be considered as indications of levels in relatively small areas (i.e. harbours or river mouths).

From the final reports by the principal investigators it seems that factors like sex, body size, temperature, salinity and depth (i.e. taken in the intertidal zone or not) are more important than the sampling season.

Mullus barbatus and/or *Mullus surmuletus* are available all over the Mediterranean and are suitable indicators of environmental levels of mercury, as mercury is not regulated in the axial muscle of finfish. These species can be very useful for monitoring of continental shelves. *Thunnus thynnus thynnus*, as a migratory predator at the top of the food-chain, seems to be suitable for the monitoring of the levels of mercury on a Mediterranean basis and for the assessment of the eventual risks to human health from mercury. For *Mullus*, sex and particularly age and size, are the principal factors affecting mercury levels at the same environmental

concentrations. Attention should be paid to the possibility of variation of the bioavailability of mercury due to the sampling depth. Also, for Thunnus, the size or age appears to be an important parameter affecting the mercury levels. The possibilities of different body burdens of tuna of Atlantic and Mediterranean origin would, however, have to be taken into account.

4.6.2 Other metals

The soft parts of molluscs, especially Mytilus, are recognized as good indicators of environmental levels of cadmium, zinc, lead and probably copper. For teleosts and probably crustaceans the situation is somewhat different, as these organisms seem to regulate metabolically the concentration of certain metals irrespective of the degree of ambient contamination. Phillips (1977) in a review of the use of biological indicators to monitor trace metal pollution, concluded that several elements are strictly regulated in the muscle of finfish. The results obtained during the pilot phase are, however, most useful as baseline data for the assessment of the human intake of trace metals through seafood. Other organs like the kidney or liver in the teleosts are also suitable for monitoring the environmental levels of trace metals which are regulated in the muscle.

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MED POL III : BASELINE STUDIES AND MONITORING OF DDT, PCBs and OTHER
CHLORINATED HYDROCARBONS IN MARINE ORGANISMS (prepared by FAO)

1. INTRODUCTION

The evaluation contained in this document is based on the final scientific reports submitted by the participating research centres, as well as on data provided on LOG FORMS for computer treatment. As at 1 July 1980, 16 of the participating 24 research centres had submitted their final reports. Of the remaining nine centres three had submitted the latest scientific report during 1979 as part of the normal reporting routine of the pilot project.

During the first half of the pilot phase the number of analyses carried out was rather limited; this made possible the evaluation of results from all participants without the use of computer facilities. A preliminary evaluation on a Mediterranean basis was also presented and discussed at the Mid-term Expert Consultation, Dubrovnik, 2-13 May 1977. As the participating centres improved their analytical capabilities during the second half of the pilot phase, the number of analyses performed increased considerably. It was, therefore, apparent that, for the preparation of the final report, the use of computer facilities for data treatment would be necessary.

The LOG FORMS, which serve as the basis for entering the data into a computer system, were completed and provided in a usable form by 16 centres. A total of about 7000 data lines, each giving one analytical value as well as information on location and biological parameters, was reported.

A common system for analysis, storage and presentation of all MED POL data is envisaged but is, at the time of preparation of this report, only at the early stage of implementation. FAO therefore made use of an existing computer system designed essentially for the Fisheries Commodities Data Base, with supplementary print programmes to generate tables in order to meet the requirements of the pilot project.

The results presented in this report are mainly based on tables giving concentrations by species and compounds for different sampling stations and MED POL areas which were produced by the FAO Fisheries Information Data and Statistics Service. It is, however, envisaged that the data will be transferred to, and utilized by, the Mediterranean data processing system in Geneva, as and when operational.

2. METHODOLOGICAL CONSIDERATIONS

2.1 Selection of the species

The marine organisms selected in the Operational Document as mandatory species are *Mytilus galloprovincialis* (Mediterranean mussel) and/or *M. edulis*, *Mullus barbatus* (striped mullet), *Parapenaeus longirostris* (deep-water pink shrimp) and/or *Carcinus mediterraneus* (Mediterranean shore crab). The basis for this selection was that these organisms are representatives of different ecotypes, they are of considerable economic importance and they are common in almost the whole of the Mediterranean.

As can be seen from table 1, results on *Mytilus galloprovincialis* and *Mullus barbatus* were reported by 15 and 16 centres, respectively. However, in some areas of the Eastern Mediterranean, e.g. Israel and Cyprus, *Mytilus* was reported as being unavailable. In Turkey, only one of the two participating centres reported results on *Mytilus*, while the other centre did so only for the pilot project MED II. As regards the centres which have not yet reported results, it seems likely that they will be able to collect samples of *Mytilus*. With this slight reservation, it can be concluded that this species has proved, as far as availability is concerned, to be a useful organism for monitoring purposes.

Mullus barbatus was sampled by all centres with one exception, the Biological Institute in Dubrovnik, which had selected another member of the Mullidae family, *Mullus surmuletus* (red mullet) as an alternative species. The conclusion on the usefulness of *Mytilus* for monitoring is therefore undoubtedly valid for *Mullus barbatus* as well.

As regards *Parapenaeus longirostris*, this species was sampled by only four centres, thus rendering the results less useful for the evaluation of levels of contamination on a Mediterranean basis. The reason for this limited sampling could be that *Parapenaeus* requires more sophisticated fishing techniques than the previously mentioned species. This was possibly also the reason why the alternative species *Carcinus mediterraneus* was sampled by more centres (eight) than *Parapenaeus*.

The total number of additional species that were sampled is close to 40, but the number of samples and the frequency of sampling is, though variable, generally low. Table 1 and 2 show all the species and the number of centres that have collected samples. Only species whose full scientific names have been given are included. Most of the species have been sampled by only one centre. Some, however, have been chosen more frequently, and *Engraulis encrasicolus*, *Sardina pilchardus*, *Merluccius merluccius*, *Mullus surmuletus*, *Mugil auratus*, *Patella coerulea* and *Pagellus erythrinus* have been sampled by three or more centres.

Of these *Sardina*, *Merluccius*, *Mugil* and *Patella* were recommended as additional or alternative species in the Operational Document and at the Mid-term Expert Consultation. Most of the additional species (about 40) are also sampled for analysis of heavy metals (MED II) but not necessarily by the same research centre.

Table 1. Species sampled and compounds analysed

Research Centre	Final report	Species					Elements					
		<i>Mytilus galloprovincialis</i>	<i>Mullus barbatus</i>	<i>Parapenaeus longirostris</i>	<i>Corcinus mediterraneus</i>	Other	PCB	DDT	DD	DDE	Dieldrin	Other
Fisheries Department, Nicosia	X		X				X	X	X	X	X	X
Institute of Oceanography and Fisheries, Alexandria												
Centre for Post-graduate Studies and Research, Alexandria												
Laboratoire de chimie appliquée à l'expertise, Montpellier	X	X	X		X		X	X	X	X	X	X
Institut scientifique et technique des pêches maritimes, Sète	X	X	X		X		X	X	X	X	X	X
Institute of Oceanographic and Fisheries Research, Athens	X	X	X				X	X	X	X	X	X
Department of Food Hygiene, University of Thessaloniki	X	X	X				X	X	X	X	X	X
Laboratory of Analytical Chemistry, University of Thessaloniki												
Benaki Institute of Phytopathology, Athens												
Israel Oceanographic and Limnological Research Ltd., Haifa	X	X	X		X		X	X	X	X	X	X
Laboratory of Hydrobiology and Fish Culture, Siena	X	X	X				X	X	X	X	X	X
Institute of Marine Biology - CNR, Venice	X	X	X		X		X	X	X	X	X	X

continued

Table 1. Species sampled and compounds analysed (continued)

Research Centre	Final report	Species					Elements							
		<i>Mytilus galloprovincialis</i>	<i>Mytilus barbatus</i>	<i>Paraperanus longirostris</i>	<i>Corcinus mediterraneus</i>	Other	PCB	DDT	DDD	DDE	Dieldrin	Other		
Centre de Recherche marine, Beyrouth														
The University of Malta, Msida														
Institut scientifique des Pêches maritimes, Casablanca	X	X	X				X	X	X					
Instituto de Investigaciones Pesqueras, Barcelona		X	X				X	X	X					
Instituto Químico de Sarría, Barcelona	X	X	X				X	X	X					
Institut national scientifique et technique d'océanographie et de Pêche, Salammbô														
Hydrobiological Research Institute, Istanbul														
Marine Science Department (METU), Erdemli-Içel	X	X	X				X	X	X					
Institute for Oceanography and Fisheries, Split	X	X	X				X	X	X					
The Biological Institute, Dubrovnik	X	X					X	X	X					
"Rudjer Bošković" Institute, Zagreb	X	X	X				X	X	X					
Marine Biological Station, Portorož	X	X	X				X	X	X					

Table 2. Additional species sampled.

<u>Species sampled</u>	<u>Number of centres</u>	<u>Sampled also in MED II</u>
<u>Arca noae</u>	1	X
<u>Belone belone</u>	1	X
<u>Boops boops</u>	2	X
<u>Boops salpa</u>	2	
<u>Callinectes sapidus</u>	1	
<u>Carcinus maenas</u>	1	
<u>Conger conger</u>	1	X
<u>Dentex macrophthalmus</u>	1	X
<u>Engraulis encrasicolus</u>	3	X
<u>Lithophaga lithophaga</u>	1	X
<u>Loligo vulgaris</u>	1	X
<u>Maena maena</u>	1	X
<u>Merlangius merlangus</u>	1	X
<u>Merluccius merluccius</u>	5	X
<u>Monodonta turbinata</u>	1	
<u>Mugil auratus</u>	3	X
<u>Mugil capito</u>	1	X
<u>Mugil saliens</u>	1	X
<u>Mullus surmuletus</u>	5	X
<u>Nephrops norvegicus</u>	1	X
<u>Oblada melanura</u>	1	X
<u>Ostrea edulis</u>	2	X
<u>Pagellus acarne</u>	1	X
<u>Pagellus erythrinus</u>	3	X
<u>Patella coerulea</u>	3	X
<u>Penaeus kerathurus</u>	1	X

Table 2. Additional species sampled(continued-2)

<u>Species sampled</u>	<u>Number of centres</u>	<u>Sampled -also in MED II</u>
<u>Sardina pilchardus</u>	3	X
<u>Sardinella aurita</u>	1	
<u>Saurida undosquamis</u>	1	X
<u>Scomber scombrus</u>	1	X
<u>Solea vulgaris</u>	1	
<u>Thunnus thynnus thynnus</u>	2	X
<u>Trachurus mediterraneus</u>	1	X
<u>Trachurus trachurus</u>	2	X
<u>Trisopterus minutus capelanus</u>	1	
<u>Upeneus moluccensis</u>	2	X
<u>Upogebia littoralis</u>	1	X
<u>Venerupis aureus</u>	1	
<u>Xantho hydrophilus</u>	1	
<u>Xiphias gladius</u>	1	X

An evaluation on a Mediterranean basis of the levels of contamination in all the additional species is impossible because of the limited number of samples. Nevertheless, the results can be useful for the assessment of local pollution and provide baseline information. For some migratory species the data may also give an indication of body burdens in the Mediterranean.

In a few cases results of analysis of zooplankton, sediments and water have also been reported.

2.2 Pollutants analysed

All research centres, with one exception, that have reported data, have made analyses of PCBs.

For DDT, DDE and DDD, results were received from all centres (table 1). As regards dieldrin, this pollutant was analysed by only 11 centres, which may be due to the fact that the analytical procedure for dieldrin is somewhat different from that for PCBs and DDT. As dieldrin is related to aldrin, being its epoxide, some centres have analysed both compounds, or aldrin as an alternative to dieldrin. Endrin, which is also derived from aldrin, was analysed by two centres. Lindane, the γ -isomer of hexachlorocyclohexane (BHC or HCH) has been analysed by five centres, some of them also analysing the α -, β -, and γ - isomers of BHC (HCH).

While only one centre analysed the pesticide heptachlor, five centres made analyses of its conversion product heptachlorepoxyde.

2.3 Areas studied

According to the Operational Document, the baseline studies and monitoring were to be carried out primarily in the coastal waters. Furthermore, the sampling stations were to be selected by the participating research centres so that the results obtained could be used to characterize the level of pollutants in certain areas. The sampling frequency was to be seasonal.

The number of sampling stations selected by the different centres varies considerably, from two stations to over 20. In the latter case, however, the samples were collected only occasionally. In fact very few centres have strictly followed the agreed sampling frequency with regard to seasonal sampling. Figure I shows the different areas that have been monitored or where monitoring is planned but data have not been reported.

The northern Mediterranean coast is relatively well covered by a number of research centres, but those from the southern Mediterranean cover only a small part of the coast and some of them have not been able to produce any data. Table 3 shows the number of research centres and sampling stations for the different MED POL areas.

Table 3. Number of research centres and sampling stations.

MED POL area	Research centre	Sampling stations
I	1	8
II	3	16
III	-	-
IV	1	8
V	5	>31*
VI	-	-
VII	-	-
VIII	4	28
IX	1	8
X	1	18
XI	1	3
XII	1	2
<hr/>		
Total	18	>122
<hr/>		

* One centre did not indicate the co-ordinates for the sampling stations.

No data were reported for areas III (South-Western), VI (Ionian) and VII (Central) while three or more centres reported results from areas II (North-Western), V (Adriatic) and VIII (Aegean). For the remaining areas results were reported by one centre in each area.

2.4 Methodology

Sampling and sample preparation were generally carried out in accordance with the recommendations given in the Manual of Methods in Aquatic Environment Research, Part 3 - Sampling and Analysis of Biological Material; FAO Fisheries Technical Paper No. 158. In a few cases however, samples were obtained from the market. These samples, if not handled with special care, risked contamination before arrival at the laboratory.

The samples were either homogenized with anhydrous Na_2SO_4 or, as in most cases, lyophilized before extraction. Extraction of the samples was carried out either with a blender or Soxhlet. The solvents used were also

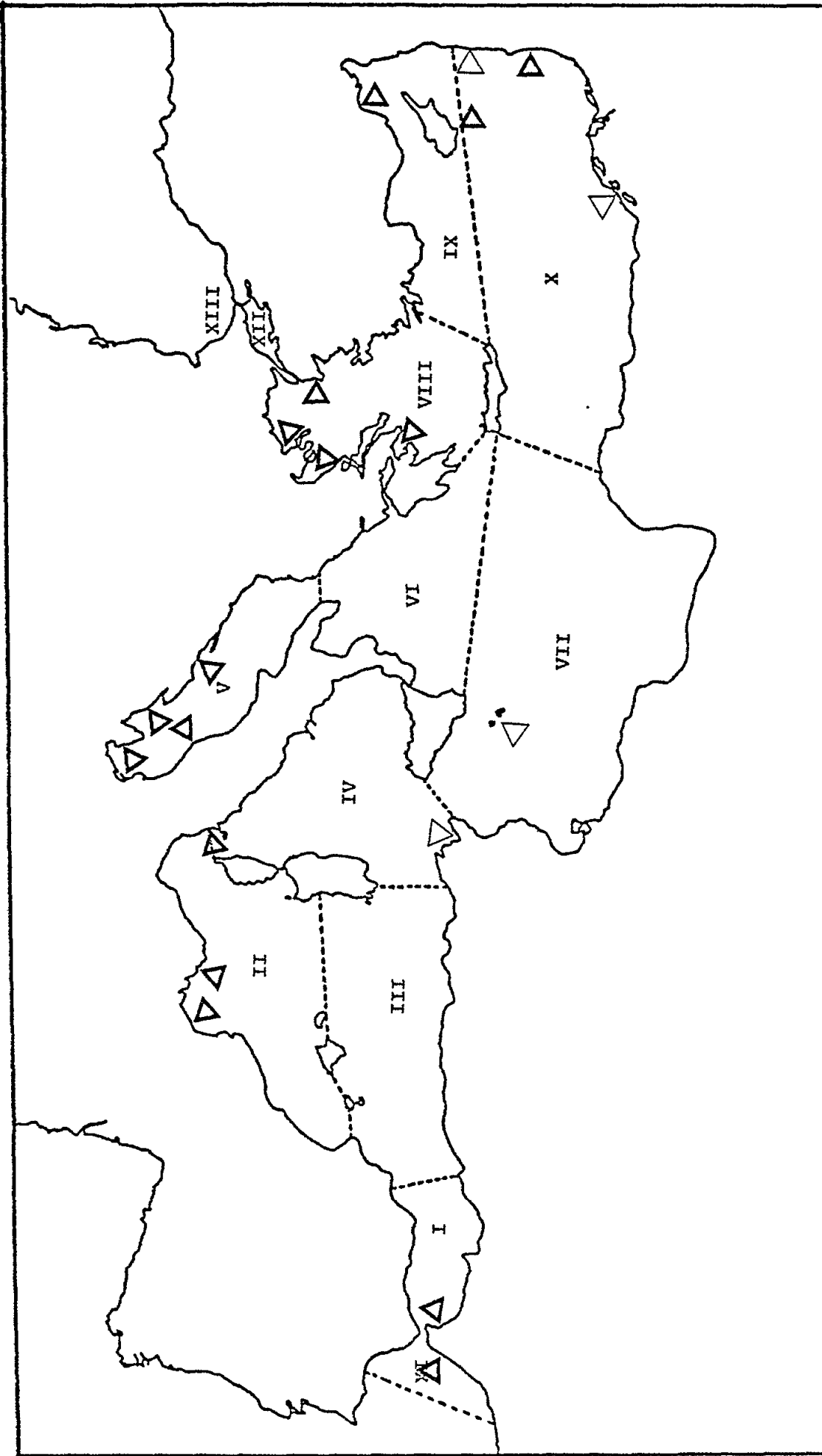


Figure 1 Sampling areas for MED III

- | | | | |
|--------------------|--------------|---------------------|-----------------|
| I. Alboran | V. Adriatic | IX. N. Levantin | XIII. Black Sea |
| II. North-Western | VI. Ionian | X. S. Levantin | |
| III. South-Western | VII. Central | XI. Atlantic | |
| IV. Tyrrhenian | VIII. Aegean | XII. Sea of Marmara | |
| △ Data reported | | △ No data reported | |

different, i.e. n-hexane or petroleum ether, but in most cases Soxhlet extraction with n-hexane was used. Since the extractable organic matter (EOM) is dependent on the solvent used, the different solvents used may affect the results, at least for some organochlorine residues.

Several different clean-up procedures were used of which the most common were:

- (i) Partitioning with either hexane-acetonitrile or petroleum-ether;
- (ii) Clean-up with sulphuric acid which, however, destroys dieldrin as this pesticide is not acid stable;
- (iii) Elution on florisil or alumina.

Although all these methods are generally accepted as clean-up procedures, they may not necessarily give the same results for all chlorinated hydrocarbons. Therefore the participating research centres have made evaluations of the loss of chlorinated hydrocarbons due to pretreatment.

For the separation of some chlorinated insecticides from PCBs, many research centres used silica-gel chromatography with different eluents. In the subsequent gas-chromatographic analyses with electron capture detectors, columns containing various types of supports and stationary phases were used.

Sometimes the samples were analysed on two types of columns for control of the identification.

For confirmation many centres have used the alcoholic saponification with KOH, while the perchlorination of PCBs to decachlorobiphenyl (DCB) was not reported by any centre.

The quantification of the PCBs was generally carried out by matching the chromatograms of the samples with those of known quantities of Aroclor 1254 or 1260. Sometimes other commercially available PCBs such as DP5 and DP6 were used.

3. INTERCALIBRATION EXERCISE

An extensive evaluation of the intercalibration exercise (MED POL XI) is presented in document UNEP/WG.46/3 Part II.

The following evaluation is therefore restricted only to questions directly related to treatment of the monitoring data.

The participating centres were provided with three different intercalibration samples as well as standards for the most common organochlorine residues. Analyses of all three samples were reported by 10 of the 18 centres that have reported data. Of the remaining eight centres

six reported results for one or two samples, while the other two did not carry out any intercalibration (table 4). To allow for a sufficiently reliable evaluation of the results from the individual centres, preferably two or three intercalibration samples should have been reported.

For each sample and compound, the arithmetic mean and standard deviation (SD) of the results reported by the participating centres have been calculated.

In order to exclude "outliers" Dixon's test was used. As a basis for estimating the reliability of the data and their fitness for inclusion in the evaluation of the monitoring exercise the following criteria were used:

- (i) results within one standard deviation from the mean (after Dixon's test) to be considered as "acceptable";
- (ii) results deviating more than one standard deviation from the mean to be considered as "not acceptable".

For the overall evaluation of the three intercalibration samples, the average of two "acceptable" results and one "not acceptable" was considered as acceptable. With two "not acceptable" and one "acceptable" the average was considered as "not acceptable". In the cases where only two samples were reported on and one result was "not acceptable" the judgement was based on how much the values deviated from the mean.

When considering these principles for accepting the data for evaluation it became evident that the quantity of data would be noticeably reduced. However, for an evaluation of the levels of contamination on a Mediterranean basis, it is preferable to have a smaller number of data that are reasonably comparable. Out of a total of 17 research centres the results on PCBs and DDT and its derivatives from five centres were deleted due to unacceptable values or lack of intercalibration results. As a consequence, only results from areas II, IV, V, VIII, IX and X could be used. Due to the limited number of reports, results for dieldrin and aldrin could be used only from areas II, IV, V, X and II, IV, IX, X, respectively. For the other contaminants an evaluation of the intercalibration results was not possible.

A comparison of the results in this intercalibration exercise with those that have been reported in the International Council for the Exploration of the Sea (ICES) North Sea baseline studies, shows that the coefficient of variation between the laboratories is larger in the Mediterranean than in the ICES area (ICES, 1978). This was to be expected however, as all laboratories in the ICES study are well established, while many centres in the Mediterranean have only recently begun gas-chromatographic analysis of chlorinated hydrocarbons. As was pointed out for the ICES studies, a regular repetition of the exercises will certainly further improve the quality of the data.

Table 4. Participation in intercalibration of samples MA-M-1 (oyster), MA-A-1 (copepod) and MA-A-2 (fish).

Research Centre	Data reported	MA-M-1	MA-A-1	MA-A-2
Fisheries Department, Nicosia	X			
Institute of Oceanography and Fisheries, Alexandria				
Centre for Post-graduate Studies and Research, Alexandria				
Laboratoire de chimie appliquée à l'expertise, Montpellier	X	X	X	X
Institut scientifique et technique des pêches maritimes, Sète	X	X	X	X
Institute of Oceanographic and Fisheries Research, Athens	X	X	X	X
Department of Food Hygiene, University of Thessaloniki	X	X	X	
Laboratory of Analytical Chemistry, University of Thessaloniki				
Penaki Institute of Phytopathology, Athens	X	X	X	
Israel Oceanographic and Limnological Research Ltd., Haifa	X	X	X	X
Laboratory of Hydrobiology and Fish Culture, Siena	X	X		
Institute of Marine Biology - CNR, Venice	X	X	X	X
Centre de Recherche marine, Beyrouth				
The University of Malta, Msida				
Institut scientifique des Pêches maritimes, Casablanca	X			
Instituto de Investigaciones Pesqueras, Barcelona	X	X	X	
Instituto Químico de Sarria, Barcelona	X	X	X	X
Institut national scientifique et technique d'océanographie et de Pêche, Salambô				
Hydrobiological Research Institute, Istanbul	X	X		
Marine Science Department (MEIU), Erdemli-Içel	X	X	X	X
Institute for Oceanography and Fisheries, Split	X	X	X	X
The Biological Institute, Dubrovnik	X	X	X	X
"Rudjer Bosković" Institute, Zagreb	X	X	X	X
Marine Biological Station, Portorož	X	X	X	X

4. RESULTS OF THE BASELINE STUDIES AND MONITORING

4.1 Introduction

The levels of contamination presented in this section are, based only on data reported on LOG FORMS received before 15 July 1980. Data from the very first phase of the pilot project, before the LOG FORMS were developed, have not been key-entered unless these data have been transferred to LOG FORMS by the reporting centre.

Data presented for the different contaminants and organisms are mean values of all results reported for the various stations in the relevant MED POL area, with due consideration given to the intercalibration results. They do not take into account the differences between the conditions prevailing at the individual sampling stations (i.e. levels of pollution). Bearing in mind the wide extent of heterogeneous conditions within each MED POL area, it is obvious that the overall averages of the levels reported should not be interpreted as mean values for an area. References to (author, final report) refer to the individual summary reports prepared by the principal investigators, and presented in document UNEP/WG.46/Inf.6.

The reporting centres have used different detection limits depending on the conditions under which the analyses were carried out. For the purpose of reporting in the present document, intermediate detection limits have been selected arbitrarily and may not be the same as the ones reported by the individual centres. Sufficiently high detection limits have been given to ensure the best reliability for evaluation of the data.

4.2 PCBs

Levels of PCBs in the obligatory species, by area, are reported in Figure 2. The highest average values for *Mytilus galloprovincialis* were reported in samples from stations in area II (North-Western) (table 5).

Table 5. Average levels of PCBs in *Mytilus galloprovincialis*

area	no. of centres	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)
II	2	17	307	266	22-1 200	53 (17)
IV	1	13	95	114	2.5- 420	32 (13)
V	4	159	84	221	2.5-2 622	48 (159)
VIII	2	12	61	12	40- 80	48 (11)

* Number of specimens in brackets.

As the number of samples is quite small and the data are scattered, a comparison between the different areas is not possible.

The levels are similar to those reported for *Mytilus edulis* in the North Sea by ICES as part of the baseline survey of 1972 (ICES, 1974). The highest mean value reported in this study was 390 ug/kg in samples collected off the coast of the Netherlands. Similar values were also reported in the monitoring exercises during 1974, 1975 and 1976, with the highest mean values about 300 ug/kg, which is of the same order as the value for area II in the Mediterranean (ICES, 1977a and 1977c).

Levels reported from the Canadian coast in the ICES North Atlantic baseline study were however much lower with concentrations between 3 and 17 ug/kg, ICES (1980).

The highest average values in *Mullus barbatus* were reported in samples from stations in areas II and IV (Tyrrhenian Sea), Table 6.

Table 6. Average levels of PCBs in *Mullus barbatus*.

area	no. of centres	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)	average* weight (g)
II	2	33	814	1 496	30-8 000	144 (33)	56 (33)
IV	1	33	477	770	50-3 950	142 (33)	62 (33)
V	4	86	234	473	0.5-3 117	134 (84)	33 (84)
VIII	2	51	113	204	0-1 110	138 (51)	42 (43)
IX	1	6	9	19	0.4- 52	187 (6)	-
X	1	42	69	75	0- 284	143 (42)	31(42)

* Number of specimens in brackets.

There is a considerable variation between the values with an overall range from 0-8000 ug/kg, the latter value reported from area II. The difference between the averages is also quite pronounced, with the mean value in area II being two orders of magnitude higher than in area IX (North Levantine). A statistical evaluation shows that the average level in area II is significantly higher than the averages in all other areas except area IV. Area IV shows a significantly higher average than areas V, VIII, IX and X.

The concentrations in *Parapeneus longirostris* are very low in all three areas studied, while samples of *Carcinus mediterraneus* collected in area II have a mean concentration as high as 1,448 ug/kg (table 7).

Table 7. Average levels of PCBs in *Parapeneus longirostris* and *Carcinus mediterraneus*

area	no. of centres	no. of samples (n)	mean conc. ug/kg FW	standard deviation	range	average* length (mm)	average* weight (g)
<i>Parapeneus longirostris</i>							
VIII	2	30	12	12	0- 51	133 (27)	13 (27)
IX	1	3	1.5	1	0- 2.5	177 (3)	26 (3)
X	1	11	31	57	0- 157	102 (11)	4 (11)
<i>Carcinus mediterraneus</i>							
II	1	10	1 448	1 295	300-3 600	41 (10)	-
V	2	31	87	93	0.5- 540	45 (31)	-

* Number of specimens in brackets

Due to the low concentrations in *Parapeneus* the scale in Figure 2 is an order of magnitude lower than for the other species. As the chlorinated hydrocarbons being essentially non-polar, have a high affinity to lipids, organisms with a higher fat content like *Mullus barbatus* normally show a higher concentration than, for instance, i.e. *Mytilus galloprovincialis* and *Parapeneus longirostris*. In particular *Parapeneus*, used for the analysis, has a very low fat content in the abdomen.

Although not all areas have been covered and the number of samples is quite small, the results from the obligatory species give clear indication that the concentration of PCBs is higher in area II than in the eastern Mediterranean particularly.

Several additional species have also been analysed for PCBs although most of them in only one or two areas. The average concentrations based on three or more samples for each species are shown in table 8.

The highest values were reported for *Engraulis encrasicolus* in area II with a mean concentration of 385 ug/kg. The concentrations in *Merluccius merluccius* sampled in areas V (Adriatic) and X (South Levantine) are similar to, or lower than, those from the ICES North Atlantic baseline

Mytilus
galloprovincialis

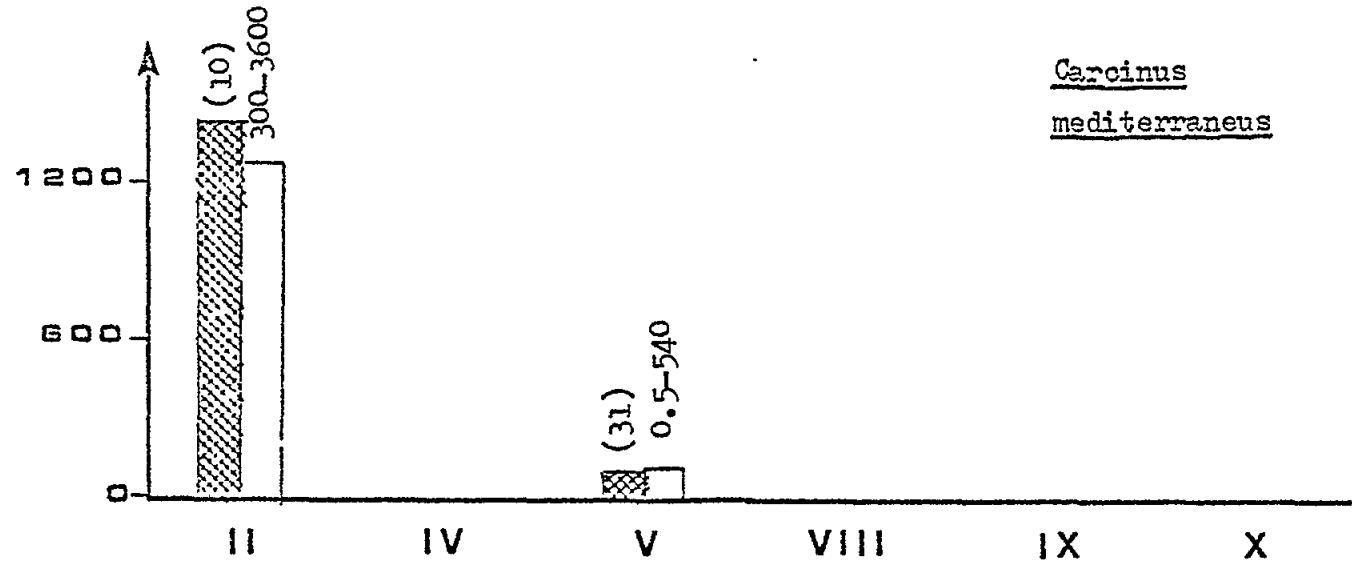
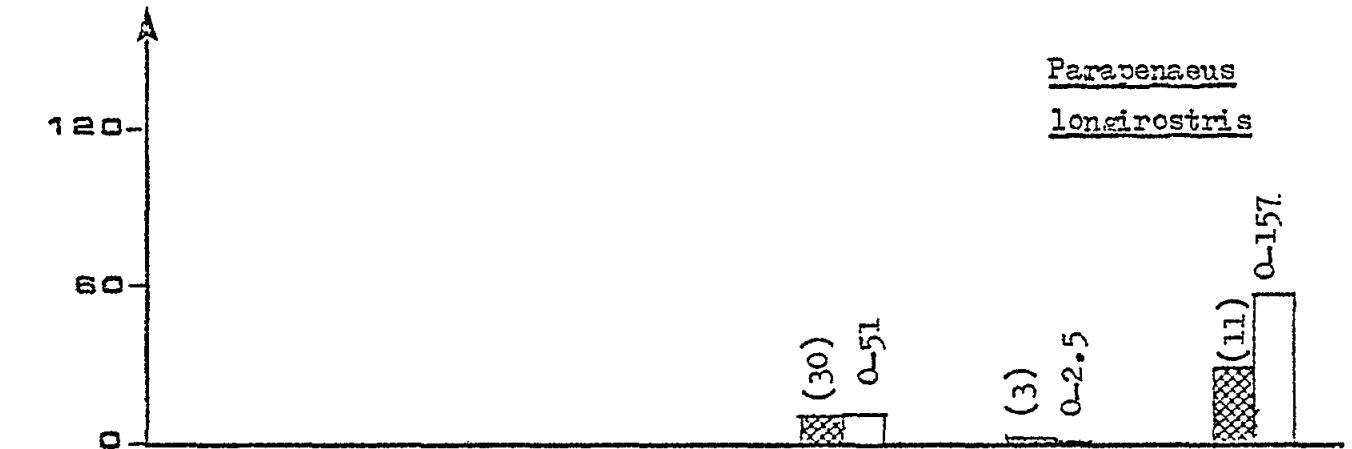
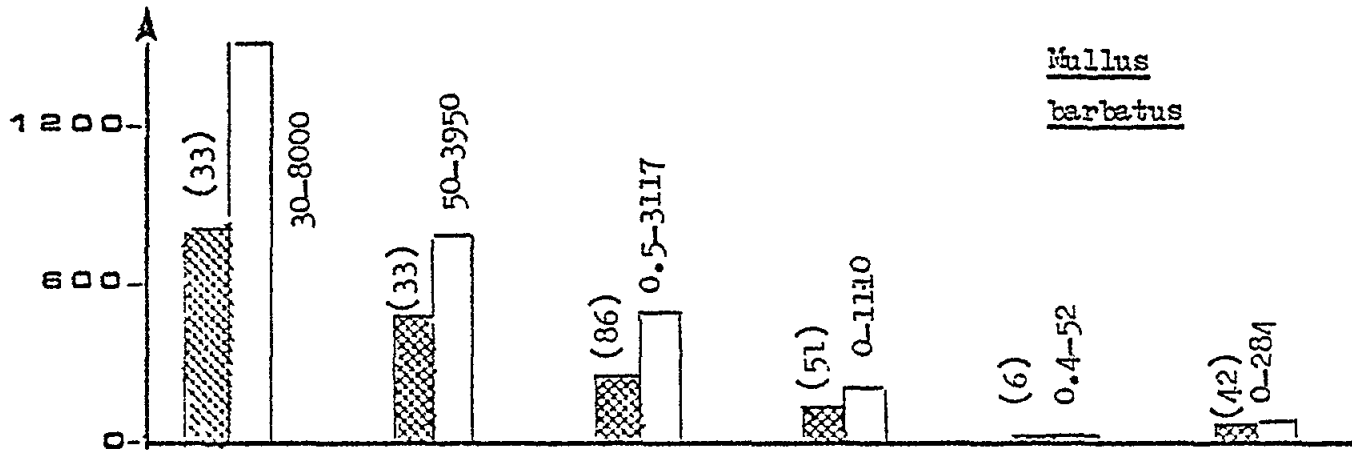
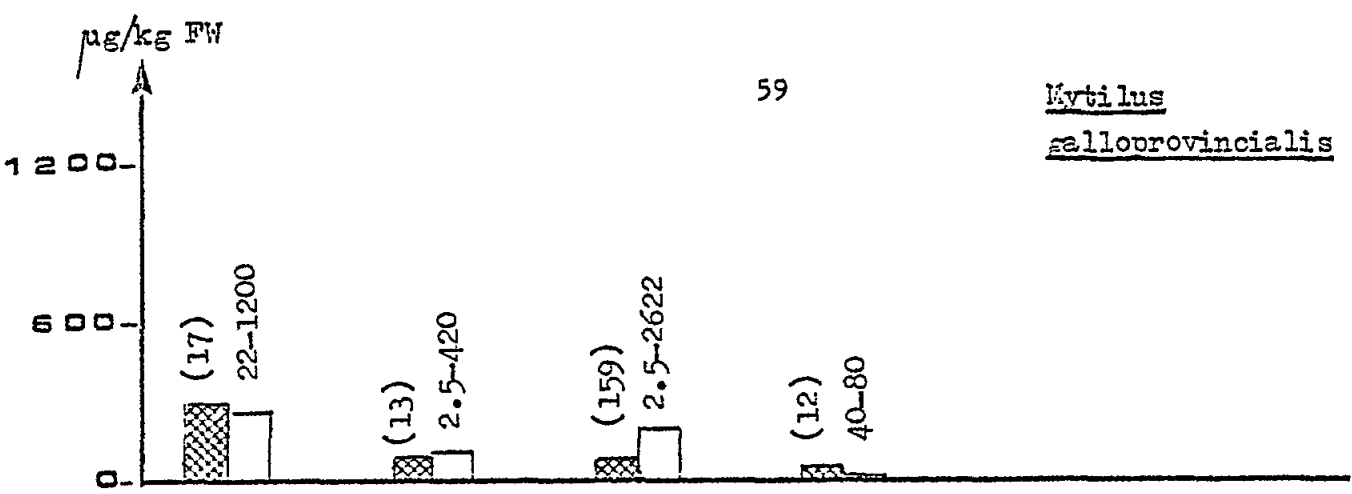


Figure 2. Average levels of PCB in different species by MED POL areas.

() n
 [hatched box] arithmetical mean
 [empty box] range
 [empty box] standard deviation

Table 8. Overall averages of levels of PCB in non-obligatory species.

Sampling areas	Species	No. of samples (n)	Mean conc. $\mu\text{g}/\text{kg}$ F.W.	Standard deviation	Range
II	<u>Engraulis encrasicolus</u>	6	385	151	140 - 160
IV	<u>Engraulis encrasicolus</u>	10	153	63	40 - 260
	<u>Mullus surmuletus</u>	6	87	17	60 - 110
	<u>Nephrops norvegicus</u>	28	25	17	8 - 90
V	<u>Engraulis encrasicolus</u>	8	106	98	21 - 325
	<u>Loligo vulgaris</u>	4	128	77	30 - 235
	<u>Merluccius merluccius</u>	6	26	20	5 - 52
	<u>Mugil auratus</u>	4	330	422	64 - 1060
	<u>Mullus surmuletus</u>	9	101	130	5 - 441
	<u>Ostrea edulis</u>	8	13	8	5 - 30
	<u>Pagellus erythrinus</u>	4	44	35	2.5 - 96
	<u>Patella coerulea</u>	4	10	4	2.5 - 14
	<u>Penaeus kerathurus</u>	7	45	31	20 - 118
	<u>Sardina pilchardus</u>	8	303	153	129 - 602
	<u>Trachurus trachurus</u>	4	151	92	34 - 287
	<u>Venerupis aureus</u>	15	7	8	0.5 - 30
	<u>Xantho hydrophilus</u>	10	93	71	7 - 242
IX	<u>Mugil saliens</u>	5	18	29	0.5 - 77
X	<u>Boops boops</u>	4	44	22	19 - 55
	<u>Maena maena</u>	5	77	91	7 - 254
	<u>Merluccius merluccius</u>	5	29	23	0 - 70
	<u>Pagellus erythrinus</u>	12	231	287	36 - 994
	<u>Saurida undosquamis</u>	15	190	297	11 - 1190
	<u>Sohyraena sohyraena</u>	3	275	167	80 - 487
	<u>Trachurus mediterraneus</u>	3	72	33	27 - 100
	<u>Ueneus molluccensis</u>	16	145	187	3 - 800

study of 1975 (mean concentrations from 20-390 ug/kg), ICES (1977b). Samples of *Merluccius merluccius* from the Portuguese coast collected in 1976 had however mean concentrations of only 9 to 19 ug/kg, ICES (1980).

As regards the forms of PCBs present in the organisms, it appears from the final reports of the principal investigators and the LOG FORMS that PCBs are usually present as mixtures of highly chlorinated compounds. Most results have been reported as Aroclor 1254 or Aroclor 1260 or a mixture of the two. This is to be expected, however, as the PCBs with lower chlorine content are more easily eliminated from the organism (WHO, 1976).

4.3 DDT and its derivatives

Overall averages of levels of p.p'-DDT, p.p'-DDE and p.p'-DDD based on three or more samples of obligatory and non-obligatory species are shown in tables 9, 10 and 11. The values are considerably less scattered than for PCBs. In *Mytilus galloprovincialis* the mean values of p.p'-DDT in samples from the different areas vary between 2.3 and 22 ug/kg. The mean concentrations of p.p'-DDD and p.p'-DDE are of the same order, varying between 7 to 49 and 5 to 18 ug/kg, respectively. Concentrations of the same order or slightly lower were reported for *Mytilus edulis* from the ICES North Sea baseline study of 1972 (ICES, 1974). In the subsequent monitoring exercises of 1974, 1975 and 1976 the concentrations of both p.p'-DDT and p.p'-DDE were generally lower than 10 ug/kg (ICES, 1977a, 1977b and 1977c).

For *Mullus barbatus* it can be seen from figure 3 that almost all the mean concentrations of p.p'-DDT, p.p'-DDE and p.p'-DDD are of the same order. In particular, the levels of p.p'-DDT and p.p'-DDE are very similar. But the variation between the individual samples is considerable as can be seen from the standard deviations which are usually of the same order as, or higher than, the mean. No difference between the areas can be distinguished on the basis of these results.

For the other species the major concentrations are generally less than 30 ug/kg. One exception is *Thunnus thynnus thynnus* which shows average concentrations for p.p'-DDT and p.p'-DDE of 343 and 352 ug/kg, respectively. The concentration of p.p'-DDD is somewhat lower (107 ug/kg) but still one order of magnitude higher than for the other species. This can be expected considering the role of tuna as predator, its high level in the food-chain, its long life and its relatively high fat content in the muscle.

4.5 Other chlorinated hydrocarbons

As was mentioned in section 2.2 many centres did not report data on dieldrin. The results reported show however that the concentration of dieldrin is generally low in all organisms analysed with the highest mean values around 6 ug/kg (table 12). Many of the individual values were below 1 ug/kg.

Table 9. Overall averages of levels of ⁶²p - DDT in obligatory and non-obligatory species.

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
II	<u>Boops boops</u>	7	21	20	5 - 69
	<u>Maena smariss</u>	5	33	13	13 - 49
	<u>Engraulis encrasicolus</u>	6	45	22	13 - 72
	<u>Mullus barbatus</u>	27	28	35	8 -170
	<u>Mytilus galloprovincialis</u>	113	22	23	3 -150
	<u>Solea vulgaris</u>	10	10	7	1 -18
	<u>Thunnus thynnus</u>	21	343	362	25-1401
	<u>Trisopterus minutis capellanus</u>	4	5	2	2.5- 7
	IV	<u>Engraulis encrasicolus</u>	10	22	12
<u>Mullus barbatus</u>		33	23	17	6 - 89
<u>Mullus surmuletus</u>		6	6	3	4 - 13
<u>Mytilus galloprovincialis</u>		12	7	5	1.2- 17
<u>Neohrops norvegicus</u>		28	1.8	1.6	0.5- 5
V	<u>Boops boops</u>	3	8	7	1 - 17
	<u>Carcinus mediterraneus</u>	31	1.7	1.4	0.2- 5
	<u>Engraulis encrasicolus</u>	8	14	6	3.7-2.4
	<u>Loligo vulgaris</u>	4	12	7	7 - 24
	<u>Merluccius merluccius</u>	8	5	4	0.6- 12
	<u>Mugil auratus</u>	4	39	20	23- 73
	<u>Mullus barbatus</u>	102	17	26	0.2-205
	<u>Mullus surmuletus</u>	11	9	11	0.5-40
	<u>Mytilus galloprovincialis</u>	180	15	77	0-1014
	<u>Ostrea edulis</u>	10	2	2	0.3- 6
	<u>Pagellus erythrinus</u>	4	8	6	2 - 18
	<u>Patella coerulea</u>	4	0.5	0.4	0.3-1.3
	<u>Penaeus kerathurus</u>	7	1.5	0.8	0.3-2.8
	<u>Sardina pilchardus</u>	8	36	18	7 - 67
	<u>Trachurus trachurus</u>	4	25	23	1 - 56
<u>Venerupis aureus</u>	15	0.5	0.8	0.2-3.6	
<u>Xanto hydrophilus</u>	10	1.7	1.4	0.5-5	

Table 9. Overall averages of levels of p,p - DDT in obligatory and non-obligatory species (Continued-2)

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
VIII	<u>Mullus barbatus</u>	51	23	25	4 - 110
	<u>Mytilus galloprovincialis</u>	12	2.3	1.7	0 - 5
	<u>Parapenaeus longirostris</u>	29	0.9	1.4	0 - 6
IX	<u>Carcinus mediterraneus</u>	6	1.6	0.7	0.4- 2.6
	<u>Mugil auratus</u>	15	10	8	0.8- 2.7
	<u>Mugil saliens</u>	11	34	20	5.5- 6.8
	<u>Mullus barbatus</u>	17	38	29	0.5- 92
	<u>Parapenaeus longirostris</u>	4	4.2	3.5	0.3 - 9
	<u>Penaeus kerathurus</u>	10	4.8	0.9	3.5 - 6
X	<u>Boops boops</u>	4	0.9	1.3	0.4- 3.1
	<u>Maena maena</u>	5	7	4.4	0 - 13
	<u>Merluccius merluccius</u>	5	6	5	0 - 14
	<u>Mullus barbatus</u>	44	8	9	0 - 37
	<u>Pagellus erythrinus</u>	12	6	6	0 - 15
	<u>Parapenaeus longirostris</u>	10	0.1	0.2	0 - 0.8
	<u>Saurida undosquamis</u>	15	4.2	4.9	0 - 16
	<u>Sphyræna sphyræna</u>	3	37	38	0 - 89
	<u>Trachurus mediterraneus</u>	4	4.7	1	3 - 6
	<u>Upeneus molluccensis</u>	16	7	9	0 - 32

Table 10. Overall averages of levels of p,p- DDD in obligatory and non-obligatory species.

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
II	<u>Boops boops</u>	7	9	8	6 - 26
	<u>Carcinus mediterraneus</u>	10	10	9	1.2 - 26
	<u>Maena smaris</u>	5	19	14	7 - 44
	<u>Mullus barbatus</u>	12	38	52	0 - 180
	<u>Mytilus galloprovincialis</u>	108	15	13	5 - 125
	<u>Solea vulgaris</u>	10	12	10	1 - 24
	<u>Thunnus thynnus</u>	21	107	98	5 - 117
	<u>Trisopterus minutis capelanus</u>	4	5	4	2 - 10
V	<u>Engraulis encrasicolus</u>	3	10	5	5 - 117
	<u>Loligo vulgaris</u>	4	11	11	3 - 29
	<u>Mullus barbatus</u>	5	28	40	2.2 - 107
	<u>Mullus surmuletus</u>	3	7	6	2 - 15
	<u>Mytilus galloprovincialis</u>	11	49	124	0 - 440
	<u>Pagellus erythrinus</u>	3	1.1	0.5	0.4 - 1.5
	<u>Sardina pilchardus</u>	4	21	16	4 - 46
	<u>Trachurus trachurus</u>	4	11	11	0 - 30
VIII	<u>Merluccius merluccius</u>	6	10	3.5	3.6 - 15
	<u>Mullus barbatus</u>	78	14	25	0 - 140
	<u>Mytilus galloprovincialis</u>	90	7	7	0 - 45
	<u>Parapenaeus longirostris</u>	29	0.8	1.4	0 - 7
	<u>Thunnus thynnus</u>	4	323	422	26 - 1052
IX	<u>Carcinus mediterraneus</u>	6	4.2	3.7	0 - 10
	<u>Mugil auratus</u>	7	8	7	1.5 - 22
	<u>Mugil saliens</u>	11	24	12	7 - 47
	<u>Mullus barbatus</u>	17	18	14	0 - 44
	<u>Parapenaeus longirostris</u>	4	2.2	1.3	0.5 - 4.2
	<u>Penaeus kerathurus</u>	3	2.2	1.0	1.0 - 3.4
X	<u>Maena maena</u>	5	7	6	0 - 17
	<u>Merluccius merluccius</u>	5	1.4	2.1	0 - 5
	<u>Mullus barbatus</u>	44	1.6	3.8	0 - 21
	<u>Pagellus erythrinus</u>	12	2.2	3.4	0 - 11
	<u>Parapenaeus longirostris</u>	11	0.4	0.8	0 - 2.7
	<u>Saurida undosouamis</u>	15	3.5	6	0 - 24
	<u>Sohyraena sphyraena</u>	3	17	19	0 - 44
	<u>Trachurus mediterraneus</u>	4	2	2	0 - 4.3
	<u>Upeneus molluccensis</u>	16	1.7	2.3	0 - 7

Table 11. Overall averages of levels of p,p' DDE in obligatory and non obligatory species.

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
II	<u>Boops boops</u>	7	6.7	2	3 - 10
	<u>Carcinus mediterraneus</u>	10	36	24	14 - 72
	<u>Engraulis encrasicolus</u>	6	47	19	16 - 66
	<u>Maena smaris</u>	5	28	8	14 - 40
	<u>Mullus barbatus</u>	34	29	14	11 - 70
	<u>Mytilus galloprovincialis</u>	114	13	9	2.2 - 42
	<u>Solea vulgaris</u>	10	7	4	1.2 - 12
	<u>Thunnus thynnus</u>	21	352	415	23 - 1582
	<u>Trisopterus minutis capelanus</u>	4	3.7	0.7	3 - 4.6
IV	<u>Engraulis encrasicolus</u>	10	24	13	5 - 50
	<u>Mullus barbatus</u>	33	33	18	7 - 93
	<u>Mullus surmuletus</u>	6	11	3	6 - 15
	<u>Mytilus galloprovincialis</u>	13	6	4	2 - 17
	<u>Nephrops norvegicus</u>	28	3.8	1.8	1.1 - 8
V	<u>Carcinus mediterraneus</u>	4	2.5	3.0	0.1 - 6.2
	<u>Engraulis encrasicolus</u>	4	22	12	6 - 40
	<u>Loligo vulgaris</u>	4	33	25	6 - 61
	<u>Merluccius merluccius</u>	8	5.4	5.4	0.3 - 20
	<u>Mugil auratus</u>	4	17	8	5 - 25
	<u>Mullus barbatus</u>	43	8	12	0.1 - 75
	<u>Mullus surmuletus</u>	10	12	12	0.1 - 33
	<u>Mytilus galloprovincialis</u>	145	5	13	0.1 - 118
	<u>Ostrea edulis</u>	10	1.2	0.8	0.1 - 2.8
	<u>Pagellus erythrinus</u>	4	7.2	4.3	0.6 - 13
	<u>Patella coerulea</u>	4	10	5	2.3 - 17
	<u>Sardina pilchardus</u>	4	133	49	80 - 211
	<u>Trachurus trachurus</u>	4	35	23	15 - 70
	<u>Venerupis aureus</u>	15	0.2	0.2	0.1 - 0.8
<u>Xantho hydrophilus</u>	10	7	8	3.3 - 24	

Table 11. Overall averages of levels of ⁶⁶p,p' DDE in obligatory and non obligatory species (Continued - 2)

sampling areas	species	no. of samples (n)	mean conc. $\mu\text{g}/\text{kg}$ F.W.	standard deviation	range
VIII	<u>Carcinus mediterraneus</u>	3	23	3	20 - 26
	<u>Merluccius merluccius</u>	4	18	4.5	12 - 26
	<u>Mullus barbatus</u>	88	33	39	1 - 255
	<u>Mytilus galloprovincialis</u>	99	10	12	1 - 75
	<u>Pagellus erythrinus</u>	3	46	25	28 - 82
	<u>Parapenaeus longirostris</u>	31	1.6	5	0 - 25
	<u>Thunnus thynnus</u>	4	601	659	161-1737
IX	<u>Carcinus mediterraneus</u>	7	22	15	0.3 - 4.5
	<u>Mugil auratus</u>	17	16	11	1.4 - 45
	<u>Mugil saliens</u>	11	70	30	33 - 115
	<u>Mullus barbatus</u>	16	53	42	0.9 - 117
	<u>Parapenaeus longirostris</u>	4	3.1	1.6	1.0 - 5.4
	<u>Penaeus kerathurus</u>	10	36	11	28 - 52
X	<u>Boops boops</u>	4	0.9	0.8	0 - 2.0
	<u>Carcinus mediterraneus</u>	4	3.1	3.5	0.7 - 8
	<u>Maena maena</u>	5	6	3	2.3 - 10
	<u>Merluccius merluccius</u>	5	15	9	7 - 32
	<u>Mullus barbatus</u>	44	15	12	2 - 67
	<u>Pagellus erythrinus</u>	11	14	10	4.9 - 39
	<u>Parapenaeus longirostris</u>	11	1.5	2.6	0 - 9
	<u>Saurida undosquamis</u>	15	13	8	4.6 - 30
	<u>Sphyræna sphyræna</u>	3	21	5	16 - 28
	<u>Trachurus mediterraneus</u>	4	10	4.4	3.2 - 15
	<u>Upeneus molluccensis</u>	16	40	35	5 - 106

Table 12. Overall averages of levels of dieldrin in obligatory and non-obligatory species.

sampling areas	species	no. of samples (n)	mean conc. ug/kg F.W.	standard deviation	range
II	<u>Mullus barbatus</u>	11	6.2	5.3	0.5 - 19
	<u>Mytilus galloprovincialis</u>	2	3.5	-	1 - 6
IV	<u>Engraulis encrasicolus</u>	4	5	2.6	1.2 - 7
	<u>Mullus barbatus</u>	9	6	3.6	0.5 - 12
	<u>Mytilus galloprovincialis</u>	6	2.8	2.6	0.5 - 6
	<u>Nephrops norvegicus</u>	7	0.9	0.5	0.5 - 1.8
V	<u>Carcinus mediterraneus</u>	31	0.5	0.6	0 - 2.4
	<u>Engraulis encrasicolus</u>	4	1.1	0.6	0.5 - 1.9
	<u>Merluccius merluccius</u>	8	0.3	0.2	0 - 0.7
	<u>Mullus barbatus</u>	67	1.7	4.1	0.1 - 17
	<u>Mullus surmuletus</u>	8	0.4	0.2	0 - 0.7
	<u>Mytilus galloprovincialis</u>	145	0.8	4.4	0.1 - 56
	<u>Ostrea edulis</u>	8	0.4	0.5	0.1 - 2.0
	<u>Patella coerula</u>	5	1.1	1.0	0.1 - 2.4
	<u>Penaeus kerathurus</u>	7	0.3	0.1	0.2 - 0.5
	<u>Sardina pilchardus</u>	4	0.8	0.5	0 - 1.4
X	<u>Mullus barbatus</u>	35	0.4	1.1	0 - 5.5
	<u>Carcinus mediterraneus</u>	4	3.1	4.5	0.4 - 10

$\mu\text{g/kg}$
FW

68

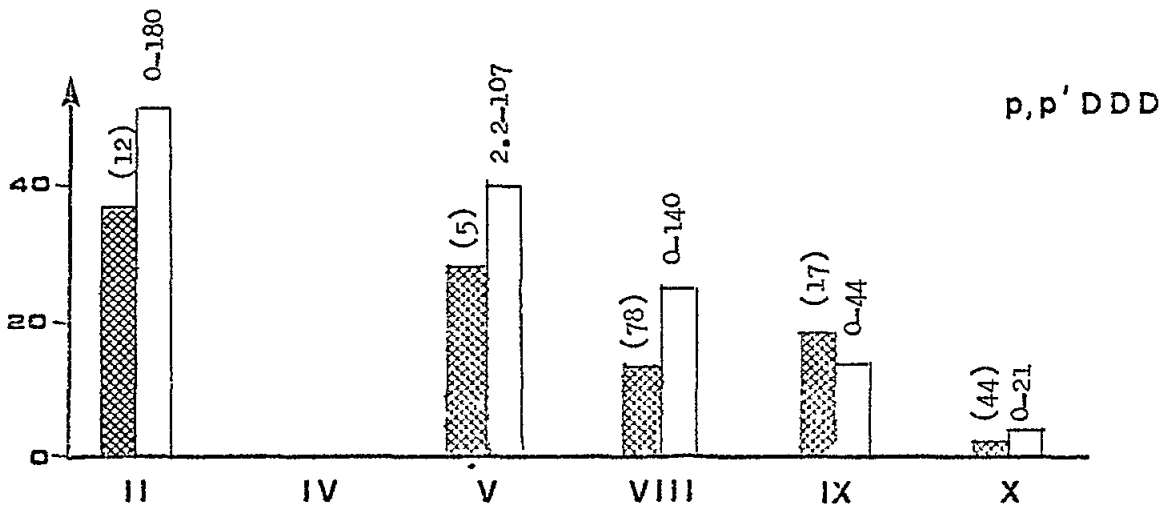
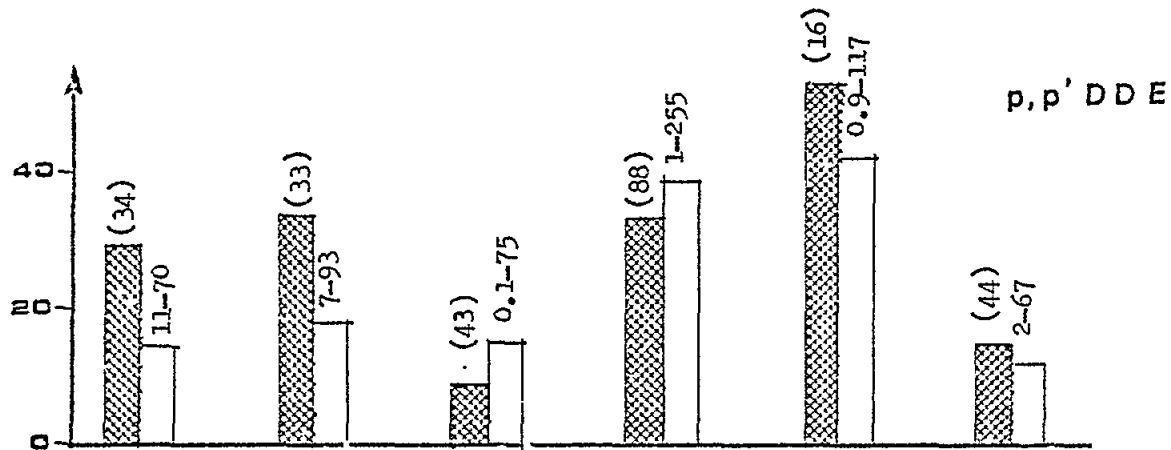
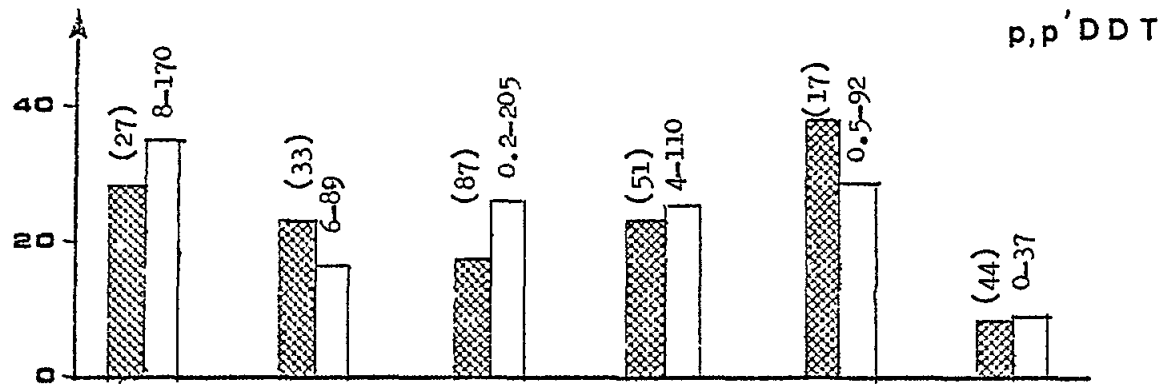


Figure 3. Average levels of DDT, DDE and DDD in Mullus barbatus by IED POL areas.

() n
▨ arithmetical mean

range
□ standard deviation

Aldrin has only been analysed in samples from four areas but the results available indicate that the concentrations in marine organisms in the Mediterranean are generally low (table 13).

For the other compounds analysed it has not been possible to take into account the intercalibration exercise when evaluating the data, but the concentrations are generally low. For heptachlor and heptachlorepoxide almost all values are lower than 1 ug/kg. For hexachlorcyclohexane and its -isomer lindane some results are presented in tables 14 and 15. Considerng the analytical difficulties when analysing at these low levels, these data should only be regarded as indications of orders of magnitude.

4.6 Discussion

The results presented in this evaluation and in the final reports of the research centres should primarily be considered as baseline information on the levels of chlorinated hydrocarbons in marine organisms in the Mediterranean. These results may be used to evaluate health hazards from consumption of seafood and possible adverse effects on the marine ecosystem. The information is also an important basis for the planning of future long-term monitoring activities using marine organisms.

From the data presented it can be concluded that a distinction can be drawn between PCBs on the one hand and chlorinated insecticides on the other. For PCBs there is a considerable scatter of the data with ranges of several orders of magnitude. There is also a clear tendency towards high values especially in the Tyrrhenian Sea and the North West Mediterranean. For most of the chlorinated insecticides the concentrations are quite low and close to, or below, detection limits. DDT and its derivatives, which usually have concentrations above detection limits, show an even distribution in the obligatory organisms over the whole Mediterranean. A possible explanation for this difference between the compounds may be that PCBs, being of industrial origin, enter the Mediterranean to a large extent through point sources, while chlorinated insecticides enter the sea through run-off or atmospheric fall-out. PCBs have only been used in considerable quantities for the last 20 years or less, and are still in use, while the utilization of DDT in particular is prohibited or restricted in many countries around the Mediterranean. DDT and other chlorinated insecticides therefore have a tendency towards a more uniform distribution in the Mediterranean compared to PCBs, for which the results indicate very high levels in some industrialized areas.

Concerning the use of organisms for monitoring chlorinated hydrocarbons there is, in contrast to trace metals, very little evidence to show the existence of metabolic regulation of these compounds. In general, chlorinated hydrocarbons are taken up in direct relation to their environmental abundance, and are stored in the body lipids of all organisms. The selection of organisms for monitoring chlorinated hydrocarbos may thus take into account other factors, such as availability and the time integration capacity.

Table 13. Overall averages of levels of Aldrin in samples of obligatory and non-obligatory species.

Sampling areas	Species	No. of samples (n)	Mean conc. $\mu\text{g}/\text{kg}$ F.W.	Standard deviation	Range
II	<u>Mullus barbatus</u>	9	0.5	-	0.5-0.5
IV	<u>Engraulis encrasicolus</u>	4	0.6	0.2	0.5-1.0
	<u>Mullus barbatus</u>	9	1.5	1.9	0.5-5.0
	<u>Mytilus galloprovincialis</u>	6	2.0	2.1	0.5-5.0
	<u>Nephrops norvegicus</u>	7	0.6	0.2	0.5-1.0
IX	<u>Mugil auratus</u>	14	1.2	0.6	0.2-2.3
	<u>Mugil saliens</u>	6	1.8	0.7	0.9-2.7
	<u>Mullus barbatus</u>	5	0.5	0.4	0.0-1.0
	<u>Parapenaeus longirostris</u>	4	1.4	1.0	0.0-2.8
X	<u>Maena maena</u>	5	4.2	3.9	0.0-10
	<u>Merluccius merluccius</u>	5	0.1	0.2	0.0-0.4
	<u>Mullus barbatus</u>	44	1.5	4.7	0.0-28
	<u>Pagellus erythrinus</u>	12	2.9	6.4	0.0-22
	<u>Parapenaeus longirostris</u>	11	0.2	0.6	0.0-2.2
	<u>Saurida undosquamis</u>	15	1.6	4.7	0.0-19
	<u>Trachurus mediterraneus</u>	4	0.1	0.1	0.0-0.3
	<u>Upeneus moluccensis</u>	16	0.1	0.4	0.0-1.9
	<u>Carcinus mediterraneus</u>	5	1.6	2.8	0.0-6.5

Table 14. Overall averages of levels of hexachlor cyclohexane in obligatory and non-obligatory species.

Sampling areas	Species	No. of samples (n)	Mean conc. $\mu\text{g}/\text{kg}$ F.W.	Standard deviation	Range
V	<u>Carcinus mediterraneus</u>	27	0.9	-	0 - 8
	<u>Engraulis encrasicolus</u>	7	0.4	0.4	0 - 10
	<u>Loligo vulgaris</u>	3	0.6	0.5	0 - 1.3
	<u>Mullus barbatus</u>	63	2.6	2.8	0.2 - 12
	<u>Mullus surmuletus</u>	4	1.2	1.7	0 - 4.0
	<u>Mytilus galloprovincialis</u>	43	1.1	1.0	0 - 5.0
	<u>Penaeus kerathurus</u>	7	0.2	-	0 - 0.4
	<u>Sardina pilchardus</u>	7	2.5	2.1	0.2 - 6.0
VIII	<u>Merluccius merluccius</u>	6	1.5	0.6	0.8 - 2.5
	<u>Mullus barbatus</u>	4	5	8	0.8 - 50
	<u>Mytilus galloprovincialis</u>	55	1.9	1.5	0.4 - 5
	<u>Parapenaeus longirostris</u>	7	0.7	0.3	0.2 - 1.1
IX	<u>Carcinus mediterraneus</u>	6	20	-	12 - 34
	<u>Murex salians</u>	7	13	6	5 - 22
	<u>Mullus barbatus</u>	5	3.9	3.9	1.0 - 11

Table 15. Overall averages of levels of lindane in obligatory and non-obligatory species.

Sampling areas	Species	No. of samples (n)	Mean conc. $\mu\text{g}/\text{kg}$ F.W	Standard deviation	Range
II	<u>Carcinus mediterraneus</u>	4	19	14	2 - 36
	<u>Mullus barbatus</u>	17	3.0	4.4	0.5 - 20
	<u>Mytilus galloprovincialis</u>	7	4.8	6	0.5 - 20
IV	<u>Engraulis encrasicolus</u>	4	6.7	3.4	4.2 - 12
	<u>Mullus barbatus</u>	9	1.5	1.4	0.5 - 5
	<u>Mytilus galloprovincialis</u>	6	1.7	0.9	0.5 - 3
	<u>Nephrops norvegicus</u>	7	0.5	-	-
V	<u>Carcinus mediterraneus</u>	27	0.2	-	-
	<u>Engraulis encrasicolus</u>	4	0.1	-	-
	<u>Mullus barbatus</u>	62	0.7	0.9	0 - 3.3
	<u>Mytilus galloprovincialis</u>	36	0.4	0.4	0 - 2.0
	<u>Sardina pilchardus</u>	4	0.7	0.9	0.2 - 2.3

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MED POL IV : RESEARCH ON THE EFFECTS OF POLLUTANTS ON MARINE ORGANISMS
AND THEIR POPULATIONS (prepared by FAO)

1. INTRODUCTION

The purpose of pilot project MED POL IV was to study the effects of pollutants on marine organisms and their populations, giving priority to determining toxicity levels by "bioassay" methods. The project also provided data on the dynamics of pollutants and their synergistic and antagonistic effects. In addition, research was done on morphological and anatomical changes and changes in reproduction and behaviour. Physiological studies were carried out to elucidate the functional responses of organisms to pollutants, and analyses were made to show possible genetic changes in stressed populations.

The results described in this report on MED POL IV are based on the eleven final reports submitted by participants in the project.

2. METHODOLOGY

2.1 Selection of species

It was agreed that the experiments should be made on a small number of species previously recommended for use in pilot projects MED II and MED III. These species, which may be described as "mandatory", were the following: *Mullus barbatus*, *Mytilus galloprovincialis* and/or *M. edulis*, *Parapenaeus longirostris* and *Carcinus mediterraneus*. In the end, only *Mytilus galloprovincialis* was used by three laboratories.

It had also been recommended that a number of other organisms should be studied, and 18 of them had been designated. Of these "alternative" species, the following 13 were chosen: *Phaeodactylum tricornutum*, the sponge *Geodia cydonium*; the polychaetes *Capitella capitata*, *Scolelepis fuliginosa*; the echinoderms *Paracentrotus lividus*, *Arabacia lixula*; the arthropods *Acartia clausi*, *Idotea balthica basteri*, *Penaeus kerathurus*; and the fishes *Mugil cephalus*, *Sparus auratus*, *Dicentrarchus labrax*, *Scyliorhinus canicula*.

In fact, the laboratories chose a much larger number of species, which had not been contemplated. It may even be said that some of these "additional" species were chosen by a larger number of laboratories than the preceding ones. In all, the following 42 additional species were selected: *Nereis caudata*, *Nereis succinea*, *Nereis diversicolor*, *Cardium glaucum*, *Venerupis aureus*, *Abra ovata*, *Patella lusitanica*, *Murex trunculus*, *Murex brandaris*, *Monodonta turbinata*, *Monodonta articulata*, *Cerithium scabridum*, *Sepia*

officinalis, Artemia salina, Acartia tomsi, Tisbe holothuriae, Tisbe bulbisetosa, Sphaeroma serratum, Jassa falcata, Hyale spp., Orchestia mediterranea, Echinogammarus stocki, Leptomysis mediterraneus, Pagurus sp., Palaemon sp., Palaemon elegans, Palaemon serratus, Palaemonetes varians, Xantho hydrophilus, Microcosmus sulcatus, Mugil auratus, Mugil capito, Mugil (Lyza) saliens, Maena maena, Maena smaris, Boops boops, Boops salpa, Halobatrachus didactylus, Coryphaena hippuris, Sardina pilchardus, Blennius pavo and Trachurus trachurus. Thus, in all, 56 species were selected.

2.2 Pollutants analysed

Generally speaking, the substances recommended for study were used. Some laboratories specialized in the study of heavy metals and others in the study of chlorinated hydrocarbons and organophosphorus compounds. The following pollutants were selected:- Heavy metals: mercury (sulfate, chloride, acetate, methylate); copper (sulfate, chloride, acetate, nitrate); cadmium (chloride, sulfate, acetate, nitrate); chromium (hexavalent and trivalent); zinc; aluminium; selenium; thallium. Polychlorinated biphenyls (including Aroclor 1254), organophosphates and carbamates, aldrin, dieldrin, permethrin, DDT, various herbicides and insecticides. Petroleum from various sources, anionic, non-ionic and cationic detergents. Miscellaneous substances: 3,4-benzopyrene, 20-methylcholanthrene, 9,10-dimethyl 1,2-benzanthracene, 6-phenolbarbital, cyanides and, in a few cases, sea-water polluted by various sources.

2.3 Methodology

The research methods used were very varied. They may be said to range, in increasing order of technicality, from research on short-term lethality in a static environment to sophisticated biochemical studies. This classification is no criterion for either the quality or the value of the research carried out.

Among the methods most commonly used were: Short-term static tests and, less frequently, tests with various "continuous flow" systems for the measurement of lethal concentrations or minimum lethal times (50%, 100%); Long-term static or "continuous flow" tests for the observation or quantitative assessment of longevity, mating egg production, larval development, duration of larva stages, instar periods and more physiological phenomena such as respiration and food assimilation.

Behaviour was taken into account and sometimes recorded by chemography. Histological and cytological methods were used to study external and internal malformations and organ deterioration. The absorption of pollutants by various organs was shown by atomic absorption spectrophotometry or, after the marking of the pollutants, by autoradiography and liquid scintillation spectrometry.

Biochemical techniques, sometimes the most effective, were applied. Use was made of electrophoresis (particularly in genetics) and various methods of measuring cholinesterase inhibition, protein synthesis, ATP and numerous enzyme activities, such as pyruvate kinase, malate dehydrogenase, benzo (a)

pyrene dehydrogenase (BPMO), 5-aminolevulinic acid dehydrogenase (ALA-D), lactic dehydrogenase (LDH), alkaline phosphatase (AP and AC), glutamate oxalate transaminase (GOT) and glutamate pyruvate transaminase (GPT). Liver esterases were studied by electrophoretic and histochemical methods. The usual haematological characteristics were studied and measured, particularly in fishes. The methods used appear to be conventional.

3. INTERCALIBRATION EXERCISE

There was no intercalibration properly so called. Moreover, none was planned. Two laboratories did, however, have analyses of pollutants in organs made by laboratories which are taking part in projects MED II and III and which have carried out intercalibration exercises.

4. RESULTS

4.1 Mandatory species: Mytilus galloprovincialis

Heavy metals: it was shown that the combined effects of mercury chloride and temperature caused an increase in the toxicity of mercury when the temperature rose (synergism), while tests on the combined effects of mercury chloride and salinity levels showed that decreases in salinity (by up to 25%) caused a reduction of mercury toxicity (antagonism).

Studies on copper salts showed a rapid accumulation of copper in tissues (up to 40 ug/g in the gills in 7 days), a reduced rate of protein synthesis (from 5% to 70% in 7 days), a fall in ATP and a considerable concentration of proteins of molecular weight 11,000 - 12,000 (similar to thioneins and chelatins) in the gills.

Tissues	Exposure to Cu ²⁺ (0.008 ppm)			
	3 days		7 days	
Gills	0.89	0.81 (- 9 %)	0.64	(-28 %)
Digestive gland	1.41	1.23 (-13 %)	0.99	(-30%)
Mantle	2.60	2.10 (-20 %)	1.77	(-32 %)

The ATP content of the tissues examined is expressed in u moles ATP/g of wet weight. The values obtained are the mean of at least 4 results.

One pesticide (Slimicide C30), at a concentration of 0.02 mg/l, has harmful effects on the development of the eggs of *M. galloprovincialis*; in 96 hours, the 50% effective concentration (EC 50) is 0.07 mg/l.

4.2 Alternative species

Phaeodactylum tricornutum

Heavy metals: Mercury caused a substantial decrease in chlorophyll production at concentrations as low as 0.01 ppm after 24 hours.

Cadmium in concentrations of between 5 and 75 ppm impedes growth and cell multiplication. This is clearly apparent after 48 hours; at more than 25 ppm, the number of cells decreases. It does not seem to make much difference which salts of these metals are used (chloride, acetate, sulfate, nitrate).

Capitella capitata

Detergents: Research carried out before MED IV showed that exposure of *C. capitata* larvae to detergents caused deaths at concentrations as low as 0.01 mg/l. Teratological phenomena were also observed. Since then, it has been found that the toxicity of detergents is definitely increased (synergism) when salinity levels are much lower (18 to 22^o/oo) or higher (44 to 50^o/oo) than normal (37 to 38^o/oo). Conversely, toxicity is reduced (antagonism) when salinity levels are nearer to normal; this was observed more especially in the case of detergents of medium toxicity.

Scolelepis fuliginosa

Detergents: Data entirely similar to those on the preceding species were found in the case of *S. Fuliginosa* though no malformed larvae were observed.

Paracentrotus lividus

Heavy metals: Mercury salts were found to be acutely toxic. The 24h LC 50 was between 0.5 and 1.5 ppm and the 48h LC 50 between 0.4 and 0.8 ppm. Mercury chloride was the most toxic; it had particularly toxic effects on different larval stages of *P. lividus*. For example, a 0.10 mg/l concentration of HgCl₂ prevents formation of the fertilization membrane in 2% of cases, and the first division in 9% of cases, but stops gastrulation in 70% and metamorphosis to the pluteus stage in 100% of cases. Cadmium is markedly less toxic than mercury (48h LC 50 is between 2.2 and 3.5 ppm).

Arbacia lixula

Heavy metals: The 50% lethal concentration of mercury sulfate is 1.5 ppm in 24 hours, 0.5 ppm in 48 hours and 0.35 in 78 hours. At concentrations of between 0.1 and 0.5 ppm of Hg, pigments are discharged into the environment.

Acartia clausi

Heavy metals: Copper, cadmium and chromium are highly toxic, in descending

order, for *A. clausi*. Very low concentrations of metals (fractions of mg/l) affect its physiological processes. *A. clausi* populations from polluted areas are distinctly less affected than those from areas with clean (or little polluted) water. For example, the cell ingestion rate in 24 hours for clean-water populations is 25,550 for the control and 3,065 with 0.005 mg/l of copper, whereas for polluted-water populations it is 25,600 and 122,290 respectively.

Idotea balthica basteri

Detergents: Detergents systematically disturb all phases of the growth and life cycles of this species (number of eggs and young, length of the instar period, longevity, feeding, etc). These disturbances do not always take the form of reduced numbers of eggs, for example, or longer instar periods; there may be a speeding up. Serious histological and cytological changes in various internal organs are also observed, including stoppage of the prophase and the maturation of germinal cells in males, and abnormalities in external organs (gills, antennae, etc.).

Penaeus kerathurus

Heavy metals: The study of the effects of heavy metals on the various larval stages of *P. kerathurus* showed that, generally, the most sensitive stages were those closest to the nauplius; the protozoa stages were particularly sensitive. Thus, the 24h LC 50s for the nauplius, protozoa II and P₄ and P₆ post-larval stages were 0.0054 mg/l, 0.0095 mg/l and 0.0469 mg/l, respectively, with mercury methylate; 0.937 mg/l, 1.270 mg/l and 4.890 mg/l with cadmium chloride; and 0.103 mg/l, 0.107 mg/l and 1.470 mg/l with copper sulfate. The accumulation of cadmium in the hepatopancreas was 319.64 mg/kg, and 15 times less in the muscles. The tissues of the hepatopancreas showed deterioration.

Mugil cephalus

Chlorinated hydrocarbons and organophosphorus compounds: in concentrations of less than 1 ppm, the toxicity of paraquat is not particularly acute. But although the LT 50 at 1 ppm is 16 days, at 10 ppm it is only 1 hour. At a concentration in the environment of 1 ppm, over a period of 15 days paraquat accumulates mainly in the skin (4 ug/g) and the digestive tract (6.083 ug/g).

It was demonstrated that, in vitro, DDT stimulated liver lactate dehydrogenase and fumarase and inhibited liver -hydrogenase. The results obtained were slightly different. DDT generally slows down the working of the citric cycle and the respiratory chain, and the catabolism of fatty acids and glycolysis in the liver whereas it intensifies lactate dehydrogenase activity. Permethrin increases pyruvate kinase and malate dehydrogenase activity in the muscle. On the other hand, change was noted as regards lactate dehydrogenase or acetylcholinesterase. As organophosphorus compounds accumulate, they inhibit brain cholinesterase in *M. cephalus*.

Sparus auratus

Heavy metals: After 41 days at a concentration of 0.1 ppm of mercury chloride, the accumulation of mercury in the liver was 323.6 mg/kg (wet weight); after 80 days at 0.008 ppm, the accumulation of mercury methylate was 21.35 mg/kg. Substantial histological and haematopoietic deterioration of various internal organs were observed in each case.

In the case of cadmium, after 96 hours at 25 ppm, an accumulation of 74.76 mg/kg (wet weight) was found in the liver; after 60 days at 3.0 ppm, 140.07 mg/kg had accumulated. Substantial histopathological deterioration occurred in the gills, liver, pancreas, intestine and kidneys.

At a concentration of 0.20 mg/l of Cu, after 77 days 20 mg/kg (wet weight) of copper had accumulated in the liver. Deterioration of the epithelium of the intestine was considerable.

Dicentrachus labrax

Heavy metals: Up to 329.25 mg/kg (wet weight) of mercury accumulate in the liver after 62 days at 0.1 mg/l; about half as much accumulates in the kidney and spleen. Serious cytohaematological and histopathological deterioration follows. The same occurs with cadmium, which may accumulate in various organs, especially the kidney (12.79 mg/kg after 96h at 50 mg/l).

Scylliorhinus canicula

Heavy metals: The action of lead on 5-aminolevulinic acid dehydrogenase activity in erythrocytes was measured. In vitro this activity decreased steadily to 64% of normal at a concentration of 0.1350 mg of lead per ml of blood. In vivo, it decreased to 61.8% of normal at a dose of 43 mg/kg of lead. At a concentration of 0.25 mg/l of lead, the activity was reduced to 40-44% of normal and, at a concentration of 1 mg/l, 10-25% of normal.

4.3 Additional speciesVenerupis aureus (Tapes aureus)

Heavy metals: With mercury chloride, an increase in temperature produces synergistic phenomena, while a decrease in salinity (from 37 to 25^o/oo) has an antagonistic effect, mercury being less toxic if the salinity of the environment is lower.

Detergents: It was found that without the addition of detergents there was no mortality if salinity was lowered to 25^o/oo, lethal salinity being 20^o/oo. If detergents are added, their toxicity is reduced when salinity is lowered, but shortly before the lethal salinity level is reached, the toxicity of the detergent produces synergistic phenomena and mortality is greatly increased.

Patella lusitanica

Heavy metals: In terms of acute toxicity, mercury is slightly more toxic than cadmium.

	Hg	Cd
LC 50 24 h	38-48 ppm	39-60 ppm
LC 50 48 h	20-28.5 ppm	21.5-29 ppm

Mercury acetate is the most toxic of the mercury salts, while cadmium acetate is less toxic than cadmium sulfate.

Murex trunculus

Pesticides: With paraquat, mortality occurs only at concentrations of more than 0.1 ppm. At 1 ppm, the LT 50 is 18 days, but at 10 ppm, it is only 10 hours. Up to 5 ppm, aldrin and dieldrin have no apparent effect on the various properties of haemocyanin.

Murex brandaris

Pesticides: The acute toxicity of paraquat is the same as for the preceding species. Its accumulation in *M. brandaris* is proportional to the concentration of paraquat in the test environment.

Monodonta turbinata

Crude oil: At a concentration of 20,000 ppm, the LT 50 of surface and mixed oil is 68 hours, whereas for floating oil at the same concentration, it is 120 hours. Sublethal effects include: loss of gregarious instinct, increase (tenfold) in the time spent at the water-air interface and a considerable reduction in emersion time. the "interface period" seems to depend on the proportion of fractions with a high boiling point (experiments conducted with crude oil distillates).

Monodonta articulata

Heavy metals: The 24h LC 50s of mercury sulfate, chloride and acetate are 8 ppm; the 48h LC 50 of mercury sulfate is 6 ppm. With regard to behaviour, it was found that emersion time increased after 24 hours and that the period of activity at the interface decreased when the mercury concentration reached 0.03 ppm. Oxygen consumption decreases at a concentration of 0.01 ppm of mercury. The acute toxicity of cadmium is less than that of mercury. At concentrations between 0.01 and 1.0 ppm, there is an increase in emersion time and the period of activity at the interface; oxygen consumption does not seem to be affected.

Sepia officinalis

Heavy metals: The 24h LC 50s are: HgCl_2 , 23.7-28 ug/l; CH_3HgCl , 17-19 ug/l; $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, 6-8 mg/l; and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.17 mg/l.

Artemia salina

Heavy metals: Starting at 0.1 ppm, mercury salts reduce egg fertilization. The reduction reaches 50 to 95% at 1 ppm. While there is no mortality of adults up to 0.7 ppm, the same is not true of larvae. With cadmium, fertilization is reduced by 20 to 60% at 1.0 ppm. The growth of larvae is slowed down and their mortality rate is high. The LT 50s vary between 50 and 120 hours for cadmium concentrations between 1.0 and 0.025 ppm. A copper concentration of 5 ppm reduces fertilization by 85%. It was also found that the growth rate of larvae is restricted by a copper concentration of 0.025 ppm; the LT 50s range from 10 to 35 hours at concentrations of 10 to 1 ppm. Acclimatization of larvae increases their tolerance.

Anti-petroleum products: For 13 of these products, the 24h LC 50s are between 1 and 500 ppm and the 48h LC 50s, between 0.5 and 250 ppm.

Petroleum: The toxic water-soluble fractions cause 20 to 40% mortality.

Tisbe bulbisetosa

Polychlorinated biphenyl (Aroclor 1254): Aroclor is toxic only in concentrations of more than 10 ug/l; at 500 ug/l, males are more sensitive to it than females. No particular phenomena related to acclimatization were observed. At 10 ug/l, fertility and the formation of nauplii do not seem to be affected, but the duration of the biological cycle is extended. The survival period of nauplii is definitely affected. The number of nauplii is ultimately reduced.

Concentration of Aroclor 1254	Control	1.6 ug/l	16 ug/l	80 ug/l
% Survivors	63.33	38.33	19.58	11.67
Sex ratio	1.05	1.14	1.47	1.33

Subsequent mating and offspring do not seem to be affected. There may be some prior selection of breeders which have become resistant to PCBs.

Orchestia mediterranea

Dispersants: The 24h LC 50s are between 25 and 7,200 ppm and the 48h LC 50s, between 15 and 200 ppm.

Echinogammarus stocki

Heavy metals: The influence of tank-storage time appears to be considerable.

Detergents: The test temperature affects the toxicity of the detergent appreciably.

Leptomysis mediterraneus

Pesticides: The 96h LC 50 of slimicide C30 is 0.11 mg/l.

Cyanides: The 96h LC 50 is very low: 45 ug CN⁻/l.

Palaemon sp.

Pesticides: The LT 50 of paraquat is 10 days at 1 ppm and 36 hours at 10 ppm. Of three herbicides, propanil is the most toxic and mecoprop the least: at 8 ppm, propanil kills 78.8% of specimens in 96 hours; at 10 ppm, molinate kills 72% of specimens in 96 hours; a concentration of 100 ppm of mecoprop is needed to kill 88.5% of specimens in the same time.

Palaemon serratus

Heavy metals: The interaction between mercury and selenium showed some notable effects. When *P. serratus* exposed to a concentration of 4 mg/l of mercury was treated with selenium for 4 days, the LT 50 increased considerably. In addition, the loss of Se and Hg by the *Palaemon* is less when they are subjected to the simultaneous action of the two metals.

Petroleum: The AP and AC activity of the hepatopancreas is affected by the water-soluble fractions.

Palaemon elegans

Heavy metals: For young *P. elegans* larvae, the 24h LC 50 of mercury salts is between 0.6 and 1.5 ppm and the 48h LC 50 between 0.3 and 0.5 ppm; mercury acetate is the most toxic. There is a close correlation between the mortality rate and the concentration of mercury chloride. Homozygotes are more resistant than heterozygotes to low (0.02-0.08 ppm) and high (0.26-0.40 ppm) concentrations.

For *P. elegans* larvae, the 24h LC 50 of copper citrate decreases as temperature rises (86 ppm at 20°C and 46 ppm at 23°C); but the same is not true of the 48h LC 50, which is 25 ppm at 20°C and at 23°C.

Pagurus sp.

Pesticides: At 1 ppm, the LT 50 for paraquat is 3 days and, at 10 ppm, 36 hours. Heavy accumulations of paraquat were found after 3 days of exposure to various concentrations:

Concentration of paraquat in water	Amount of paraquat in body (ug/g)
5.0	14.63
2.5	9.21
1.0	3.16

Xantho hydrophilus

Petroleum: The soluble fractions affect AP and AC activity in the blood plasma.

Mugil auratus

Heavy metals: Cadmium is toxic for the young of *M. auratus*: in 96 hours, the mortality rate is 33.3% at 18 mg/l and 40% at 32 mg/l; the mortality rate is 100% after only 24 hours at a concentration of 56 mg/l. The inhibition of ALA-D activity is proportional to the concentration of lead. It was found that the zinc had a strong restorative effect on ALA-D activity affected by other metals (mercury, copper, cadmium and aluminium).

Phenol: High concentrations of phenol cause neurotoxic symptoms, haemorrhaging, tissue oedema and various forms of liver deterioration, which are confirmed by increased LDH, GOT and GPT activity in the blood, in which proteins are also affected.

Mugil capito

Heavy metals: Thallium does not affect the metabolism of K^+ , but causes a significant increase in Na^+ and Cl^- exchange through the gills.

Lyza saliens (Mugil saliens)

Anti-petroleum products: Juvenile *L. saliens* die in 48 hours at a concentration of about 1,000 ppm. For 3 out of 4 products, the LT 50 is between 5.5 and 7.2 hours at 5,000 ppm, and for the fourth, 13 hours.

Maena maena

Pesticides: For this species, slimicide C30 has a 96h LC 50 of 0.34 mg/l.

Maena smaris

Pesticides: Organophosphorus compounds caused cholinesterase activity of 2,500 in the brain of *M. smaris* after only 2 hours exposure.

Boops boops

Pesticide: Permethrin increases the maximum rate of pyruvate kinase, malate dehydrogenase, succinate dehydrogenase and cytochrome oxidase; it does not affect lactate dehydrogenase in the muscles of this fish.

Halobatrachus didactylus

Heavy metals: There is a substantial accumulation of the salts of various metals.

Accumulation rate (mg/kg of wet weight):

Organs	Mercury (0.1 mg/l for 35 days)	Cadmium (50 mg/l for 96 hours)
Liver	70.86	5.21
Kidney	39.84	12.79
Spleen	37.50	
Blood	3.60	1.20
Intestine		39.05
Muscle		0.15

Substantial cytohaematological and histological deteriorations occur, particularly of the blood, liver and kidney.

Coryphaena hippuris

Pesticides: Permethrin has the same effects on *C. hippuris* as on *B. boops*.

Sardina pilchardus

Pesticides (organophosphates and carbamates) have various inhibiting effects. All liver esterases are completely inhibited by para-oxon, but not by phosalone.

Blennius pavo

Petroleum: As the result of an oil spill, the BPMO levels of *B. pavo* populations increased eight times. This was confirmed by an experimental test with No. 2 diesel oil at a concentration of 170 ppm.

5. DISCUSSION AND CONCLUSION

It is, first of all, interesting to summarize the various approaches adopted and the biological phenomena considered by the different laboratories. A certain selection must, of course, be made. It cannot and will not be determined by the extent or evidence of the results obtained by the laboratories; special account will, of course, be taken of the studies which, by the species and pollutants selected and the bioassays carried out, come closest to the most clearly defined objectives of pilot project MED IV.

5.1 Toxicity tests

The tests used may be divided into short-term and long-term tests, but most of the laboratories carried out research on short-term toxicity. It appears that in most cases the object of this research was to determine the limits of the toxicity of pollutants used for other studies on organisms which were available to the laboratories, or which they wished to use as test organisms in other studies. Consequently, the researches varied very widely.

For instance, a great deal of attention was given to the effects of detergents produced by the petrochemical industry on various marine invertebrates, polychaetes and molluscs (*Mytilus* and *Tapes*) with sudden or gradual changes in salinity. These studies dealt with synergistic and antagonistic action (3510).

Studies of the toxic effects of heavy metals on populations of the copepod *Acartia clausi* (3602) revealed differences in their resistance to pollutants. Some of these populations were from a very polluted area, while others were from an area which may be described as "clean". The differences are certainly connected with genetic data.

One laboratory (3609) found very significant differences in the short-term resistance of *Murex*, *Pagurus* and *Mugil* to paraquat (herbicide).

Another laboratory (MA01) made a long study of the short-term toxic effects of heavy metals on various invertebrates (gasteropods, sea urchins and shrimps), making a special effort to determine the toxicity of the various salts of these metals.

Attention was also given to the synergistic effects of an oil (diesel No. 2D) and a polychlorinated biphenyl on the benthic isopod *Eurydice truncata*, whose nychthemeral activity is particularly well known (9503).

While much research was carried out on adult specimens, some was also done on juveniles. For example, the effect of cadmium chloride on young *Mugil auratus* and the short-term action of anti-petroleum products on *Mugil saliens* (9502) were determined.

This brings us to the research on larval stages. The effects of detergents and heavy metals on the growth cycle of the sea urchin *Paracentrotus lividus* was studied. The mortality at different stages was noted, together with the lengthening of the normal duration of the different phases of the growth cycle (3510).

One laboratory studied the effects of various salts of heavy metals on 9 larval stages of the shrimp *Penaeus kerathurus*. It supplemented its research by using, for the same purpose and with the same pollutants, larval stages of the cephalopod *Sepia officinalis* and the fish *Sparus auratus* (2901).

Studies were made of the survival of *Tisbe bulbisetose* nauplii in an environment polluted by Aroclor (PCB) (4804) and of the effects of metals on the fertilization of *Artemia salina* eggs (MA01).

It seems permissible to believe that, biologically speaking, these "short-term" researches on larval stages are really "long-term", because of the rapid succession of the various stages observed. In any event, such data must also be taken into account in the studies on development.

The idea of "short-term" and "long-term" research was thus found to be rather ambiguous. It will also be noted that rather little research was done to determine the long-term toxic effects of pollutants on organisms.

Generally speaking, research on long-term toxicity served rather as support for other studies - physiological, behavioural, histopathological, genetic studies, etc. - which will be considered later.

5.2 Pollutant dynamics

Some attention was devoted to accumulation phenomena, but, generally speaking, their study does not seem to have generated much enthusiasm. The studies were carried out by a small number of laboratories and covered heavy metals and pesticides.

Studies by two laboratories (3609 and 9503) showed that organochlorinated compounds are extremely unstable in the experimental environment and are able to attach themselves to all substrates present. One laboratory (3609) expressed concern about the accumulation of heavy metals, which is greater in specimens living in polluted environments. Attention was also given to the accumulation of salts of mercury and cadmium in various organs (muscle, blood, intestine, liver, spleen, kidney) of three species of fish and one cephalopod (2901).

The accumulation of detergents marked with tritium was clearly shown in most of the internal organs of the isopod *Idotea balthica* (3510). There is clear evidence that these accumulations, which are sometimes substantial, cause damage to the organs in which they are present, as will be seen below. It would be interesting, but certainly hazardous and difficult, to try to establish an objective correlation between the levels of pollutant accumulations and the extent of organ deterioration.

5.3 Physiological and behavioural effects

Particular attention was devoted to these effects and to enzymatic problems and most of the laboratories made a significant contribution to their study. It may even be thought that the work carried out in this field by one laboratory (9504) goes beyond the normal activities of MED IV.

General physiology

One laboratory (MA01) studied the growth and chlorophyll production of the alga *Phaeodactylum tricorutum* in the presence of heavy metal salts, and the consumption of oxygen by gasteropods.

The number of erythrocytes, the quantities of haemoglobin and the haematocrit value in *Halobatrachus didactylum* subjected to the effects of mercury were also measured (9502).

It is assumed that oil droplets blocking the anterior part of the digestive tract of *Eurydice truncata* affect the digestion process (9503).

Behaviour

One laboratory (3602) studied the nutritional activity of copepods, while much of the work of another (MA01) was devoted to the study of the reaction of *Monodonta* gasteropods to mercury and cadmium salts, and to crude oil. The studies dealt more specifically with the phenomena of withdrawal of the animal into its shell and gregarious behaviour, and the limits of impairment of such behaviour were determined. Reduction of mobility of the sea urchin *Strongylocentrotus lividus* when treated with crude oil was also studied.

5.4 Changes in enzyme activity

Enzymes

Much research on enzymes was carried out, and most of the laboratories devoted at least a small proportion of their work to it. Such biochemical research even constituted the main activity of some centres (3609, 9502 and 9504). The approach differed very widely, not only as to the species, which comprised both invertebrates and fishes, and the pollutants which were mostly heavy metals or organochlorinated compounds, but also to the enzymes, since changes in the activity of several dozen enzymes were studied in both respiratory and digestive organs.

Particular attention was given to the action of organochlorinated compounds. Thus results were obtained on the anti-cholinesterase activity of phosphorylated esters in the brain and blood of *Mugil cephalus* (3609). One laboratory (MA01) studied the action of permethrin on various enzymes (pyruvate kinase, malate dehydrogenase, succinate dehydrogenase and cytochrome oxidase) of three species of fishes, Boops, *Coryphaena* and *Mugil*, and another (9502) studied the action of DDT and aldrin on six enzymes in *Mugil cephalus* (particularly in the liver).

The action of lead on 5-aminolevulinic acid dehydrogenase in the blood of *Scyliorhinus* was also studied.

Enzyme studies served as a basis for some genetic research (4706).

5.5 Morphology and histology

One laboratory (3510) had previously studied the teratological effects of detergents on the morphology of larvae of the polychaete *Capitella capitata* and the isopod *Idotea balthica*. It found histological deterioration in various internal organs of *Idotea*, particularly the gonads, and demonstrated the lethal teratological effects of detergents and heavy metals on *Paracentrotus lividus* larvae.

Many cytohaematological and histological deteriorations were found in the digestive and excretory organs of fish subjected to the action of heavy metals (2901).

5.6 Development: reproduction and population genetics

Under this heading may be considered the studies of the larval stages of *Paracentrotus lividus*, which showed an increase in the duration of the development stages. Studies of *Idotea balthica basteri* showed similar phenomena, with either lengthening or shortening of the instar period, which was always different from that of the control specimens (3510).

Other studies (3602, 2901) showed that the reproductive potential of species of crustaceans was severely affected (by hypermortality of the larvae).

One laboratory (3602) which carried out genetic research considers that the differences observed in the effects of pollutants on two populations of the copepod *Isabe acartia*, one living in a polluted environment and the other in a non-polluted environment, may be of genetic (phenotypic) origin. The study of 20 loci of *Palaemon elegans* showed that phosphate glucomatase was highly polymorphic, whereas in three others it was slightly so (4706).

6. CONCLUSION AND RECOMMENDATIONS

In general, it may be noted that, within each research centre and at the overall level, some selection was made in regard to pollutants, organisms and the studies themselves.

Pollutants

It may be noted that most of the centres used heavy metals and/or pesticides (or herbicides), i.e. the pollutants studied more specifically as part of MED POL II and MED POL III; this is quite normal, since many of the MED POL IV centres are also taking part in MED POL II and MED POL III. Some laboratories used hydrocarbons, but it was entirely exceptional for a laboratory to choose petrochemical detergents.

An effort was made by some laboratories to use the different physical and chemical forms in which pollutants may be present (particularly in the case of heavy metals). Such research and observation of absorption (primarily of chlorinated hydrocarbons) should be encouraged, with a view to evaluating the effective concentrations and toxicity of the pollutants to which animals are exposed.

Organisms

The species selected were very rarely those which had been designated as mandatory. It may even be considered that the alternative species did not receive the attention that might have been expected, since five of them were not used at all. On the other hand, 41 of the "additional" species were chosen.

It seems necessary to try to understand why the laboratories proceeded in this way.

The explanation is not difficult as regards the mandatory species which, it must be emphasized, were particularly ill-chosen for this pilot project. That point had, moreover, already been stressed by the participants in the meeting of principal investigators (Dubrovnik, May 1977). *Parapenaeus longirostris* is a fairly deep water species. Its laboratory acclimatization and, a fortiori, its use as a test species raises difficulties which have not yet been overcome and may not be in the near future. Moreover, although it is a species that is said to be present all over the Mediterranean, its real distribution is localized, and its geographical and seasonal abundance varies widely. The requirements for catching it are not easy to meet.

Similar, though less complex, problems arise with regard to *Mullus barbatus*. *Carcinus mediterraneus* seems to be abundant. It is easy to gather, provided laboratories are situated near lagoons or estuaries, where it usually lives. It is precisely this preferred biotope which raises problems; in the Mediterranean, *C. mediterraneus* is not normally a true marine species.

None of these three species was used.

The fourth species (omitting at the outset *Mytilus edulis*, about which the least that can be said is that it is rare in the Mediterranean) is *Mytilus*

galloprovincialis. This species is fairly abundant (especially in polluted waters) in the northern part of the Mediterranean, but rare along the African coast, where *Perna perna* (sometimes included in the genus *Mytilus*) is found in some places.

It seems to be totally absent from the south eastern part of the Mediterranean, approximately south of a line from Izmir to Tunisia. Moreover, it raises many problems for those using it for experimental purposes. Three laboratories used it, but not very intensively.

Of the 18 "alternative" species, 13 were used. Since these species were originally proposed by those who had already worked on them or planned to do so, it is not surprising that a fair proportion of the species finally chosen were in this category.

The additional species were varied, but were in fact often closely related to, if not of the same genus as, the "alternative" species. In this connection, it is perhaps to be regretted that the laboratories did not make more systematic efforts to show "resemblances" and/or "differences" in the results obtained with those (zoologically speaking) allied species.

Effects studied

Acute toxicity was studied extensively, both in adults and in larvae. A broad range of continuing bioassays was developed for the study of sublethal effects. Most of this research was based on the study of enzyme activity. Many laboratories seem to have been keenly interested in enzymology, and some of their research goes well beyond the framework of project MED IV.

From a brief survey of what has been done, it may, of course, be concluded that the results are perhaps not what was requested in the report of the FAO(GFCM)/UNEP Expert Consultation held at Rome from 23 June to 4 July 1975.

The species recommended first were hardly used at all. It may well be that they were difficult to use and in appropriate (even if the centres were able to obtain them and keep them alive in the laboratory). The list of additional species, which was rather long, was used extensively and, ultimately, considerably lengthened. It would be useful to review the tests, so that species may be better selected in the light of the experience gained.

Too little research has been done on heterotrophic micro-organisms and phytoplankton, and more attention should be devoted to them. Similarly, little use is made of zooplankton (real), whereas zoobenthos and nekton (especially fish) are widely used.

With regard to the effects studied, interest was shown in the direct toxicity and enzymology. Research on the physiology of nutrition and respiration generated little interest (except in so far as it relates to enzymology).

As the programme expanded, it became clear that more attention was being devoted to the frequently lethal effects of pollutants on the morphology of larvae and adults, since reproductive phenomena (changes in the development cycle, reductions in the number of larvae, abortions, etc.) directly affect populations, either by enabling them to increase or by gradually reducing them, which in time will affect ecosystems.

Too few laboratories studied the problem in terms of "populations". They experimented with populations of the same species, but of different origins (for example, populations taken from clean water and populations taken from polluted water) or with similar species living in different environments.

Thus it may fairly be said that few centres stressed the value of their research for the marine environment. Most of the research did not take special account of the marine environment, as has already been clearly shown. Not only were organisms studied more than their populations, but little seems to have been done to investigate species which are representative of particular aspects of the polluted or unpolluted natural environment. The same seems to apply to pollutants, whose presence or abundance in, and have potential danger to, the environment does not seem to have been considered as a criterion for selection.

An effort should therefore be made to establish a more rational and effective correlation between laboratory results and observations - experimental, if possible - which can be made in the natural environment.

It is obvious that, in the natural environment, pollutants are not only generally numerous in their joint action on populations, but do not act independently of one another. It is therefore regrettable that so few studies were carried out on interactions (synergism and/or antagonism), however difficult and perhaps somewhat "unrealistic" such studies may be; though their lack of realism is, after all, not necessarily any greater than that of other in vitro research.

It is also to be regretted that so few studies were carried out on problems of accumulation, particularly through food chains. Due allowance must, however, be made for the difficulty of developing such chains with some semblance of realism and for the delicate problems involved in measuring accumulations at the different levels of the chain. This might, perhaps, be made easier by the use of tracer molecules.

In conclusion, it may be said that, although the laboratories used classical methodological principles and, on the whole, took the usual experimental precautions, there was, nevertheless, a regrettably wide variety not only in the choice of species and pollutants but also in the choice of methods, so that it is rather difficult to attempt any rigorous and detailed comparison of the results obtained.

MED POL V : RESEARCH ON THE EFFECTS OF POLLUTANTS ON MARINE COMMUNITIES
AND ECOSYSTEMS (prepared by FAO)

1. INTRODUCTION

This pilot project has focused its research programme on pollution-induced modifications of marine communities, usually in comparison with biocoenotic conditions in similar but non-polluted habitats. Whenever possible and practical, the studies of communities were accompanied by simultaneous measurements of basic physico-chemical environmental conditions and detections of the presence of pollutants, both in sea-water and on the sea bed.

The account of the results obtained through the pilot project is based on the results reported from the fourteen participants in the project.

2. AREAS INVESTIGATED

Since pollution mostly affects marine ecosystems in neritic zones, and also for practical reasons, the investigations were limited, with few exceptions, to coastal marine environments as indicated in figure 1.

Unfortunately the project was not able to cover all areas of the Mediterranean. However, many polluted areas of the Mediterranean influenced by big rivers (Nile, Po and Rhone), large cities (Alexandria, Algiers, Athens, Izmir, Marseille) and adjacent industrial agglomerations were quite effectively investigated, as well as reference "clean" and insignificantly polluted areas for useful comparisons.

3. COMMUNITIES STUDIED

Practically all the investigations within this project were carried out in neritic zones of the Mediterranean Sea, and by far the greater part of the research, with few exceptions (Gulf of Marseilles, Adriatic), was concentrated on inshore waters. About half the national programmes focused their research on pelagic communities and half on benthic. The above-mentioned exceptional programmes organized their investigations as a complex ecosystem approach which included both pelagic and benthic communities. The same approach was also used for studies of the effects of artificial pollution on an experimental lagoony ecosystem (Strunjan, Adriatic).

Among benthic communities the greatest attention was paid to soft bottom communities of the infralittoral and circalittoral zones. Only three national programmes included investigations into hard-bottom communities, these usually being made in transects from intertidal to circalittoral zones.

In addition some rather elementary research was done on lagoonary ecosystems. One programme was devoted entirely to studies of "fouling communities" on experimentally exposed substrata (Gulf of Athens).

Investigations into pelagic communities were focused mainly on phytoplankton, its structure, standing crops and productivity, while some programmes included zooplanktological research as well, and only one programme was entirely involved in zooplanktonic communities.

As previously mentioned, most of the community studies were accompanied by more or less systematic measurements of environmental conditions in the areas investigated.

4. POLLUTION OF INVESTIGATED AREAS

A summary of the types of pollution and the areas studied is given in table 1. As a rule, almost all the areas investigated represent coastal marine environments under the influence of large inputs of pollutants, the origins of which are rather big cities (Alexandria, Algiers, Athens, Izmir, Marseilles, Rijeka, Split and Thessaloniki), their harbours, maritime traffic and important industrial activities. Although biodegradable municipal sewage usually makes up the main constituent of effluents, these discharges also contain a large variety of industrial pollutants. The identification of the types and composition of pollutants responsible for observed ecosystem modifications, in the sense of their physico-chemical and toxicological properties, was therefore not possible. The nature of the pollutants was even more difficult to identify in cases where, in addition to the above-mentioned sources, the areas investigated also receive discharges of big and heavily polluted rivers such as the Rhone and the Po. The only areas found to be polluted by effluents that could be identified were the coastal waters of Cyprus (discharges from the beverages industry) and experimental lagoons in Strunjan, Adriatic (domestic sewage of known rate and composition).

5. METHODS

5.1 Environmental measurements and analysis

The majority of the collaborating research centres used standard oceanographic procedures and more or less systematic year-round frequency of observations for the following parameters:

- temperature
- salinity
- turbidity (Secchi disc)
- pH
- dissolved oxygen
- BOD
- nutrients (N.P)
- total seston

Some centres applied in situ measurements of temperature, turbidity, salinity and dissolved oxygen.

Sediments were analysed by a number of research centres for granulometric composition and some geochemical determinations such as carbon content etc., by appropriate standard methods, but usually the sampling of sediments was performed by gear designed for benthos, which is not quite adequate for that purpose.

Some research centres made efforts to monitor specific pollutants such as faecal coliforms (bacteriological tests as recommended by MED VII), trace elements (polarographic and AAS determinations), anionic detergents (colorimetrically), organic carbon (IR analyses) and phenols (colorimetrically).

5.2 Pelagic investigations

In general, all research centres used methods that were at least comparable, usually the same as those recommended by UNESCO - IBP for both phytoplankton and zooplankton sampling, as well as for the determinations of standing crops and biomass.

Phytoplankton was collected by large inert-plastic samplers, biomass as chlorophylls determined fluorometrically or by trichromatic spectrophotometry, and density and community structures were studied by the Uttermohl technique or by regular microscopy of concentrates made by membranous filtration. The functional primary productivity was measured according to C14 assimilation or by diurnal oxygen dynamics.

Zooplankton was sampled by IBP - recommended nets, usually as vertical hauls. Biomass was determined gravimetrically as total dry weight and/or its organic fraction after ashing. Abundance and faunistic structure of the zooplankton was studied by well-known procedures of sorting, identification and counting zooplankton samples, usually at species level.

One research centres also measured total pelagic biopotential as adenilphosphates (ATP, ADP, AMP) by the Holm-Hansen bioluminescent method.

5.3 Benthic investigations

Due to important differences between the benthic habitats investigated, and also taking into account the unequal technical means and facilities at the disposal of the collaborating research centres, the methods used for investigating the benthos, and in particular the sampling, were not as comparable as for the pelagic studies.

However, at least the sampling of soft bottom communities was performed by a fairly similar technique i.e. with two types of grab samplers: Van Veen and "Orange-peel", delivering 5-40 l of sediment. In addition, a newly developed quantitative benthos-nektoncorer for the sampling of shallow lagoony communities and a number of dredges such as "Charcot-Picard" and "Spatangue" were used.

Hard bottom communities were sampled only orientatively by rock-dredges, while quantitative sampling was performed as a rule by divers. Samples were usually collected from 400 cm² of substrate surface.

Samples were always sieved through 0.5-2.0 mesh, preserved in formalin or ethanol and processed later on in a laboratory by well-known procedures of sorting, identification and quantitative analyses of taxonomic structures of communities. Biomass was determined quite variably: as wet weight, total dry weight or ash-free dry weight.

Based upon data on the quantitative taxonomic structure of communities, the results were evaluated according to dominance, affinity and diversity indices, using a number of different mathematical expressions such as those of Sorrensen, Margaleff and Shannon-Weaver.

5.4 Experimental research

Two participating research centres devoted their programmes entirely to experimental investigations, one on the modifications of the whole lagoony ecosystem caused by artificial discharges of sewage, the other on successions of fouling communities at artificial substrate exposed to variably polluted environments. The methodological details on the performance of experiments are described in the relevant reports, but most of the methods applied for experimental measurement and sampling of communities were about the same as those described above.

6. RESULTS

A summarized inventory of subjects investigated is given in tables 1 and 2. The majority of the results obtained can be considered within the following four typical approaches.

6.1 Complex ecosystem investigations

This approach means that polluted ecosystems were studied simultaneously from the aspects of physico-chemical environmental conditions and pelagic as well as benthic communities. Heavily polluted areas of the whole North Adriatic and of the Gulf of Marseilles were studied in this way. Results are comparable mutually as well as with other approaches and particularly with the results of artificially polluted experimental lagoons, and are reported below as conclusions.

6.2 Investigations into pelagic communities

Results obtained by pelagic investigations made in coastal waters of, e.g. the Middle and South Adriatic, are fully comparable with those of the above ecosystem approach and lead to mutual conclusions as reported below. Due to specific environmental and biogeographic conditions, results obtained in coastal waters of Alexandria cannot be correlated as above. The modified dynamics of phytoplankton blooms, the frequency of which is increasing, are reported and explained by the changed hydrology of the Nile as well as by increasing pollution.

6.3 Investigations into soft bottom benthic communities

Since practically all the national programmes that focused their work on benthic communities used about the same sampling technique, their results are comparable mutually as well as with the results of complex ecosystem investigations as outlined above. There are, of course, quite important differences between observed communities due to the variety of habitats and biogeographic zones, yet a number of trends and phenomena in common were observed, as reported in the conclusions.

6.4 Experimental research

There is no methodological connection between the following two experimental programmes executed by this project:

- Studies of recruitment and successions of fouling communities on experimentally exposed artificial substrata in the Harbour of Piraeus (polluted by domestic sewage) and in the Harbour of Lavrion (industrially polluted by elemental phosphorus etc.) demonstrated strong inhibitions in the latter environment, since developed communities were significantly less diverse than in the first case, although here too the environment was heavily polluted, by sewage in this instance. These specific observations are, of course, not comparable with other programmes of this pilot project.
- Experiments of long-term artificial discharges of domestic sewage (300 l/day) into the lagoony ecosystem of Strunjan gave results on pollution-induced environmental, pelagic and benthic modifications, which are fully comparable with those obtained by the particular complex ecosystem approaches of this project reported above.

Environment:

Investigated marine environments receiving significant inputs of pollutants in the form of a mixture of domestic sewage, urban run-off and some industrial effluents show some obvious deviations from natural conditions in the shape of fluctuating and decreasing salinity, increasing turbidity, higher concentrations of organic matter and nutrients, particularly nitrogen and silicium compounds, silting of bottom substrata etc. All the modifications mentioned can be considered more or less as the primary effects of the input of pollutants.

However, more important environmental stresses appear as the secondary consequences of modified trophic conditions which can, in most cases, be considered arbitrary as eutrophication. As a rule, an increase in amounts of dead organic matter mainly deposited on the sea bed was observed, the decomposition of which leads to decreased oxygenation or even to anoxic conditions, with an obvious formation of H_2S in the bottom layers of the sea-water and a remarkably increased content of black sulphides even on the surface of sediments.

Anoxic conditions appear in very shallow inner parts of bays or in lagoons which are heavily polluted. They are usually periodic phenomena.

In eutrophicated environments, during the periods of active primary productivity, there were extremely sharp diurnal oscillations of the oxygen, CO_2 and pH values observed, e.g. up to 10 ml/l O_2 at noon and less than 2 ml/l during the night, while pH fluctuated from 8.0 to 8.7 and total CO_2 from 1.5 to 2.6 mmol/l (national programme 4). The remarkable consequences of an extraordinary bloom in North Adriatic phytoplankton were observed in early summer 1977 (national programme 14), with oxygenation decreased in the bottom layers (only 13 per cent saturation) and pH 7.8, while in surface layers it reached the extremely high value of 8.8.

Although there are obvious modifications in the concentrations and dynamics of nutrients, they are clearly recognizable only in rather localized sites of pollution sources, while for larger areas significant differences were not proved. As was shown, e.g. by pollution experiments in the lagoons of Strunjan, pollution-born nutrients are rapidly taken up by plant consumers, absorbed by sediments and dispersed. Therefore, data on concentrations and distribution of nutrients cannot be considered as a measure of eutrophicated conditions, unless they are accompanied by information on populations of primary producers, etc.

Pelagic communities:

Considering eutrophication processes as observed in the areas investigated, it is evident that, in large areas such as the North Adriatic and the Gulf of Marseille, combined pollution and riverborne enrichment increase overall primary productivity as expressed in terms of biomass (chlorophylls), density of phytoplankton populations and functional assimilation rates ($C14$). Trends indicate a fairly steady increase in productivity. There also seems to be an increase in the intensity and frequency of bloom outbreaks which are no longer in line with the previous spring and autumn maxima and also appear during the summer period. Similar observations have also been made in more restrained areas such as the inshore and lagoony formations of Alexandria, the Saronikos Bay (Aegean Sea) and the Bay of Kastela (Mid-Adriatic).

Quite different seems to be an immediate influence of pollutants on phytoplanktonic communities as was observed in discharge areas of municipal

effluents of Marseille (Cortiou) and as was found also by pollution experiments in Lagoons. Although pelagic biomass, in terms of chlorophylls, was quite high, this was not the case with phytoplankton densities, which were even lower than those found in comparable, natural or slightly polluted, environments. The high biomass might be due to allochthonous pigments (debris of terrestrial vegetation in effluents: national programme 6) or to specifically increased populations of microflagellates which escape routine phytoplankton counts (national programme 4). There is, however, little doubt about the fact that mixed municipal effluents in the "immediate contact zones" inhibit conventional phytoplankton communities. In such environments both density and diversity of species are very low and, apart from microflagellates, there are very few highly resistant species that can survive in them. These are the euglenoid *Eutreptia* spp., dinoflagellates *Prorocentrum* sp., *Gymnodinium* spp., diatoms *Nitzschia* spp. and tychopelagic naviculoids, etc.

Typical "bloom species" which have been reported as the major causes of the eutrophication phenomena in pollution-enriched areas are actually quite common neritic species of the diatoms *Skeletonema costatum*, *Leptocylindrus danicus*, *Nitzschia seriata* and *Chaetoceros*. Blooms (red tides) are caused, however, by a number of dinoflagellate species, a still unidentified chrysophyte species and heterotrophic *Noctiluca*.

Zooplankton communities seem to be less affected than phytoplankton communities except under an immediate pollution stress which drastically reduces species diversity as well as abundance and standing crops. Larger enriched areas also show relatively decreased diversity, although standing crops and abundance of some tolerant neritic species may significantly increase. Such arbitrarily "indicative species" the copepods *Acartia clausi*, *Oithona nana*, *Euterpina acutifrons* and the cladoceran *Penilia avirostris* were found in almost all investigated areas.

Benthic communities:

- (a) Hard-bottom communities were investigated only in the Adriatic and in the Gulf of Marseilles. Although it is quite difficult to compare situations found in these biogeographically different zones some phenomena are common to both:
- Habitats within the immediate influence of effluent discharges are practically free of any macrobenthic fauna except some barnacles, *Balanus* spp.
 - Moderately polluted habitats are characterized by rich nitrophylic vegetation composed usually of green algae *Enteromorpha* spp. and *Ulva rigida*. As a rule such substrata are also covered by deposits of organic detritus and mineral particles inhabited by a number of highly resistant species of polychaetes, e.g. *Platynereis dumerili* and amphipods; in one case also dense populations of the ophiuroid *Ophiocomina nigra* was reported. Mediollittoral and upper

infralittoral zones are often densely covered by a number of euryvalent filtrator organisms such as the mussel *Mytilus galloprovincialis*, the ascidian *Pyura* spp. and the recently introduced exotic oyster *Crassostrea gigas* (North Adriatic).

- Slightly polluted habitats may show higher values of standing crops and overall productivity combined with decreased diversity and a general simplification of communities. However, significant scientific evidence is rarely obtained.

(b) Soft bottom communities were at the centre of investigations, and from quite comparable results some general conclusions can be drawn.

Regarding inshore benthic communities of sedimentary bottoms affected by important amounts of mixed domestic-industrial pollutants, the following three levels of biocoenotic degradation were found in common:

- Azoic zone where no living benthic organisms are found. Such zones were observed in the immediate vicinity of sewage outlets and in the most polluted harbours. Azoic refers to the absence of macrofauna although such areas might be inhabited by highly resistant species of meiofaunal nematods, harpacticoids and oligochaetes.
- Heavily polluted zones are characterized by communities composed of highly resistant organisms which can survive in an environment where practically all environmental factors sharply oscillate, waters are turbid, sedimentation rates and silting are very intensive, oxygenation is low and bottom layers are often anoxic. The main components are those species of polychaetes which can be considered to some degree as "pollution indicators", such as *Capitella capitata* and *Scololepis fuliginosa* in all observed areas, and *Notomastus latericeus* in Aegean areas and *Dorvillea rudolphi*, *Nereis caudata* in the North-Western area were found as well.
- Moderately or slightly polluted zones can be considered as subnormal and usually eutrophicated environments, inhabited by communities composed of a great number of species known to be ecologically quite resistant. Due to the high trophic potential of such environments, standing crops are abundant and the productivity of benthic communities is high, mainly on the part of molluscs, polychaetes, echinoderms and crustaceans. For these reasons, and since those sensitive species, which would in natural conditions form part of those communities, have disappeared, the diversity of such communities is rather low, as was proved by the results of this pilot project. The taxonomical structures of such communities were found, however, to be very different from site to site - for obvious reasons of different habitats and biogeographical situations.

With regard to sea-grass communities, mainly the dominant vegetations of *Posidonia oceanica* or *Cymodocea nodosa*, the reports made clear that in many localities of the Mediterranean these communities are degraded or are totally disappearing in areas of important urbanistic and industrial development. Not only pollution effects, but also man-made modifications of hydrologic and sedimentation conditions are blamed for this phenomenon, and the overall ecological consequences might be responsible for one of the most negative impacts on coastal and lagoony environments of the Mediterranean. Artificial discharges of purely domestic sewage (300 l/day) into the experimental lagoons of Strunjan, dominated by the vegetation of *Cymodocea nodosa*, demonstrated how easily and quickly this community could be totally destroyed: within one year all sea-grass was replaced by nitrophyllic green algae, and two years after the experiment was discontinued none of the sea-grass vegetation had reappeared.

7. CONCLUSIONS AND RECOMMENDATIONS

The research carried out under the pilot project has certainly contributed towards a better understanding of the impact of pollution on Mediterranean marine ecosystems. The results pointed out a number of extremely degraded coastal environments in focal sub-areas in immediate contact with pollutants, where communities of macro-organisms are almost totally exterminated, and regressively modified in large sub-areas where pollution effects are traceable. Examples of such local ecological disasters are found in the inshore waters of Alexandria, Athens, Izmir, Marseilles and Thessaloniki. Results also indicate that massive combined loads of coastal and river-borne pollution are causing considerable modifications of whole ecosystems in the North Adriatic and possibly in the Golfe du Lyon, showing clear trends towards a general eutrophication and consequent ecological disequilibria. Man-made modifications of sea-grass communities were pointed out as being an expanding phenomenon of general importance.

These above conclusions, of course, cannot be generalized for obvious reasons, and particularly because the investigations of this pilot project did not cover as many Mediterranean areas as would be desirable.

Table 1 : Basic information on realized programmes of participating research centres to MED PUL V

RESEARCH CENTRE (code)	AREAS INVESTIGATED	SOURCES	POLLUTION TYPES	SUBJECT OF INVESTIGATIONS
1 (AL01)	Bay of Algiers Bay of Bou Ismail Lake of Mellah	Algiers (2 million) None None	Domestic sewage Port - Industry - -	Some environmental measurements. Sedimentological analyses. Soft bottom communities.
2 (CY01)	Limassol Bay	Limassol (65,000)	Domestic sewage Biodegradable industrial effluents -	Soft bottom communities Demersal fish populations Systematic environment survey Sedimentological analyses
3 (2701)	Coastal waters of Alexandria	Alexandria (2 million)	Domestic sewage Industry-rivers	Zooplankton-hyoneuston Fish-landing facilities Environmental survey
4 (2702)	Harbour of Alexandria Lake Menzalah	Alexandria (2 million)	Domestic sewage Port-industry River discharges	Pelagic communities Some environmental measurements
5 (3510)	Gulf of Marseilles (Cortiou)	Marseilles (1 million)	Domestic sewage Port-industry	Pelagic communities Systematic environmental survey Analyses of pollutants Complex ecosystem approach
6 (3510)	Gulf of Marseilles (Cortiou) Gulf of Fos	Marseilles (1 million) River Rhone	Domestic sewage Port-industry Industry-polluted river	Soft and hard bottom communities Environmental measurements Sedimentological analyses Complex ecosystem approach

RESEARCH CENTRE (code)	AREAS INVESTIGATED	SOURCES	POLLUTION TYPES	SUBJECT OF INVESTIGATIONS
7 (3601)	Saronikos Bay	Athens (1 million)	Domestic sewage Port-industry	Soft bottom communities Some environmental measurements Sedimentological analyses
8 (3602)	Harbour of Piraeus Harbour of Lavrion	Piraeus (190,000) Industry	Domestic sewage Industrial effluents	Development and successions of fouling communities on experimentally exposed substrata
9 (3603)	Bays of Thermaikos Kavala Strymonikos	Thessaloniki (350,000) Industry None	Domestic sewage Industrial effluents - -	Soft bottom communities Systematic environmental survey Sedimentological analyses
10 (8903)	Gulf of Izmir	Izmir (650,000)	Domestic sewage Port-industry	Soft bottom communities Environmental survey
11 (9502)	Bay of Kastela Sibenik Channel Bay of Rijeka	Split (200,000) Sibenik (100,000) Rijeka (300,000)	Domestic sewage Ports Industry	Pelagic communities Systematic environmental survey Soft and hard bottom benthic communities
12 (9503)	Mid-Adriatic (Reference Area) Coastal waters of Dubrovnik Bay of Gruz	None Dubrovnik Gruz (100,000)	- Domestic sewage Port	Pelagic communities Environmental measurements

RESEARCH CENTRE (Code)	AREAS INVESTIGATED	SOURCES	POLLUTION	TYPES	SUBJECT OF INVESTIGATIONS
13 (9504)	North Adriatic	River Po etc.		Complex pollution	Pelagic and benthic communities
	Open waters	Rijeka		Domestic sewage	of soft and hard bottoms
	Bay of Rijeka	(300,000)		Port-industry	Systematic environmental survey
	Istria coastal waters	Small local pollution		-	Complex ecosystem approach
14 (9505)	Lagoon of Strunjan	Experimental		Purely domestic	Pelagic and benthic communities
	Gulf of Trieste	discharge 300 litres/day		sewage	Pollutants analyses
					Systematic environmental survey
					Complex ecosystem approach

MED POL VI : PROBLEMS OF COASTAL TRANSPORT OF POLLUTANTS
(prepared by IOC)

I. INTRODUCTION

The main aim of the pilot project is the investigation of water circulation in coastal areas, and the exchange of water between the coastal and offshore regions, so as to provide the necessary information on one of the main physical processes contributing to the coastal transport of pollutants in the Mediterranean Sea. Special attention is paid to the movement of the surface layer since this contributes to the rapid spread of certain pollutants. Many pollutants are often discharged in a body of relatively low-density water (e.g., effluent outfalls and river outflows) into this surface layer.

The main problems associated with the coastal transport of pollutants arise from the relatively high concentrations that may occur because of either the flow of pollutants from localized coastal sources and the subsequent transport and dispersion in the coastal region, or the transport into, and along, the coastal region, from open waters, of pollutants that are still in a relatively concentrated form (usually petroleum products, but cargoes of vessels carrying other hazardous substances may pose equally serious threats in the case of accidents).

This evaluation is based on the Progress and Final Reports of the participating Research Centres submitted to IOC. Some results presented by MED POL VI participants at the joint ICSEM/UNEP Workshop on Pollution of the Mediterranean, Anatalya, 24-27 November 1978, are also taken into account. No attempt has been made to look at the very large amount of previous and present research relevant to the problems of coastal transport of pollutants in the Mediterranean conducted by non-participants in the MED POL VI project.

Since the studies made by the participating Research Centres are extremely limited in area, it is inappropriate, at this stage, to make a region-wide synthesis of the results submitted.

II. AREAS STUDIED

The areas studied by the Research Centres are generally highly localized and usually those in the vicinity of each Centre. To understand the exchange of water between the coastal and offshore regions, some Research Centres are also conducting work in the offshore as well as the coastal region.

Such studies should be greatly expanded. Also, the number of coastal areas should be increased to include important industrial sites, important fishing or fish reproduction areas and other areas of importance; e.g., those given over to tourism.

III. MATERIAL AND METHODS

The basic parameters monitored are:

- currents, above and below the thermocline if this exists;
- salinity and temperature, to provide data on the water stratification (these parameters have also been used by some institutions for geostrophic current calculations);
- surface wind, which is a major driving force in many coastal circulation systems;
- bathymetry, when not already available, since this has a major influence on coastal circulation;
- river discharge, where applicable.

Other complementary data (e.g., dissolved oxygen, nutrients) were collected by some institutions.

The techniques used for current measurements included:

- driftcards or drifters;
- drogues;
- tracers and dyes (e.g., rhodamine);
- current meters.

IV. RESULTS AND THEIR INTERPRETATION

The bulk of the observations was made using recording current meters near the sea surface or at moderate depths, sometimes near the bottom. Observations using drifters or driftcards were often made in conjunction with recording-current-meter readings.

Many of the Research Centres encountered difficulties in mooring the current meters, particularly for extended periods, so that there were occasional losses; and there were some logistical problems in meter maintenance. Likewise, several countries encountered difficulties in reducing the data stored on the recording tapes of the meters. A reliable, possibly centralized, tape-reading and data-analysis service would greatly improve the yield of results from the recording current meters.

To assess current patterns in a given area, an appropriately large array of meters is required; many Research Centres were not in a position to set up such an array, not having a sufficient number of meters, or the means of servicing it.

The use of floating drift-cards or sea-surface drifters is a particularly useful method of observing sea-surface currents, with a low cost/benefit ratio; but it is important to incorporate wind data covering the same time and place of a drift-card experiment (DRIFTEX) in the assessment of the returns. A thorough computer programme to analyse DRIFTEX data was developed by the Instituto de Investigaciones Pesqueras, in Barcelona, under contract to the IOC, and applied to data from the Ligurian Sea and the Eastern Mediterranean.

Drogues, requiring greater logistical support, but otherwise as useful as drifters, were deployed by only two Research Centres.

Only two Centres used more than two methods to measure surface currents; their studies were more detailed and localized, therefore more intensive. It would seem to be necessary to do this to deal properly with pollutant transport problems in the present context.

It seems very doubtful that calculated (geostrophic) currents based on temperature-salinity distributions are reliable in the Mediterranean where the boundary conditions (coastline and bottom) and the vigorous vertical mixing in certain seasons and areas compromise such calculations.

The Principal Investigators have, generally, stretched their interpretations and conclusions somewhat beyond what their data justify. It is recommended that each Research Centre be encouraged to produce a comprehensive review covering its own observations of coastal water circulation and stratification, and using the published results of other research workers on the exchange of water between their coastal region and the offshore regions.

Little work has been reported on the more complex problem of dispersion and diffusion of pollutants within the water mass.

Coastal transport is only one state in the cycle from pollutant source to sink. Within the long-term programme consideration should be given to other stages, including possible pollutant transfer between the various basins within the Mediterranean, and between the Mediterranean and the Atlantic, as well as the transfer across the boundaries of the marine environment (e.g., land-sea, air-sea and sediment-sea).

Two questions, among others, that need to be answered are:

Do pollutants entering the surface water ever leave the Mediterranean in the intermediate water?

Does the water leaving the Adriatic Sea flow into the deep Ionian waters to be held in the eastern basin, or into the intermediate layer and thence eventually into the western basin and finally into the Atlantic?

The correct analysis of all these factors governing the transport of pollutants in the Mediterranean will require the development of hydrodynamic and mathematical models of the Mediterranean Sea.

MED POL VII : COASTAL WATER QUALITY CONTROL

(prepared by WHO)

1. INTRODUCTION

The main objective of MED POL VII is the assessment of the potential health hazards connected with the coastal waters of the Mediterranean, needed for the rational design and efficient implementation of national programmes for the control of coastal pollution from land-based sources in the area.

The elements of the programme of work are as follows:

- a. The monitoring of selected coastal areas;
- b. The initiation and promotion of scientific studies on the epidemiological evidence of health effects caused by pollution in coastal areas;
- c. Principles and guidelines for coastal water pollution management;
- d. The development and propagation of relevant technical documentation;
- e. Training and technical assistance.

The present chapter is intended to analyse, evaluate and discuss the practical and theoretical scientific results of the work carried out and implemented since the actual initiation of the Pilot Project in July 1976 up to October 1979. Special attention is given to the monitoring programme which constitutes the larger and main scientific activity of the Pilot Project.

2. THE MONITORING OF SELECTED COASTAL AREAS

2.1 Areas monitored

The monitoring included two aspects: (a) the surveillance of beaches and bathing waters; and (b) the surveillance of shellfish culture waters and shellfish flesh.

The collaborating laboratories represent 14 Mediterranean countries out of a total of 18. Moreover, the distribution of the collaborating institutions did not represent a well balanced representation of all the coastal areas.

2.2 Methods and material used

For the monitoring of the selected coastal areas standard methods agreed by the principal investigators were used, (Report of WHO/UNEP Expert Consultation on Coastal Water Quality Control Programme in the Mediterranean (Geneva, 15 - 19 December 1975). EHE/76.1. WHO 1976; Guidelines for Health Related Monitoring of Coastal Water Quality. Report of a meeting of WHO/UNEP joint group of experts (Rovinj, Yugoslavia, 23 - 25 February 1977) WHO 1977; Health Criteria and Epidemiological Studies Related to Coastal Water Pollution. Report of a meeting of WHO/UNEP joint group of experts (Athens, 1 - 4 March 1977) WHO 1977; Mid-term Review of the Joint WHO/UNEP Co-ordinated Pilot Project on Coastal Water Quality Control in the Mediterranean. Report of the meeting of principal investigators of collaborating laboratories (Rome, 30 May - 1 June 1977) WHO 1977; Coastal Water Pollution Control. Report of a joint WHO/UNEP Workshop (Athens, 27 June - 1 July 1977) WHO 1977; Monitoring of Recreational Coastal Water Quality and Shellfish Culture Areas. Report of a joint WHO/UNEP Seminar (Rome, 4 - 7 April 1978) WHO 1978; Second Report on Coastal Quality Monitoring of Recreational and Shellfish Areas (MED VII) - Report of a Workshop jointly convened by WHO and UNEP (Rome, 17 - 19 January 1979) WHO 1979; and Third Report on Coastal Quality Monitoring of Recreational and Shellfish Areas (MED VII) - Report of a Meeting of Principal Investigators jointly convened by WHO and UNEP (Rome, 20 - 23 November 1979) WHO 1980).

2.3 Results and their interpretation

2.3.1 Parameters investigated

a. Recreational waters

The great majority of collaborating laboratories used the three bacteriological indicators specified: i.e., total coliforms, faecal coliforms and faecal streptococci included in the minimum compulsory programme.

Similarly, but to a lesser extent, the collaborating laboratories monitored, in addition to the bacteriological data, air, sea and sample temperatures during transport, and salinity.

However, only a relatively small number of laboratories monitored some of the parameters describing general conditions in the monitoring area at the time of sampling. These parameters concerned meteorological, hydrographic and dynamic conditions and visual observations on pollution traces.

Few collaborating laboratories monitored additional parameters with a view to collecting more specific information or to developing new parameters more sensitive and more representative of the pollution by faecal material. In these laboratories pathogens, like salmonella, shigella, *Vibrio cholerae*, enteric viruses and other micro-organisms such as bacteriophages, bacteria that grow on nutrient agar, total bacterial count, *V. parahaemolyticus*, dinoflagellates, are being investigated (table 1).

Table 1 - Optional parameters, carried out by some of the institutes collaborating in MED VII

Code	Microbiological	Chemical	Biological
27.02			
35.04			
35.08		Nutrients(occasionally)	
36.06	<u>V. parahaemolyticus, Salmonella</u>	DO	
36.07	<u>V. parahaemolyticus, Salmonella</u> <u>Shigella, Fungi, Sulphite</u> reducer, clostridia, Coagulase- positive staphylococci	PH	
36.11	Total and faecal coliforms, faecal streptococci in the sediments, fungi in the sand - <u>V. para haemolyticus</u> <u>Salmonella, Shigella, Vibrio</u> <u>cholerae</u>		
47.02	<u>Enterovirus</u>		
47.03	<u>Salmonella, enterovirus, bacterial</u> count		
47.04	<u>V. parahaemolyticus, Salmonella</u>		
47.05	<u>V. parahaemolyticus, V. cholerae,</u> <u>Salmonella, Shigella</u>	COD,pH	
48.01			
4806/48.12			
48.09	<u>Salmonella</u> <u>Salmonella</u>	NH ₄ , NO ₂ , NO ₃ , P, MBAS Nutrients	phytoplankton
48.11	<u>Virus</u>	Nutrients-pH	chlorophyle
48.15	<u>Virus</u>		
52.01	<u>Vibrio - Salmonella</u>	pH	
MA.03			
MO.01	<u>Salmonella</u>	Nutrients	
56.03			
29.05			
29.06			
88.03	<u>Sulphite reducer, clostridia,</u> total bacteria, <u>Pseudomonas</u> <u>aeromonas</u>		
89.05			
95.02		Nutrients	phytoplankton
95.04		pH	
95.05		Nutrients	phytoplankton chlorophyll

Collaborating laboratories 56.01 and AL.01 joined the Pilot Project only recently and are not included in this table.

From the results so far obtained it appears that higher counts have been experienced for total coliforms than for faecal coliforms and enterococci. But the enterococci count was also reported to invariably give the lowest count values with respect to the other two compulsory parameters.

Although the concentration of total coliforms might not be the best indicator of contamination of sea-water with faecal material, some results obtained show a close correlation with the location of outfalls which discharge faecal material into the sea, or material which seems to enhance the survival and reproduction of micro-organisms in the sea.

From the experience so far acquired it appears that the faecal coliform test may largely replace the traditional total coliform parameter for water quality measurements in recreational waters.

However, some results show that faecal streptococci are a good indicator of pollution. Their survival and frequency of discovery is similar to those of enteroviruses with $r = 0.9113$ and peaks of $r = 0.94$. It was also noted that when warm, industrial, alkaline wastes are present, large numbers of enterococci may be isolated while coliforms may be absent.

In one of the studies, the correlation analysis between the various bacteria and the enteroviruses was carried out. The results with the details of the regressing line are given in figures I, II and III. A significant correlation was found between the ratios of total coliforms to faecal coli, total coliforms to faecal streptococci and faecal coli to faecal streptococci.

Considering that the selected indicators of pollution are relatively sensitive to the marine environment, it appears advisable to investigate and eventually to use a more suitable organism. To this end, some studies are being carried out on salmonella, E. coli, bacteriophages and enteric viruses. No definite results are yet available.

While in some studies it appeared that the microbial concentration level in the sea was low in the summer as compared to other seasons, the contrary was observed for sediments. This is apparently due to increased daylight and solar radiation which may not reach sediments.

However, in other studies, higher mean values were noted during the summer season. This was attributed to the increase in coastal pollution due to the number of summer tourists accommodated along the coast.

The operational document proposed the following as compulsory parameters for the identification of effluents or outfalls in a minimum programme as mentioned in section 2.2: biochemical oxygen demand, BOD_5 ; settleable solids (SS); and the volume of the discharge.

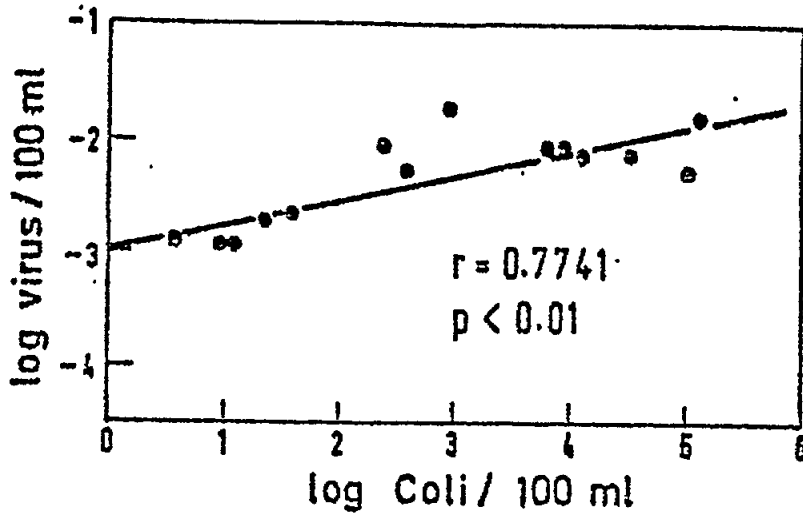


Figure 1: Correlation between Coliforms and Viruses found at beaches.

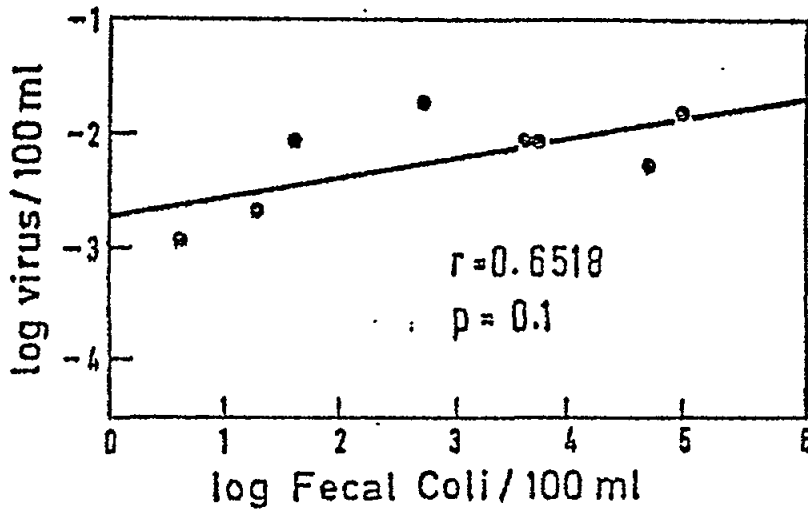


Figure 2: Correlation between Fecal Coli and Viruses found at beaches.

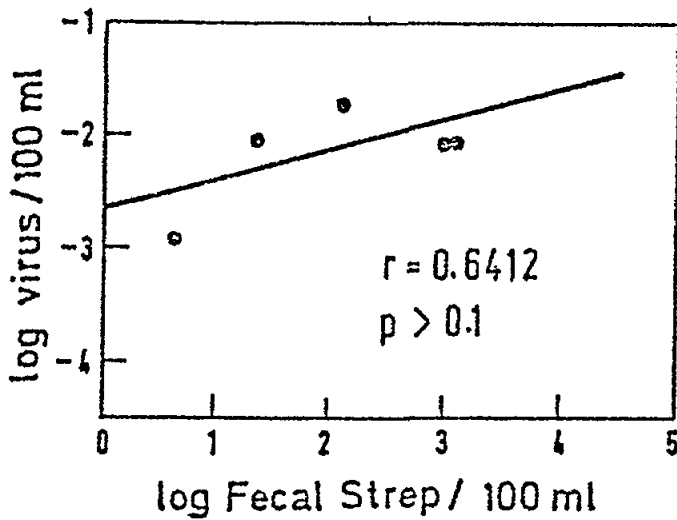


Figure 3: Correlation between Fecal Streptococci and Viruses found at beaches.

These parameters were not widely applied, owing to the fact that in some of the monitored areas there were no effluents or outfalls of importance nearby. However, it was considered by some of the collaborating laboratories that the above parameters were insufficient for the assessment of the pollution in rivers and outfalls. They proposed to include pH, COD and TSS (total suspended solids) as well.

b. Shellfish areas

Here again the great majority of collaborating laboratories used the four bacteriological indicators, i.e. total coliforms, E. coli, Streptococcus faecalis and total heterotrophic bacteria, included in the minimum compulsory programme.

To a lesser degree, the collaborating laboratories included physical and chemical parameters such as temperature, dissolved oxygen and meteorological factors in the parameters monitored. Once more, this was mainly due to the absence of the necessary facilities, equipment and personnel.

In the results of one of the collaborating laboratories it was found that the positivity of V. parahaemolyticus in shellfish increased during the warmer months and decreased markedly during the cold ones. This seems to confirm the well-established view that V. parahaemolyticus is a natural inhabitant of sea-water and does not correlate with pollution.

From the experience gained during the Pilot Project, it appears that the most important parameters in shellfish monitoring are faecal coliforms and faecal streptococci. Their importance is related to the hygienic and sanitary aspects of the control of shellfish. However, it has been found that although faecal streptococci and faecal coliforms are both indicators of faecal pollution, the value of their analyses cannot always be correlated. Thus, high values of enterococci were found in shellfish with less than few E. coli per gram of flesh.

The testing of Salmonella in shellfish flesh is receiving some attention, and consideration is under way to include it among the compulsory parameters.

The following parameters: temperature of the sea-water, salinity, rainfall with reference to date of sampling, are considered to be the most important accompanying parameters and should be included in the compulsory parameters.

c. Fish

Although not specifically referred to in the "Operational Document" some investigations are being carried out on fish. In polluted waters, fish might concentrate bacteria and viruses from the water in their organs and muscles and become a public health hazard. The result of a preliminary study carried out by one of the collaborating laboratories indicated that when the concentration of coliforms in the water was $10^2/100$ ml and the total bacteria count was 1×10^5 /ml, coliform bacteria were recovered from all the organs of fish as well as the muscles. The bacterial concentration in the organs was higher than in the water in which the fish lived. In view of the correlation between the concentration of bacteria in water and the recovery of bacteria from fish organs, the question arises as to whether fish grown in recommended concentrations of faecal coliforms might not constitute a public health hazard.

2.3.2 Methodology

a. Recreational waters

Realizing the importance of developing and applying similar methodologies and materials for the analysis of the various parameters, the Pilot Project included in its first activities the preparation and distribution of a document entitled "Guidelines for Health Related Monitoring of Coastal Water Quality."

In addition to these "Guidelines", the collaborating laboratories agreed to apply a more specific methodology for each of the compulsory microbiological parameter.

In one study it appeared that the MPN and MF methods did not differ significantly. However, in other studies, the MPN results were giving higher counts. In yet another study, the comparison of the MPN with the MF method showed a fairly good correlation ($r = 0.8$). Table 2 lists the collaborating laboratories that run the MPN and the MF methods in parallel. Further investigation and results are necessary before any accurate appraisal of one or the other method can be made.

Table 2 - Methods used for testing compulsory bacteriological parameters and their respective evaluation

MPN - most probable number of multiple tube method
 MF - membrane filtration method with recommended media
 n.i.a.- no information available

Code No.	Country and designated institution	Bacteriological test:			Remarks
		Total Coliforms	Total Coliforms	Total Streptococci	
AL.01	<u>ALGERIA</u> 1. Centre de recherches Océanographiques et des Pêches, Alger	-	-	-	Only recently joined the Pilot Project
27.02	<u>EGYPT</u> 1. Centre for Postgraduate Studies and Research, Alexandria University	MF	MF	MF	
35.08	<u>FRANCE</u> 1. Scientific & Technical Institute for Sea Fisheries (ISTPM), Sète				n.i.a
35.04	2. Research Centre for Biology & Medical Oceanography (CERBOM), Nice	MF	MF	MF	

Code No.	Country and designated institution	Bacteriological test:			Remarks
		Total Coliforms	Total Coliforms	Total Streptococci	
	<u>GREECE</u>				
36.07	1. Laboratory of Hygiene, Medical School, University of Thessaloniki	MF/MPN	MF/MPN	MF	
36.11	2. Environmental Pollution Control Control Project, Ministry of Social Services, Athens	MF/MPN	MF/MPN	MF	
36.06	3. Department of Food Hygiene, Veterinary Faculty, University of Thessaloniki	MF/MPN	MF/MPN	MF	For shellfish only MPN method for coliforms and PP faecal coliforms and PP for faecal streptococci
	<u>ISRAEL</u>				
47.03	1. Environmental Engineering Laboratories, Technion, Haifa	MF	MF	MF	
47.02	2. Environmental Health Laboratory, Hadassah Medical School, Hebrew University, Jerusalem	MF	MF	MF	
47.04	3. A. Felix Public Health Laboratories, Ministry of Health, Tel Aviv	MPN/MF	MPN	MF	
47.05	4. Public Health Laboratories, Ministry of Health, Haifa	MPN/MF	MPN	MF	

Code No.	Country and designated institution	Bacteriological test:			Remarks
		Total Coliforms	Total Coliforms	Total Streptococci	
	<u>ITALY</u>				
48.10	1. Higher Institute of Health, Rome	MF	MF	MF	
48.12	2. Zoological Station, Naples				
48.06	3. Centre for Study and Research in Sanitary Engineering, Institute of Water Supply and Wastes Disposal, Naples	MF	MF	MF	
48.11	4. Institute of Water Research (CNR), Rome	MF	MF	MF	
48.15	5. Institute of Hygiene, Genoa	MPN/MF	MPN/MF	MPN/MF	
48.01	6. Institute of Hydrobiology and Fish Culture, Messina	MF	MF	MF	
48.09	7. Institute of Hygiene, Trieste	MF	MF	MF	
	<u>LEBANON</u>				
52.01	1. Marine Research Centre, National Council for Scientific Research, Beirut	MF	MF	MF	

Code No.	Country and designated institution	Bacteriological test:			Remarks
		Total Coliforms	Total Coliforms	Total Streptococci	
MA.03	<u>MALTA</u> 1. Public Health Laboratory, Ministry of Health & Environment, Valletta	MF/MPN	MF	MF	
MO.01	<u>MONACO</u> 1. Scientific Centre of Monaco, Monte-Carlo	MF	MF	MF	
56.03	<u>MOROCCO</u> 1. National Institute of Health Rabat	MF	MF	MF	
29.06	<u>SPAIN</u> 1. Laboratories and Services of the Malaga Provincial Health Authority, Malaga	MPN/MF	MPN/MF	MPN/MF	
29.05	2. Laboratories and Services of Tarragona Provincial Health Authority, Tarragona	MPN/MF	MPN/MF	MPN/MF	
88.03	<u>TUNISIA</u> 1. Institut Pasteur de Tunis, Tunis	MF	MF	MF	

Code No.	Country and designated institution	Bacteriological test:			Remarks
		Total Coliforms	Total Coliforms	Total Streptococci	
89.05	<u>TURKEY</u> 1. Environmental Engineering Department, METU, Ankara	MF	MF	MF	
95.04	<u>YUGOSLAVIA</u> 1. "Rudjer Boskovic" Institute, Centre for Marine Research, Rovinj	MF/MPN	MF/MPN	MF	
95.02	2. Institute for Oceanography and Fisheries, Split	MF/MPN	MF/MPN	MF	
95.05	3. Marine Biological Station, Institute of Biology, University of Ljubljana, Portoroz	MF/MPN	MF/MPN	MF	MPN for total and faecal coliforms for shellfish

The suitability of the proposed nutrients for the microbiological parameters was studied. From the experience gathered during the Project it appeared that the adopted m-FC medium incubated at 35°C for the determination of total coliforms was not giving satisfactory results. In this connection it was suggested that the M-Endo broth might be used.

In the "Operational Document" it is specified that the samples should be taken at a distance of 10m from the low tide mark. However, this presented some difficulties, especially to those laboratories usually concerned only with microbiological parameters and which did not have an appropriate boat for sampling.

b. Shellfish areas

Here too, in order to strengthen harmonization and comparability of results it was agreed by the collaborating laboratories to utilize the same methodology and the same nutrients more specifically for the analysis of the compulsory parameters.

The adherence to the above standardization and methodology has unfortunately not been applied by the majority of the collaborating Institutes and any comparison of the results obtained is weakened by this deficiency.

The sampling networks lacked uniformity. Density, direction, the number of sampling points did not follow some of the general guidelines.

2.3.3 Quality criteria

As part of the project the first drafts of environmental quality criteria were formulated for:

- a. recreational waters, and
- b. shellfish growing waters.

They are presented in Section 2 and 3 of the document UNEP/WG.46/7.

2.4 Quality Control Pilot Programme

The execution of the Pilot Project progressively increased the need to develop a Quality Control Programme with the aim of identifying a variety of laboratory variables and specifying essential quality control practices to assure the present and continued productions of reliable data. The programme is described as chapter 19.3 in document UNEP/WG.46/5.

3. INITIATION AND PROMOTION OF EPIDEMIOLOGICAL STUDIES

The hazards to human health from bathing waters arise primarily from the swallowing of polluted waters and from direct contact with the skin. There is

circumstantial evidence of association between disease and bathing in polluted water. However, additional epidemiological studies are required in order to better ascertain and establish the relationship of cause and effect. These studies should aim at providing the necessary data base for evaluating health effects and developing water quality criteria for the recreational use of coastal waters in the Mediterranean.

To this end a programme was developed through the pilot project and is presented as chapter 10 in the document UNEP/WG.46/5.

4. PRINCIPLES AND GUIDELINES FOR COASTAL WATER POLLUTION CONTROL

The operational document of the MED VII Pilot Project recognized the importance, complexity and need of coastal water pollution control. Effective marine pollution control will ultimately depend on modification, reduction and dispersion of wastes discharged and dumped into the sea. It will be necessary to institute and execute a series of local and regional pollution abatement programmes covering the major population and industrial centres around the Mediterranean. Such programmes should aim at the development of long-range plans covering large geographical areas.

In response to the priority needs of the Mediterranean countries, the development of principles and guidelines for coastal water quality management has been included in this Pilot Project as one of its main objectives.

A workshop as convened by WHO/UNEP on Coastal Water Pollution Control, Athens, 27 June to 1 July 1977, in order to examine the methodology for marine pollution control planning and to outline a plan of action leading to the development of a model Code of Practice for the disposal of liquid wastes into the Mediterranean.

The workshop, among other proposals, suggested an "Outline of Contents of a Code of Practice for Coastal Pollution Control in the Mediterranean", intended as a guide to the preparation of the different sections of the Code.

Considering the priority importance of pollution from land-based sources, UNEP, in collaboration with the World Health Organization and with the assistance of national Mediterranean experts, developed a Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources, which was agreed and signed at the meeting of Plenipotentiary Ministers of the Mediterranean States in Athens, 12-17 May 1980.

To assist responsible national authorities in the negotiation and eventual implementation of this protocol, a publication on "Principles and Guidelines for the Discharge of Wastes into the Marine Environment" was prepared and published under the joint sponsorship of UNEP and WHO.

5. DISCUSSION AND CONCLUSIONS

5.1 The monitoring of selected coastal areas

The nomination by the Mediterranean States of collaborating institutes and the subsequent selection of coastal areas to be monitored, did not provide a balanced representation of either the Mediterranean countries or their surrounding coastal areas. These deficiencies should be remedied for any planned follow-up to monitoring activity in any future programme.

Any proposed monitoring of quality of coastal areas should not be limited to bacteriological quality, as in the case of MED POL VII, but should cover all relevant and necessary physical, chemical, bacteriological and other parameters of quality.

In proposing a future monitoring programme of quality of coastal areas, due attention should be given to including monitoring of rivers, outfalls from major municipal sewage discharges, outfalls from industrial units and any others which may affect substantially the selected monitoring area.

5.2 Methods and materials

While it was agreed by the Principal Investigators that the compulsory parameters utilized up to now for recreational coastal waters should be maintained, they suggested that the total number of coliforms should be discontinued in the future for routine monitoring. Notwithstanding, total coliforms might be used as an indicator for cleaner waters. Thus, basically faecal coliforms and faecal streptococci should be retained as compulsory bacteriological parameters.

As far as shellfish monitoring is concerned, it is considered that the four compulsory bacteriological parameters, namely total coliforms, faecal coliforms, faecal streptococci and heterotrophic bacteria, could be reduced to two: faecal coliforms and faecal streptococci.

As far as shellfish culture areas are concerned, physical and chemical parameters may not be of great importance for routine monitoring. However, this view requires additional investigation as it is not shared by all the collaborating institutes. The importance of testing salmonella in shellfish and its inclusion in the minimum programme is being considered. However, further study is still needed before recommending it for inclusion in the minimum compulsory programme.

The results of the comparison of the compulsory membrane filtration method with the MPN (most probable number), now being undertaken by a number of laboratories, will clarify this issue. From preliminary readings, results appear to be comparable.

As far as media are concerned, there is some evidence that the m-FC broth for the detection of total coliforms in sea-water presents some difficulties in interpreting the results. A comparative study using m-Endo broth or agar is under way in order to resolve this controversy.

The Pilot Project was not a "one-shot" exercise intended to provide rigid rules and procedures for the establishment and management of a monitoring network, or required as an assessment of pollution and for providing information and data necessary for its appraisal and control. On the contrary, it was intended to develop a dynamic and at the same time, elastic approach that would permit improved efficiency and quality, and expansion of the work carried out.

5.3 Criteria and epidemiological studies

The Pilot Project did not go further than to establish two interim criteria, one for recreational water and the other on shellfish (culture areas and shellfish flesh). These should be translated into guidelines and standards. To this end, a decision as to "acceptable risk" of symptoms of varying degrees of severity or of specific diseases should be made. Such decisions on the pollution control programmes to achieve these standards are essentially political. However, the interim criteria should be consolidated or amended, following epidemiological studies, which should give the dose-response type relationship between illness and water quality.

5.4 Principles and guidelines for coastal water pollution management and control

Following the progress made in the monitoring and assessment of pollution the time has come to proceed from monitoring to pollution control. The protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources, as already mentioned, provides the legal basis for the development and implementation of a pollution control programme.

5.5 Training

Although successful, the training component was too small. This should be enlarged substantially, considering also that the Protocol referred to above will undoubtedly require the training of a great number of technical personnel at various levels and belonging to various disciplines.

The substantial results and the successful multiple role that the occasional meetings achieved, advocate their continuation in the future.

MED POL VIII : BIOGEOCHEMICAL STUDIES OF SELECTED POLLUTANTS IN
THE OPEN WATERS OF THE MEDITERRANEAN (prepared by IAEA)

1. INTRODUCTION

For the past several years the International Laboratory of Marine Radioactivity (ILMR) has been charged with co-ordinating the MED POL VIII Pilot Project in the overall framework of the UNEP-sponsored Mediterranean Action Plan. The principal purpose of MED POL VIII is to obtain baseline data on levels of pollutants in sea-water, organisms, particulate matter and sediments from the open Mediterranean Sea. These measurements are to be compared with those being made in the coastal zone as part of several other ongoing UNEP-sponsored Mediterranean pollution pilot projects.

The overall philosophy of MED POL VIII has been twofold. First, to gather as much information as possible on inputs, levels and fluxes of pollutants in all major components of the Mediterranean in order that a general model of the bio-geochemical cycles of these substances can be elaborated. These steps are considered to be essential in any attempt to assess pollutant mass balance in oceanic systems. Second, these data are intended to supplement and enhance those presently being gathered on levels in selected marine species in the coastal areas. Pollutants in water and sediment are not being measured in the four UNEP Monitoring Pilot Projects and without such information, any future attempt to calculate mass balances for pollutant inputs to the Mediterranean, or to explain abnormally high concentrations of these substances in the marine organisms being monitored, would be impossible.

The marine biogeochemical cycle of a given pollutant can be conceptualized as outlined diagrammatically in figure I. Briefly, contaminants entering the marine environment either from natural or anthropogenic sources may remain in the aqueous phase, become involved in biological cycles or precipitate out by biological and physico-chemical processes. Most of the pollutants which become associated with biotic or abiotic particulates sink under the influence of gravity and eventually reach the sediments. Once incorporated in sediments, these substances may be released back to the water column by both biotic and abiotic processes. Some pollutants such as metals and certain organic compounds may be released back into the atmosphere as volatile sea salts.

The approach used in the MED POL VIII Pilot Project has been to measure a suite of heavy metals and organochlorine compounds in the prime components

shown in figure I. To complete the picture, flux measurements of pollutants in certain matrices have also been made. This has involved studying biokinetic behaviour of certain pollutants in important marine species and assessing the vertical transport potential of biogenic detritus by collecting sinking particulates in sediment traps moored at different depths.

In order to effect the baseline measurement programme the ILMR undertook the following oceanographic cruises during the period 1975-79:

R/V Chain	3-19 May 1975 (Istanbul-Cadiz)
USNS Kane	10-14 April 1975 (Piraeus-Monaco)
Atlantis II	14-23 April 1977 (Suez-Malta)
USNS Hayes	13-23 June (Piraeus-Corsica)
Shikmona	5-12 July 1977 (Haifa-Crete) (under subcontract with the Israel Oceanographic and Limnological Research, Ltd.)
Cornide de Saavedra	15-26 July 1977 (Civitavecchia-Barcelona)
Calypso	10-20 November 1977 (Piraeus-Sicily)
Researcher	18-22 June 1979 (Port Said-Piraeus)

Sea-water, sediments and pelagic biota were sampled during these series of cruises which covered almost all of the principal geographical regions of the Mediterranean Sea (figure II). Samples were analysed for selected trace elements and chlorinated hydrocarbon compounds either at the ILMR or by the "Demokritos" Nuclear Research Centre in Greece under subcontract to the MED POL VIII project. In addition to these baseline measurements, determination of trace elements in marine aerosols and particulate matter in sea-water were carried out by the Centre des Faibles Radioactivites, CNRS, France, in order to study the flux of pollutants through the air-sea interface of the Mediterranean.

The biokinetic behaviour of arsenic, vanadium, nickel and PCBs in various marine organisms was examined in order to gain information on the fluxes of these substances once they enter biological cycles. These contaminants were chosen for study on the basis of both their recognized potential as marine pollutants and the fact that little information is known about their transfer rates through the biosphere. This information is instrumental in establishing flux rates for materials in the biotic component of the biogeochemical cycle and in supplying fundamental data for future studies on the effects of these pollutants on aquatic species. The laboratory studies on biokinetics were conducted at the ILMR in Monaco and also under subcontract at the Royal University of Malta, Msida, Malta, and the Instituto de Investigaciones Pesqueras, Barcelona, Spain.

Vertical flux studies of pollutants were undertaken by utilizing both in situ measurements and analyses of freshly produced biogenic particulates which account for a large fraction of the particulates trapped at depth. Sediment traps were deployed for periods of up to two weeks at various depths off Monaco. The material was quantified for mass flux calculations and analysed for several heavy metals and organochlorine compounds. At the same time shipbound collections of freshly produced biogenic particulates were made, using pelagic organisms which were residing in the water column directly over the traps. Pollutant concentrations in this "source" material were compared with those in material trapped at depth in order to estimate the rate at which certain pollutants are remineralized from biogenic particles as they sink.

All the above data are used as input parameters for models which are intended to delineate the biogeochemical flux of pollutants through the open Mediterranean Sea. In addition, the information on pollutant concentrations in the various components of the Mediterranean will serve as a valuable baseline for judging possible changes in these levels in future years.

2. OPEN MEDITERRANEAN BASELINE MEASUREMENTS

2.1 Heavy metals in sea-water and sediments

During the period 1975-1979, a number of sea-water samples were collected throughout various zones of the Mediterranean and analysed for selected heavy metals such as Cu, Zn, Cd and Hg (Huynh-Ngoc and Fukai, 1979). In order to understand the atmospheric transport of trace elements from land to the Mediterranean, particulate Al, Fe, Cu, Zn, Pb, Cd and As were determined in marine aerosols collected at 3 m over the sea surface, and in suspended matter collected at various depths in the region between the south coast of France and Corsica. These studies on marine aerosols and suspended matter were carried out by the Centre des Faibles Radioactivites at Gif-Sur-Yvette, France (Chesselet et al., 1979). In addition to these measurements a few deep sediments and a number of coastal sediments were collected and analysed for selected heavy metals.

The results of the measurements of heavy metals on open Mediterranean surface waters were grouped according to the different zones of the Mediterranean, which were defined for establishing the inputs of pollutant into various parts of the Mediterranean Sea (UNEP et al., 1977). The average surface concentrations for Cu, Zn, Cd and Hg were computed on the basis of the grouped results for each of these zones and are given in table 1. To compute average concentrations, the sample collection date was disregarded as it appeared that spatial differences were more significant than those with time. Since the representativeness of average concentrations presented in table 1 depends on the amount of data available, the significance of average values is different from one value to another. Despite the limited representativeness of these average values presented, the table gives some idea of the overall distribution of trace metals in the Mediterranean Sea.

Table 1. Average concentrations of copper, zinc, cadmium and mercury in various zones of the Mediterranean sea

Zone	Cu		Zn		Cd		Hg	
	n*	$\mu\text{g/l}^{**}$	n*	$\mu\text{g/l}^{**}$	n*	$\mu\text{g/l}^{**}$	n*	ng/l^{**}
II N.W. Med.	34	$<0.4 \pm 0.2$ ($<0.04-5.8$)	34	2.7 ± 0.4 ($0.02-10$)	33	$<0.15 \pm 0.03$ ($<0.02-0.70$)	7	20 ± 3 ($8-32$)
III S.W. Med.	13	$<0.10 \pm 0.04$ ($<0.04-0.60$)	13	1.2 ± 0.5 ($0.02-6.0$)	13	$<0.11 \pm 0.04$ ($<0.02-0.51$)	14	14 ± 2 ($5-30$)
IV Tyrrhenian	9	$<0.18 \pm 0.08$ ($<0.04-0.62$)	9	0.9 ± 0.3 ($0.02-2.3$)	9	$<0.11 \pm 0.04$ ($<0.02-0.33$)	10	26 ± 4 ($10-40$)
VI-VII Ionian-Central	6	$<0.7 \pm 0.4$ ($<0.04-2.5$)	6	1.8 ± 0.9 ($0.02-5.7$)	6	$<0.15 \pm 0.09$ ($<0.02-0.57$)	6	30 ± 10 ($5-80$)
VIII Aegean	4	$<0.3 \pm 0.1$ ($<0.04-0.64$)	4	3 ± 1 ($0.9-5.8$)	4	$<0.07 \pm 0.02$ ($<0.02-0.12$)	3	40 ± 20 ($15-80$)
X S. Levantin	4	$<0.04 \pm 0.01$ (<0.04)	4	0.9 ± 0.2 ($0.3-1.3$)	4	$<0.04 \pm 0.03$ ($<0.02-0.11$)	4	16 ± 2 ($12-20$)
Grand average	70	$<0.33 \pm 0.09$ ($<0.04-5.8$)	70	2.0 ± 0.2 ($0.02-10$)	69	$<0.13 \pm 0.02$ ($<0.02-0.70$)	44	22 ± 3 ($5-80$)

* n = No. of samples measured.

** = Uncertainties are expressed in terms of standard errors. Ranges are given in brackets.

Since far more than half of the samples were below the detection limit for Cu measurements and approximately half of those were below the detection limit for Cd measurements, the average values for these metals represent only the upper limits of the average concentrations. In these cases comparisons between different zones in the Mediterranean are less meaningful. However, the grand averages for the Mediterranean of these metals, $< 0.33 \text{ ug/l}$ for Cu and $< 0.13 \text{ ug/l}$ for Cd, appear to be similar to those values given for oceanic waters by Goldberg et al. (1971), Brewer (1975) and Robertson and Carpenter (1976). There was no correlation between the appearance of high Cu values and high Cd values.

The average concentration of Zn tend to differ from one zone to another; values are higher in the north-western Mediterranean and Aegean basins and lower in the Tyrrhenian and south Levantine basins, despite the large associated uncertainties. The grand average for the Mediterranean of Zn tends to be lower than the values given in the references cited above.

The zonal differences in the distribution of Hg are not clear from the average concentrations presented in table 1 due to large associated uncertainties. It appears, however, that average concentrations are lower in the southern Mediterranean such as the south-western Mediterranean and south Levantine basins. The grand average of Hg is lower than the values given in the references cited above, as well as in other values obtained for the Atlantic and Pacific by various investigators, but similar to or slightly higher than those given by Gardener (1975) for various parts of oceans and definitely higher than those obtained by Matsunaga et al. (1975) for the western Pacific.

The results of the trace element measurements on marine aerosols collected in June 1978 from the coastal zone of the north-western Mediterranean show that concentrations of Al and Fe, which are closely associated with almino-silicate brought from land, are found to be relatively low compared with those observed over oceanic regions. Considering that collections were made 3 m from the water surface, these relatively low Al and Fe concentrations suggest that an effective cleaning process of aerosols is taking place in the marine atmosphere at a very low altitude. While Cu concentration in Mediterranean aerosols is 10 times higher than those of general average for the oceanic aerosols, the concentrations of Zn are 5 to 10 times lower than the minimum value observed in the region of Fos-Etang de Berre by Viala et al. (1978). The average concentration of Pb in the Mediterranean appears to be close to the values observed over various regions in the North Atlantic.

The average concentrations of trace elements such as Al, Fe, Cu, Zn, Pb, Cd and As in suspended matter collected between the south coast of France and Corsica are, in general, similar to those measured in the Atlantic, except for Cu. No increase or decrease in these concentrations was observed with increasing depth.

Taking Al as a reference element, the enrichment of trace elements in marine suspended matter relative to terrestrial crustal matter has been

studied. It was found that enrichment factors for Cu, Cd and Pb are slightly higher than those observed in the Atlantic. It seems that among the trace elements in marine aerosol and in suspended particulate matter collected in the Mediterranean region, Pb is the only element the origin of which can be exclusively attributed to the influence of industrial pollution. While the concentrations of Cu in particulate matter are definitely higher in the Mediterranean than those observed in the Atlantic, it is not certain that the atmospheric transport of Cu is exclusively due to industrial origins. It should be emphasized that atmospheric transport flux of volcanic origin such as that coming from Etna for heavy metals like Cu is comparable with the flux from industrial activities in Mediterranean countries.

The results of trace metal measurements on suspended particulate matter in Mediterranean sea-water demonstrate that enrichment anomalies exist for Cu, Pb, Cd, Zn and possibly for Fe in this region. Nevertheless, the concentrations and degree of enrichment are of the same order of magnitude as those found in the Atlantic and Pacific oceans. This indicates that the chemical behaviour of trace metals in the Mediterranean is governed by laws similar to those controlling the distribution of these elements in the world oceans.

The vertical distribution of selected trace metals in offshore Mediterranean bottom sediments has been studied on two core samples taken from 500 m and 1,000 m depth in an area located off Villefranche in 1978. The cores of approximately 30 cm were divided into several vertical sections and selected trace metals such as Mn, Cu, Zn, Pb, etc. were measured on each section. For the Pb measurements, various procedures of sediment pretreatment were applied to differentiate between the different chemical forms of Pb associated with sediment particles. Depending on the treatment applied, acid-extractable Pb, EDTA-exchangeable Pb, total organic Pb, alkyl Pb, etc. were distinguished. The vertical distribution on these different chemical forms of Pb within the sediments demonstrates that some fractions of Pb in the upper parts of the sediment cores are introduced anthropologically; the Pb concentration decreases from the surface of the sediments to 6-8 cm depths for both sediment cores and the concentration of Pb at the surface in the shallower core (500 m) is always higher than that in the deeper core (1,000 m). Considering the expected sedimentation rate in the area under study, the vertical distribution of Pb within the sediments suggests the downward migration of certain forms of Pb in the sediments.

2.2 Trace elements in biota

During the period 1975-1977, pelagic organisms ranging in size from plankton to tuna were sampled throughout the Mediterranean and analysed for selected heavy metals (Fowler et al. 1979a). Large zooplankton and small nekton from both western and eastern basins were sorted according to individual species, thus allowing realistic comparisons to be made between the levels in similar species inhabiting different areas. In some cases, organisms were dissected to examine inter-tissue distribution of certain pollutants. In general, although occasional high concentrations were

noted, the levels encountered in the majority of the organisms were not too unlike those reported for pelagic species from other oceanic regions.

To date, mixed plankton sampled in 1977 have been analysed only for Hg and V (table 2). Mercury levels were generally low, averaging approximately 46 ppb dry (range 15-116 ppb) for the entire Mediterranean. There was a slight tendency towards lower values ($X = 28$ ppb) in the Levantine basin, although the differences between areas were not statistically significant ($P < 0.05$). In general, overall Hg levels in mixed plankton were in the same range as those measured in similar samples collected throughout the open Mediterranean on the chain cruise in 1975 (Fowler et al. 1976). Vanadium concentrations in plankton were considerably higher than mercury, with levels averaging about 0.9 ppm dry (range 0.2 to 1.7 ppm).

Euphausiids were usually the most prevalent group found at each station. Results of the heavy metal analyses of these pelagic crustaceans are given in table 3. Mercury levels averaged 138 ppb dry and were notably higher than the concentrations in the mixed plankton upon which euphausiids feed. Interstation variation in the concentration of most elements in euphausiids was less than one order of magnitude except in the case of Sc and Ag.

Several other individual zooplankton and micronekton species were analysed for selected trace elements and, in general, for any one species no striking differences or similarities in element concentration were observed (tables 4-7). In the case of Hg, for which we have the most comprehensive data, it appears that, along with mixed plankton, the smaller forms with high water content (e.g. *Pyrosoma atlanticum*, *Abylopsis tetragona* and leptocephali of eels) displayed the lowest levels. Although there were some exceptions, a trend towards higher concentrations (0.1 to 0.2 ppm Hg dry) was noted in pelagic crustaceans and molluscs, with the highest levels generally found in pelagic fish. As was the case with euphausiids, in general, relatively little variation in element concentration was noted among individual species from different stations. One notable exception was cobalt, which was consistently higher in the mesopelagic fish, *Myctophum glaciale*, from the eastern basin compared to the other regions (table 5).

Size may also be a factor to consider concerning the concentration of certain trace elements in pelagic organisms. For example, vanadium concentration in *Myctophum glaciale* collected at a single station was inversely related to size (table 5). However, the same trend was not evident with all the elements examined, and analyses of more individuals representing a wider range in weight will be necessary in order to evaluate which element shows variation in concentration with size.

An analysis of food-chain relationships of elemental concentrations was often hampered by lack of samples of complete food-chains at a given station. For this reason, several species comprising a complete, multiple food-chain were sampled from a single net haul and analysed for As and V. The data in table 8 show that in passing along the food-chain from microplankton to euphausiids to carnivorous decapods and fish,

Table 2. Total mercury and vanadium in mixed plankton from the Mediterranean Sea. Samples were collected during May - August, 1977.

Region	Station	Net mesh size (μm)	Hg/g dry	
			Hg	V
Eastern	A-1	60	0.036	0.37
	A-3a	280	-	1.45
	S-1	280	0.020	
	S-2	280	0.031	
	S-3	280	0.034	
	S-4	280	0.018	
Ionian	H-4	60	0.063	1.52
	H-4	280	0.039	1.04
	H-14	60	0.116	0.86
	H-14	280	0.048	0.91
Tyrrhenian	H-23	60	0.066	6.32
	H-23	280	0.036	6.29
	H-37	60	0.050	1.54
	H-37	280	0.041	1.67
North-western	CS-39	500	0.024	
	CS-42	500	0.015	0.22
	CS-44	500	0.021	
	CS-49	500	0.026	
	CS-51	500	0.078	
	CS-51	333	0.116	

Region	Station	Range of size (cm)	As	V	Zn	Co	Cs	Ag	Se	Sb	Rb	Sc	Fe	Hg*
µg/g dry														
Eastern	A-3a		49.9	<0.06	58	0.29	0.18	2.7	7.2	0.050	0.11	0.005	150	
	A-6a		33.8	0.24	107	0.24	0.23		4.6		0.31			
	S-2		33.7		100	0.15	0.60		4.0		0.25			
	S-3		38.4		123	0.15	0.43		4.2		0.65			
	S-4		47.2	0.84	140	0.26	0.16	0.92	2.3	0.046	0.08	0.040	80	0.028
Ionian Sea	H-4 () (1)			0.37										
	H-4 (1.5-2)													0.148
	H-14 (= 1)		56.9		84	0.15	0.12		3.6		0.32			0.106 ¹³⁴
	H-14 (1.5-2)													0.192
	H-14			(<0.07)	(39)	(0.06)	(0.06)	(0.16)	(2.9)		(0.27)			
Tyrrhenian Sea	H-23 (=1)		20.0	0.48	120	0.23	0.29	2.3	2.9	0.011	0.17	0.038	191	0.075
	H-23 (1.5-2)													0.175
	H-37 (>2)		34.9	1.24	57	0.19	0.26	1.7	3.5	0.040	0.11	0.013		0.239
H-37			(1.10)	(144)	(0.25)	(0.08)			(3.3)		(0.38)			
North-western	G5-46		29.6	0.23	39	0.23	0.33	1.2	3.4	0.050	0.11	0.070		0.189

* analysed by AAS

Table 4. Trace metals in pelagic eel leptocephali (*Anguilla* sp.)
from the eastern basin of the Mediterranean Sea.

Station	µg/g dry									
	As	V	Zn	Co	Cs	Ag	Se	Sb	Rb	Hg*
A-3a	32.1	0.36	71	0.22	0.21	1.6	4.1	0.033	0.054	
A-6a	37.3		25	0.067	0.03		2.9		0.22	0.064
S-1	17.1		25	0.073	0.70		4.5		0.17	0.059
S-2	26.9	0.15	26	0.086	0.09		4.2		0.18	0.048
S-4	22.0	2.3	20	0.47	0.35	0.86	3.6	0.050	0.14	

* analysed by AAS

Table 5. Trace metals in myctophid fish, Myctophum glaciale, from different regions of the Mediterranean Sea.

Region	Station	size (cm)	As	V	Zn	µg/g dry							Hg*
						Co	Cs	Se	Rb				
Eastern	A-6a		44.8	<0.06	69	0.21	0.090	6.1	0.31				
	S-1			0.66	51	0.24	0.080	3.5	0.22				
	S-2			1.12	80	0.22	0.080	3.1	0.31				
	S-3 S-4	(1-3.5)		0.30	93	0.12	0.070	3.0	0.25			8.097 8.116	
Ionian Sea	I-4	(2-3.5)			85	0.10	0.060	5.8	0.26				
	I-4	(6.5-7.5)		0.35	90	0.067	0.054	5.9	0.24				
	I-14	(2.5)		<0.08	73	0.067	0.056	5.4	0.21				
	I-14	(4-5)			43	0.06	0.070	5.2	0.32				
Tyrrhenian Sea	T-23	(1-3.5)			64	0.044	0.054	5.0	0.24				
	T-23	(5.9-7.5)		<0.05	76	0.054	0.033	4.1	0.25				
	T-37	(1-3)		0.98	66	0.035	0.069	4.4	0.19				
	T-37	(3-4)		0.74	66	0.035	0.069	4.4	0.19				
	I-37	(6-7)		0.60	78	0.11	0.038	5.2	0.20				
North western	CS-46												0.142

* analysed by AAS

Table 6. Trace metals in the pelagic tunicate, Pyrosoma atlanticum, from the central and eastern regions of the Mediterranean Sea.

Region	Station	Size	µg/g dry										
			As	V	Zn	Co	Cs	Ag	Se	Rb	Hg		
Eastern	A-3a		-	-	131	0.24	0.04	0.37	4.6	0.32			
	A-6a		26.8	0.32	98	0.17	0.04	0.56	6.2	0.38			
Ionian Sea	H-4	6cm	35.6	0.39	64	0.10	0.03	0.05	3.3	0.18	0.047		
	H-4	8cm									0.042		
	H-4	10cm	-	0.52	180	0.20	0.91	0.08	4.1	0.38	0.037		
	H-4	12cm	-	0.43	-	-	-	-	-	-	-		
	H-14	6-10cm	34.2	0.30	173	0.16	0.03	0.09	4.3	0.29	0.041		
Tyrrhenian Sea	H-37		-	-	136	0.13	0.03	-	4.4	0.40	0.075		

Table 7. Total mercury (µg/g dry) in various Mediterranean pelagic organisms sampled during a series of cruises in 1977.

Region	Station	COLLETERATA		MOLLUSCA		CRUSTACEA			PISCIS			
		Abylopsis tetragona	Medusa	Salpa maxima	Sepioida rondeletii	Loligo vulgaris	Squilla arctica	Squilla corniculata	whole muscle	exoskeleton	Chauliodus sp.	Lampanyctus sp.
Eastern	A-1	0.022								0.225	0.312	0.3
	A-3a	0.015										0.545
	A-6a											0.122
	S-2											
Aegean	H-1					0.163		0.206	0.153			
Ionian	H-4		0.041		0.124				0.152	0.175	0.193	0.131
Iyrrhennian	H-14	0.021							0.155	0.194		
	H-23	0.032		0.033								
	H-37	0.020							0.115			
Northwestern	CS-42			0.034								
	CS-46			0.028						0.292		

Table 8. Arsenic and vanadium in pelagic organisms from the north-western Mediterranean. Samples were collected during March 1977 off Villefranche-sur-Mer, France.

Organism	weight ratio dry/wet	ug/g dry	
		As	V
* Microplankton	.11	12.2	1.45
<u>Meganctiphanes norvegica</u>	.21	55.8	0.23
Moult	.22	2.4	10.3
faecal pellets	.14	35.9	N.A.
<u>Phronima sedentaria</u>	.10	27.2	0.45
<u>Pasiphaea sivado</u>	.24	114	0.07
<u>Mycetophum glaciale</u>	.28	12.7	<0.02

* Principally copepods, unidentified small crustaceans, chaetognaths, phytoplankton and detritus.

N.A. = not analysed

concentrations of As displayed no noticeable trend, whereas V levels clearly decreased.

Food-chains consisting of microplankton, macroplankton and pelagic fish were also sampled in the Aegean Sea (Papadopoulou, 1979). No trend of "food-chain magnification" was noted: As, Zn, Cs and V concentrations decreased at high trophic levels, whereas Se levels remained fairly constant (table 9). Dissection of fish tissues showed that As, Zn, Co and Se accumulate preferentially in liver, whereas Cs and Rb concentrations are roughly the same in muscle and liver (Papadopoulou, 1979). Similarly, V concentrations have been found to be five times higher in pelagic shrimp hepatopancreas than in muscle.

Tissues of bluefin tuna (*Thunnus thynnus/thynnus*) have also been analysed for heavy metals to gain insight into the intricate food-chain relationships involved in the transfer of pollutants to top-level pelagic predators. Levels of vanadium in tuna are given in table 10. Gut contents are normally higher than either liver or muscle indicating that vanadium does not show a biomagnification effect in passing from prey to predator. Mercury has also been analysed in muscle, and values ranging between 0.6 and 1.2 ppm wet appear similar to those which have been previously reported for Mediterranean tuna (Renzoni et al. 1979).

2.3 Vertical transport flux of trace elements

Heavy metals were also analysed in sinking particulates, which were collected in sediment traps moored at 100 m depth several kilometres off the coast of Monaco. Preliminary results for selected trace elements in particulates sampled during the summer-autumn period 1978 are given in table 11. It is immediately evident that trace metal concentrations in this material are relatively high. Much of the material trapped at 100 m was in the form of zooplankton faecal pellets. Metal levels in pure copepod faecal pellets collected near the traps are also high and are similar to concentrations found in the trapped particulates. In general, metal levels in these particulates are much higher than those in the organisms producing them (table 11). The data clearly illustrate the variation in trace element vertical flux that occurs seasonally.

2.4 Chlorinated hydrocarbons in sea-water, air and sediments

To establish the baseline levels of organo-chlorine compounds in the open Mediterranean Sea, as well as to understand major geochemical processes involved in distributing these compounds in the open Mediterranean environment, the measurements of PCBs have been carried out in sea-water, air and sediments collected during several cruises conducted in 1977-79. The collections of these samples were made on board Atlantis II, Haynes, Cornide de Saavedra, Shikmona, Calypso and Researcher (figure 11).

During these cruises, 76 surface and subsurface sea-water samples were collected, and various organic constituents were preconcentrated on X-AD-2 resin on board. The resin columns were brought back to the laboratory at Monaco and chlorinated hydrocarbons were analysed by gas chromatography

TABLE 9

Trace element concentrations in plankton and
Trachurus mediterraneus ($\mu\text{g/g}$, dry \pm standard deviation)

SAMPLE	As(2)	Zn	Co	Se	Cs	Rb	V(3)
60 μ net sample	18	-	-	-	-	-	-
250 μ net sample	18	162 \pm 5	0.060 \pm 0.002	2.0 \pm 0.3	0.99 \pm 0.035	0.32 \pm 0.08	11.1 \pm 0.4
500 μ net sample	7.7	119 \pm 4	0.36 \pm 0.014	2.2 \pm 0.3	0.37 \pm 0.013	-	4.6 \pm 0.2
<u>Euphausia</u> <u>kronnii</u>	5.4	77 \pm 3	0.17 \pm 0.07	1.8 \pm 0.3	0.55 \pm 0.020	0.17 \pm 0.05	1.62 \pm 0.03
<u>Trachurus m.</u> (flesh)(1)	7 \pm 2	19 \pm 9	0.030 \pm 0.014	2.9 \pm 0.7	0.067 \pm 0.012	0.32 \pm 0.05	0.095 \pm 0.02

- (1) For Zn, Co, Se, Cs and Rb mean of 14 specimens analysed, for As and V mean of 9 specimens.
- (2) Analytical standard deviations for As are up to 10%.
- (3) Overall standard error of the counting technique.

Table 10. Vanadium concentration (ppb) in tissues and stomach contents of Mediterranean Bluefin tuna (Thunnus thynnus thynnus) caught off the Côte d'Azur

Fish No.	Port of landing	Date	Length (cm)	Weight (kg)	ng V/g dry \pm 1 σ		
					Muscle	Liver	*stomach contents
1	Nice	21/7/77	82	10.2	18.7 \pm 1.9	158 \pm 18	469 \pm 64
2	Menton	7/8/77	84	11.0	39.2 \pm 5.0	139 \pm 18	397 \pm 34
3	Cannes	13/8/77	88	11.0	14.9 \pm 1.4	73 \pm 9	130 \pm 14
4	Antibes	21/8/77	83	12.8	9.3 \pm 0.7	26 \pm 2.4	136 \pm 12
5	Monaco	4/9/77	116	27.8	26.6 \pm 4.0	66 \pm 8	31 \pm 2

*/ Composed principally of euphausiids.

Table 11. Trace elements in biogenic particulates from the Ligurian Sea

Sample	Date	Mass flux $\text{g m}^{-2} \text{d}^{-1}$	Cd	Cu ($\mu\text{g g}^{-1}$ dry)	Fe ($\mu\text{g g}^{-1}$ dry)	Mn	Zn
Sediment trap particulates	6/78	0.77	1.3	62	27000	812	402
	7/78	0.64	N.D.	21	24100	247	125
	10/78	0.77	N.D.	23	28700	583	99
Copepod faecal pellets			N.D.	950	15400	277	915
Copepods			0.9	10.1	129	5.5	71

after the separation and cleaning procedures. Due to low levels of concentrations of organo-chlorine compounds, it was only possible to determine the PCBs. A summary of the results obtained on the PCB concentrations in Mediterranean sea-water is given in table 12. The results show that, although higher concentrations of PCBs at the surface were observed at some stations, no systematic vertical variation is generally observed. The levels of PCBs in near-surface layers are not very much different from those in deep layers beyond 2,000 m. PCB concentrations measured on these sea-water samples range from 0.1 to 2.5 ng/l with an average of 0.7 ng/l. This average value is found to be significantly different statistically from the average PCB concentration 2.0 ug/l obtained for sea-water samples collected in the same regions during 1975 (Elder and Villeneuve, 1977). This indicates that the concentration of PCBs in open Mediterranean waters decreased slightly from 1975 to 1977-79.

Since 1975 the ILMR has also undertaken the measurements of PCBs in air samples collected during the cruises as well as in those collected from a fixed station in Monaco.

The concentration of PCBs measured in six open Mediterranean air samples collected from the western Mediterranean during September 1975 ranged from 0.1 to 0.3 ng/m³. While two samples collected from a similar region in July 1977 show a range of 0.05 - 0.08 ng/m³, the data obtained for the Adriatic sea during November 1977 range from 0.04 to 0.1 ng/m³. It appears that the concentration of PCBs in the air masses lying above the Mediterranean decreased slightly from 1975 to 1977, as has been indicated for the sea-water concentration. It has been observed, however, that the effects of climatic conditions upon the PCB concentration in air are substantial. Thirty-six measurements of air samples collected from a fixed station at Monaco show that the PCB concentration in air varies within a wide range of 0.03 - 1.0 ng/m³, tending to decrease from summer to winter by a factor of 10.

The results of the PCB measurements carried out on sediment core samples collected during several cruises in the Mediterranean are summarized in table 13. PCBs were observed in all samples analysed, with considerably high concentrations in the top centimetre of some core samples. In most core samples, it is generally noted that a substantial decrease in PCB concentration occurs from the first to the second centimetre below the sediment surface, and also that a subsurface maximum of PCB concentration appears about 3 cm from the sediment surface. Although mechanisms for the appearance of these subsurface maxima in marine sediment cores have not yet been understood, their frequent occurrence only in offshore cores indicates that they are not likely to be artefacts related to the sampling procedure. It is considered that they are related to the behaviour of PCBs in sediment layers.

2.5 Chlorinated hydrocarbons in biota

Pelagic species from the central and eastern basins of the Mediterranean Sea were surveyed for PCBs and DDT. Residues levels in mixed microplankton from two cruises Atlantis II and Shikmona, (figure II), show some clear

Table 12. Concentrations of PCBs in Mediterranean seawater (in ng/l as DP5)
 - a summary table -

Cruise	Atlantis II	Hayes	Cornide de Saavedra	Shikmona	Calypso	Researcher
	April 1977	June 1977	July 1977	July 1977	Nov. 1977	June 1979
	Eastern Med.	Ionian-Tyrrhenian	Western Med.	Eastern Med.	Adriatic	Eastern Med.
0 - 100 m	0.3 - 1.4	0.2 - 2.5	0.2 - 0.6	<0.1 - 0.1	0.2 - 1.8	0.2 - 0.5
500 m	0.7 - 1.9	<0.1 - 1.0	-	0.2 - 0.3	-	0.2 - 0.3 ¹⁴⁵
1000 - 1500 m	0.4 - 1.5	0.7 - 1.1	-	-	-	0.1 - 0.2
2000 - 2500 m	0.5 - 0.7	1.5	-	-	-	-
3000 - 4500 m	1.3	0.9	-	-	-	-

Table 13. Concentrations of PCBs in Mediterranean sediments (in ng/g dry sediment as DP6)
 - a summary table -

Cruise	Atlantis II	Ilaves	Shikmona	Meteor
Date	April 1977	June 1977	July 1977	August 1979
Area	Eastern Med.	Tyrrhenian	Eastern Med.	Ionian
Station Depths	2650 - 3840 m	1000 - 2300 m	-	-
Top - 1 cm	5.1 - 8.9	0.8 - 1.3	0.6	1.2 - 1.6
1 - 2 cm	1.6 - 2.3	0.3 - 0.8	0.3	0.3 - 0.9
2 - 3 cm	2.3 - 3.1	0.6 - 1.2	0.6	0.8 - 1.0
3 - 4 cm	2.3	0.3 - 0.7	-	0.9 - 1.2
4 - 5 cm	0.9	0.3	-	0.2 - 0.3
> 5 cm	-	0.3	-	0.8 - 0.9

Depth in Sediment

differences. PCBs were significantly higher in samples from St. 3a and 6a taken aboard the Atlantis II (table 14). A careful examination of possible sources of contamination suggested that the observed differences might be real, although PCB concentrations in water from these two stations were not significantly higher than at other stations. The high DDT/PCB ratio found in plankton from St. 2 sampled by the Shikmona may also reflect a relatively recent input of DDT to this region.

The range of residue concentrations in euphausiids (9.8 to 110 ppb dry for PCB and 2.5 to 115 ppb for DDT) were similar to those measured in mixed plankton. Euphausiids from the eastern basin had higher DDT/PCB ratios than those of the central region. This is due to a greater relative decrease in DDT levels compared to PCB concentrations in going from the central to the eastern region.

Residue data in macrozooplankton and micronekton are too sparse to discern regional patterns adequately; however, some interesting observations can be made (table 15). The pelagic tunicate, *P. atlanticum*, sampled at one station in the Ionian Sea, contained far less PCB and DDT than similar-sized individuals from the Levantine basin. Different-sized mesopelagic fish, *M. glaciale*, sampled from a single population, displayed a trend towards increasing DDT/PCB and DDE/PCB ratios with increasing size of fish. Finally, the relatively high levels of chlorinated hydrocarbons (PCB = 660 ppb; DDT = 127 ppb) found in the amphipod, *Anchylomera blossevillei*, may be typical for this group of organisms. It is interesting to note that amphipods are also known to accumulate certain heavy metals to very high levels (Fowler et al. 1976).

Tuna muscle contained concentrations of PCB and DDT ranging from 34 to 331 ng/g dry and 9 to 184 ng/g dry, respectively. Gut contents, which were primarily composed of euphausiids, contained levels (PCB = 67 - 383 ng/g; DDT = 57 - 198 ng/g) which corresponded to those in tuna muscle.

Levels of organochlorine compounds in selected macrozooplankton and nekton, as well as mixed microzooplankton have been compared with those in similar species from other oceanic areas (table 16). Although the data are sparse, PCBs in macrozooplankton and nekton do not appear to differ significantly from concentrations in similar species measured elsewhere. In the case of microzooplankton there was a trend towards slightly lower values in Mediterranean samples. PCB production has decreased since the time most of the previous surveys were made. Since no information exists on PCB concentration in plankton or water from the open Mediterranean during the early 1970s, it is impossible to ascertain whether levels may have been higher prior to our 1977 survey. Far more data need to be collected over a longer time span in order to resolve whether these lower levels in plankton are due to a global decrease in PCB input with time, or actually represent real-time geographical differences in existing PCB concentrations.

2.6 Vertical transport flux of chlorinated hydrocarbons

The flux of organochlorine compounds via vertical transport of contaminated

Table 14. Chlorinated hydrocarbon residues in microplankton collected in the eastern Mediterranean during two cruises in 1977.

Cruise	Station	PCB (DP-5)	$\mu\text{g/Kg dry}^*$			$\frac{\text{DDT}}{\text{PCB}}$
			pp'DDT	pp'DDD	pp'DDE	
<u>Atlantis II</u> (4/77)	1	30	7.1	2.4	2.7	0.40
	3a	100	8.7	1.1	3.6	0.13
	6a	230	20	3.1	8.9	0.14
<u>Shikona</u> (7/77)	1	35	6.9	12	13.6	0.92
	2	19	17	58	9.8	4.57
	3	22	9.4	2.7	2.5	0.66
	4	15	6.2	6.2	6.8	1.25

* dry weight averaged 11 per cent of wet weight

Table 15. Chlorinated hydrocarbon residues in zooplankton and micronekton from the open Mediterranean. Each sample was a composite sample of several individuals collected during the Hayes and the Atlantis II cruises in 1977.

Organism	Region	Station [†]	PCB (DP-5)	µg/Kg dry			<u>Σ</u> DDT PCB
				pp'DDT	pp'DDD	pp'DDE	
SIPHONOPHORA							
<u>Abylopsis tetragona</u>	Tyrrhenian	37	22	4.8	0.8	2.5	0.36
	"	23	41	15	22	4.3	1.00
	Eastern	3a	37	9.4	5.9	3.0	0.50
POLYCHAETA							
<u>Alciopa cantrainii</u>	Ionian	14	96	35	5.9	19	0.63
AMPHIPODA							
<u>Anchylomera blossevillei</u>	Tyrrhenian	23	660	57	†† ₁₈	52	0.19
DECAPODA							
* <u>Sergestes arcticus</u>	Tyrrhenian	37	41	4.8	4.4	27	0.89
	"	23	56	22	2.4	13	0.65
* <u>Sergestes corniculum</u>	Ionian	4	21	4.5	1.2	9.7	0.74
<u>Palinurus</u> (larva)	"	14	71	35	N.D.	17	0.71
TUNICATA							
Pyrosoma <u>atlantica</u>	Ionian	4	6.0	1.4	0.4	1.0	0.47
	Eastern	3a	49	8.6	1.7	4.5	0.31
	"	6a	150	16	8.8	10	0.23
PISCES							
<u>Anguilla</u> (leptocephales)	Eastern	3a	35	6.8	3.0	6.6	0.47
	"	6a	48	3.9	5.2	15	0.50
** <u>Myctopnum glaciale</u>	Tyrrhenian	23	89	69	14	47	1.45
	"	37 (6-8cm)	27	20	4.5	13	1.38
	"	37 (4-5cm)	83	52	6.9	28	1.05
	"	37 (2-3cm)	50	20	10	9.6	0.81
	Eastern	6a	41	11	4.9	20	0.88

† Stations refer to those in Fig. 11

†† Error is + 50%

* Dry weight is 23% of wet weight

** Dry weight is 27% of wet weight

Table 16. PCB residues in mixed plankton from different oceanic areas

Region	Date	Net mesh size (μm)	Mean (range) $\mu\text{g}/\text{kg}$ wet	Reference
N.W. Atlantic shelf	1969, 1971	239	*91.2 (7.1-300)	Risebrough <i>et al.</i> (1972)
North Atlantic	1970	"	380 (300-450)	"
South Atlantic	1971	"	200 (18-640)	"
N. & S. Atlantic	1970-1972	"	200 (= 10-1000)	Harvey <i>et al.</i> (1974a)
N.E. Atlantic	1971	-	60 (10-110)	Holden (1972)
Firth of Clyde	1971	-	485 (40-2200)	"
Stockholm archipelago	1971	100	- ** (3-350)	Jensen <i>et al.</i> (1972)
Gulf of St. Lawrence	1972	73	1390 (90-3050)	Ware & Addison (1973)
"	1972	239	700 (N.D-1860)	" "
S.W. coast of Finland	1972-1973	150	190 (40-730)	Linke <i>et al.</i> (1974)
Gulf of Mexico - N. Caribbean	1971	239 or 750	95 (<3-1055)	Gian <i>et al.</i> (1973)
Gulf of Mexico	1973	333	84 (40-157)	Baird <i>et al.</i> (1975)
N.E. Pacific	1973-1975	333	40 (= 1-180)	Clayton <i>et al.</i> (1977)
Eastern Mediterranean	1977	239	7 (2-25)	Present study

* Converted at dry/wet weight = 10%

** Converted at fat/wet weight = 1%

particulate from the upper layers to the sediments has been assessed by analysing freshly produced biogenic particulates released from zooplankton and those collected, at depth with moored sediment traps (Fowler et al. 1979).

Sediment trap samples were composed almost entirely of intact faecal pellets and grey-green, amorphous organic matter which closely resembled the contents of faecal pellets. The latter material was categorized as faecal material. Two distinct types of faecal pellets were evident; small ovoid and cylindrical copepod pellets and longer, more fragile, cylindrical pellets presumably from larger zooplankton such as euphausiids or salps. Intact faecal pellets, sorted from a known volume of the sample, were found to comprise approximately 10 per cent of the total dry particulate trapped. Dry weight of the total particulate sample averaged about 30 per cent of the wet weight.

Total mass flux estimates at 100 m during four months, as well as PCB concentration in the particulates are given in table 17. The decrease in particulate flux during the summer months correlates well with the decrease of phytoplankton biomass and organic aggregates that are known to occur in this region. Using PCB concentrations and the mass flux values, it can be calculated that PCB deposition rates averaged approximately $100 \text{ ug PCB m}^{-2} \text{ y}^{-1}$. Independent estimates of PCB deposition rates calculated from PCB levels measured in Ligurian Sea sediment range from 80 to $125 \text{ ug m}^{-2} \text{ yr}^{-1}$ (Elder and Harvey, in prep.) and agree very closely with the measured values.

Freshly released copepod faecal pellets typically contained about $1,300 \text{ ug PCB kg}^{-1}$ dry (table 18). These levels were a factor of 10 higher than PCB concentrations (180 ppb dry) in the copepods that produced the pellets. The general similarity between PCB concentration in copepod pellets and the trapped material was not unexpected, in that faecal pellets and faecal material comprised the bulk of the particulates collected at depth. It is noteworthy that in all cases, particulates collected at 100 m contained rather less PCB than was present in faecal pellets released from surface-dwelling copepods. This observation suggests a partial release of PCBs from faecal matter as it sinks.

The presence of relatively high levels of PCBs in both freshly produced copepod faecal pellets and sinking faecal matter collected in situ indicated that zooplankton defecation contributes significantly to the downward vertical transport of these compounds in the Mediterranean Sea. Measured faecal pellet sinking rates suggest that copepod pellets have the potential to reach the bottom in areas of shallow depth such as most coastal regions. However, in deep waters it is probable that only rapidly sinking, large pellets from bigger forms (e.g. large copepods and euphausiids) will prove to be the principal particulate conveyor or pollutants to depth. In this case smaller pellets would play an important role in the cycling of these compounds in the upper water layers. The fact that faecal pellets collected in traps at 2,000 m correspond in size to those of the large copepods, *A. patersoni*, used in our study, lends support to this

Table 17. Estimates of PCB vertical flux in the Ligurian Sea

Date	Particulate PCB ug/Kg dry	Mass Flux $\text{g m}^{-2} \text{d}^{-1}$	PCB Flux $\text{ug m}^{-2} \text{y}^{-1}$
6/78	650	0.77	183
7/78	300	0.64	70
8/78	710	0.40	104
10/78	200	0.77	56
		\bar{X}	= 103

Table 18. PCB CONCENTRATIONS (AS DP-5) IN SURFACED PRODUCED
BIOGENIC PARTICULATE AND THOSE TRAPPED AT DEPTH.

Sample	ug/kh dry
NATURAL FECAL PELLETS (SURFACE)	
Copepods	1300
TRAPPED PARTICULATES (100m)	
June 1978	650
July "	300
August "	710
October "	200

contention. Further analyses of particle trap samples from several depths in the Mediterranean will be instrumental in testing this hypothesis.

3. BIOKINETIC STUDIES

3.1 Trace element kinetics

Information on the flux of trace elements through marine organisms is vital for a complete understanding of ambient element levels measured in species which are being used in Mediterranean monitoring programmes. For this reason, the behaviour and fate of arsenic, vanadium and nickel in a variety of Mediterranean species were examined in controlled laboratory experiments utilizing both radiotracers and stable element techniques.

Bioaccumulation, tissue distribution and depuration of arsenic were studied in Mediterranean mussels (*Mytilus galloprovincialis*) and shrimp (*Lysmata seticaudata*) with the aid of the radiotracer ^{74}As (Fowler and Unlu 1978; Unlu and Fowler 1979). Over a concentration range from approximately 2 to 100 g As/l, uptake was dependent upon the arsenic concentration in sea-water. Most of the arsenic accumulated was located in muscle tissue. Arsenic was taken up by mussels more rapidly at higher temperatures; a temperature effect of arsenic accumulation in shrimp was more difficult to discern due to an increased rate of moulting at higher temperatures. Arsenic uptake was inversely related to salinity in both species. Animal size also affected arsenic accumulation patterns; ^{74}As concentrations on a whole-body weight basis were higher in smaller than in larger individuals.

Arsenic elimination from both species appeared to follow a double exponential function. Increased temperature enhanced the rate of depuration; however, changes in salinity had little effect on the loss rate. In addition, depuration was strongly dependent on whether arsenic was accumulated with food or directly from water (figure III). Mussels living in their natural environment lost arsenic at a much greater rate than did individuals maintained in the laboratory. Increased arsenic loss from these individuals was correlated with increased byssus production and it appears that rapid turnover of arsenic in byssus is one mechanism by which contaminated mussels can rid themselves of excess arsenic.

Preliminary studies with the phytoplankton *Dunaliella marina* have shown that arsenate is rapidly metabolized to a form extractable with the lipids. Using *Dunaliella* as the primary producer in a three component food-chain it has been shown that this lipid arsenic is transferred efficiently to a herbivore (*Artemia salina*), and subsequently to a carnivorous shrimp (*Lysmata seticaudata*). It also appears that *Artemia* and *Lysmata* cannot mobilize inorganic arsenic into the lipid fraction; arsenate absorbed directly from sea-water by these organisms is converted largely to arsenite (Wrench et al. 1979).

Vanadium-48 and stable vanadium were used to study the uptake from water and elimination of vanadium in four benthic invertebrates - mussels (*Mytilus galloprovincialis* and *M. edulis*), worms (*Nereis diversicolor*), shrimp (*Lysmata seticaudata*) and crabs (*Carcinus maenas*). The highest

concentration factor (= 30) was noted in mussels after three week's exposure. Over a concentration range from approximately 2 to 100 ug V/l, uptake in mussels and shrimp was dependent upon the vanadium concentration in sea-water. Uptake in mussels and shrimp appeared to be independent of temperature over a range of 13° to 24°C but was slightly increased at low salinity (19 o/‰. Vanadium behaves differently from arsenic in that the majority of vanadium (> 90 per cent) becomes fixed to shells of mussels and crustaceans suggesting that surface adsorption plays a strong role in the bioaccumulation of this element (Ballester, 1979; Miramaud et al. in prep). Both radiotracer experiments and stable element data showed that byssus rapidly accumulated vanadium to high levels (figure IV). Because of the remarkable ability of byssal threads to take up this element, some consideration might be given to using this tissue as a biological monitor for measuring changes in vanadium levels in the natural environment.

Elimination of ^{48}V from mussels, shrimp and crabs was biphasic and could be best fitted to a double exponential excretion model. Contaminated worms, on the other hand, lost the isotope from their tissues at a rate which was best described by a single exponent. Crustacean moulting was found to play an important role in vanadium depuration as well as in the overall biogeochemical cycle of this metal in the marine environment.

In similar experiments with the mussel *Mytilus edulis*, it has been shown that Ni is assimilated to a much greater degree than V (Ballester, 1979). Enhanced bioavailability of Ni compared to vanadium was also noted in bioaccumulation experiments using bacteria and phytoplankton. Other studies in which fish and shrimp ingested food contaminated with V have demonstrated the generally low assimilation efficiency of this element in marine biota (Ballester, 1979).

3.2 Chlorinated hydrocarbon biocycling

Several different experiments were designed to assess the bioaccumulation potential, tissue distribution and depuration of PCB available from water, food and sediments (Polikarpov et al. 1979). In order to test the bioavailability of sediment-bound PCB, comparisons were made of the accumulation of a PCB mixture from sediments and from water by the benthic worm *Nereis diversicolor* (Fowler et al. 1978; Elder et al. 1979). Uptake from sediments was dose-dependent, attaining equilibrium concentration factors of approximately 3 to 4 after two months (figure V). Subsequent PCB elimination rates were concentration-dependent, with higher initial loss rates evident in the worms containing higher levels of PCBs. Accumulation of PCBs from water was much more rapid: concentration factors reached approximately 800 after only two weeks. Estimates were made of the relative importance of sediments and water as a source of PCBs to worms exposed to these contaminants in the natural environment. Calculations based on experimentally derived PCB concentration factors and ambient PCB levels in sediments and water suggest that, compared to water, sediments contribute the bulk of these compounds to the worms.

Using the typical filter-feeding mussel *Mytilus galloprovincialis*, the influence of natural off-shore water and laboratory (running sea-water

system) conditions on PCB loss from mussel tissues was studied. Before beginning the depuration phase, mussels had reached 160 ± 67 ppm PCB following a long-term accumulation from running sea-water. During depuration, the ratio of PCB in laboratory mussels to those maintained in situ increased from 1.0 at the start to 10 at 71 days, indicating a much more rapid loss of PCBs from mussels maintained under natural conditions. These results suggested that mussels living in the natural environment turn over PCB compounds at much more rapid rates than those maintained under laboratory conditions; however, the significance of this finding was questionable, since the PCB concentrations in offshore waters (1.3 ng/l) and laboratory sea-water (20 ng/l) varied by approximately a factor of 15. Therefore a controlled experiment was designed in which PCB-spiked mussels were allowed to depurate in two laboratory sea-waters with PCB concentrations averaging 40 and 190 ng/l. The results in figure VI show that mussels do indeed depurate PCBs more rapidly in water of lower PCB concentration. This effect partially explains the observations noted in the laboratory-field experiment and, thus, it is evident that PCB flux comparisons between organisms living in the environment and those living under conditions simulating the environment must take into account the effect of ambient PCB concentration even when it varies by as little as a factor of five. Nevertheless, some increase in PCB depuration rate might be expected in healthy, growing mussels living under natural conditions, but this will be difficult to determine experimentally unless PCB concentrations in laboratory sea-water and in the sea are similar.

The influence of uptake pathway on PCB accumulation and tissue distribution was examined by allowing shrimp to accumulate DP-5 from either food or sea-water and analysing their tissues during a period of one month. Regardless of the uptake pathway, the relative tissue distribution was similar (figure VII). The viscera which include the hepatopancreas reached the highest levels. Concentrations of PCB in viscera were over an order of magnitude higher than those in exoskeleton and muscle, suggesting that surface sorption plays a minor role in the accumulation of PCB from water by shrimp. Despite the fact that PCBs were rapidly absorbed into internal tissues, moulted exoskeletons contained significant amounts of these compounds. Concentration factors in moults as high as 10^5 to 10^4 clearly illustrate the importance of crustacean moulting as a process for redistributing PCBs in the marine environment. These experiments demonstrate the ease with which PCBs are transferred from the environment to benthic shrimp.

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FIGURE CAPTIONS

- Fig. I Schematic diagram of the oceanic biogeochemical cycle.
- Fig. II Sampling stations during the open Mediterranean cruises (1977-1979).
- Fig. III Loss of As from Mediterranean shrimp (Lysmata seticaudata) at two different temperatures following uptake either from water or food.
- Fig. IV Accumulation of ^{48}V in the tissues of Mediterranean mussels (Mytilus galloprovincialis) following uptake from water. Byssus (), shell (), viscera (), gill (), mantle (), muscle () and whole soft parts ().
- Fig. V Accumulation of PCB by benthic worm Nereis diversicolor from sediment spiked with 0.65 ppm (2), 9.3 ppm (3) and 80 ppm (4) dry weight. PCB levels in worms living in unspiked Mediterranean sediments is given in curve (1). Wet weight to dry weight ratios were 5.6 for worms and 2.2 for sediments.
- Fig. VI Loss of PCB (DP-5) from mussels (Mytilus galloprovincialis) in laboratory sea-water containing two different concentrations of PCB.
- Fig. VII PCB (DP-5) in shrimp tissues (Lysmata seticaudata) following long-term uptake from food and from water.

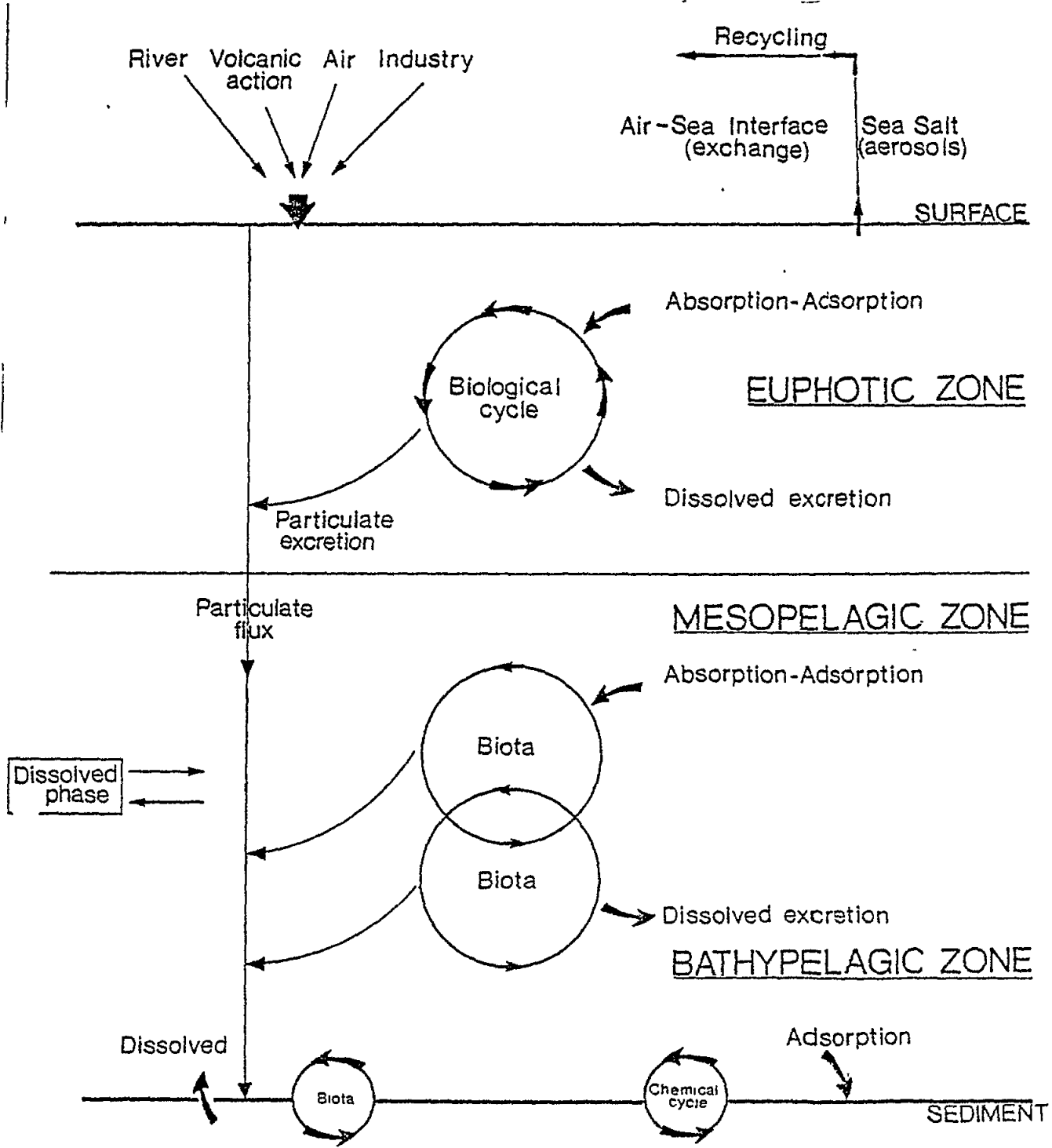


Figure 1

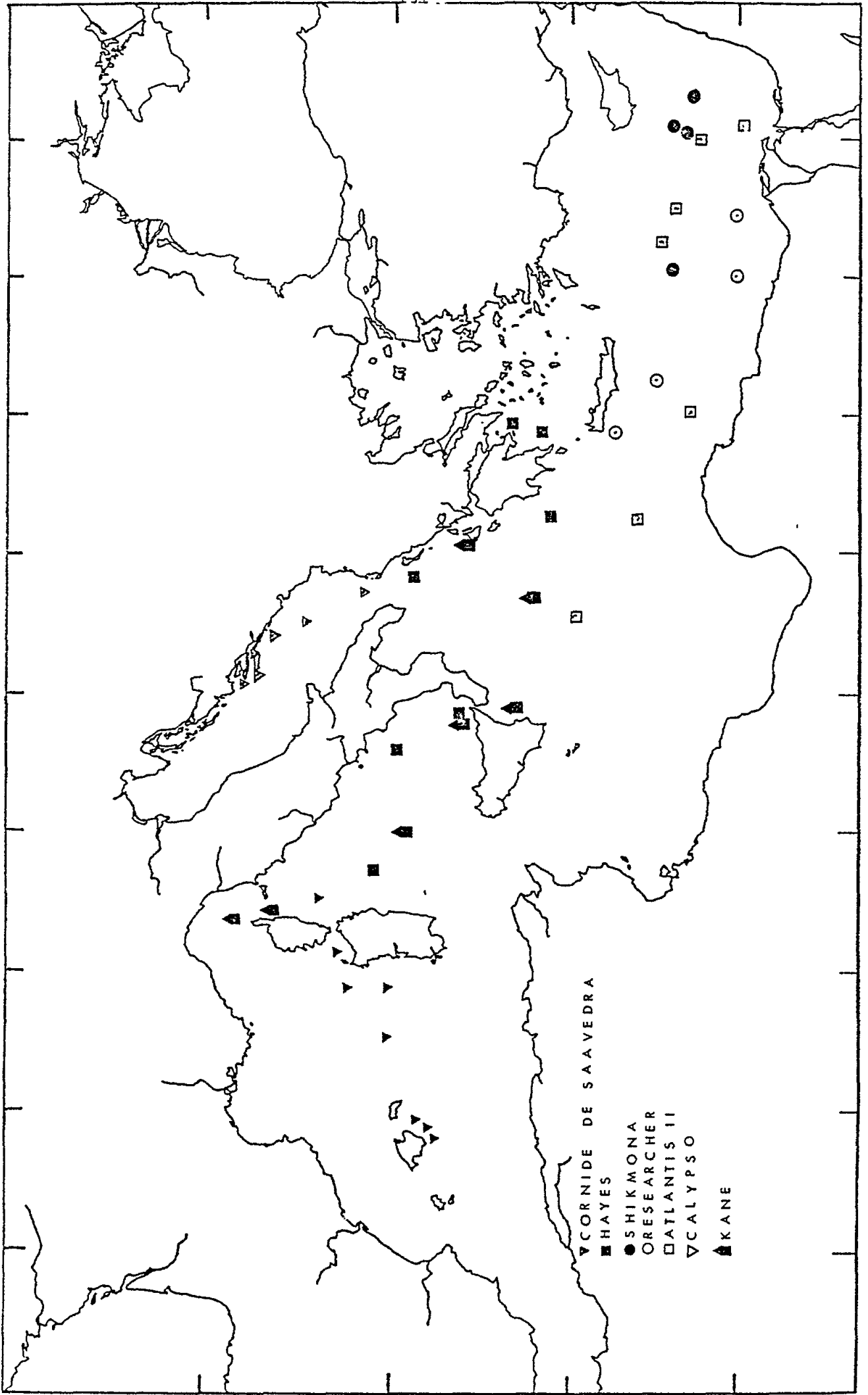


Fig. II

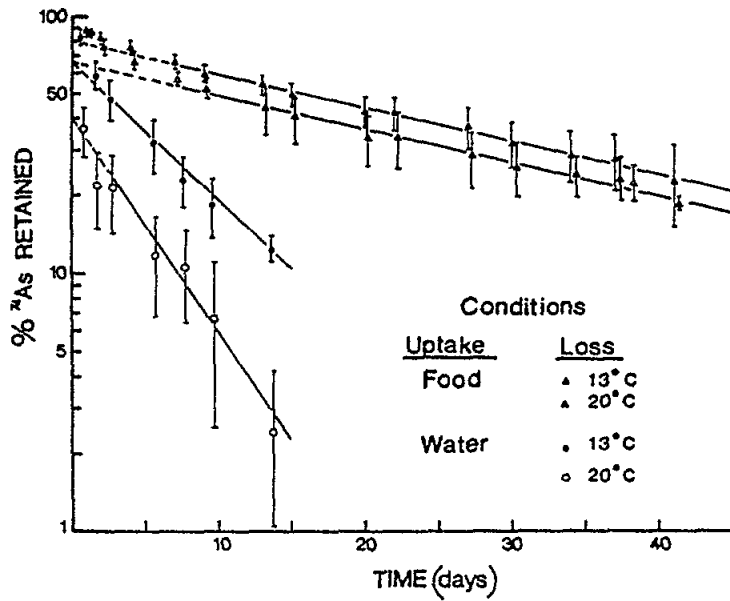


Fig. III

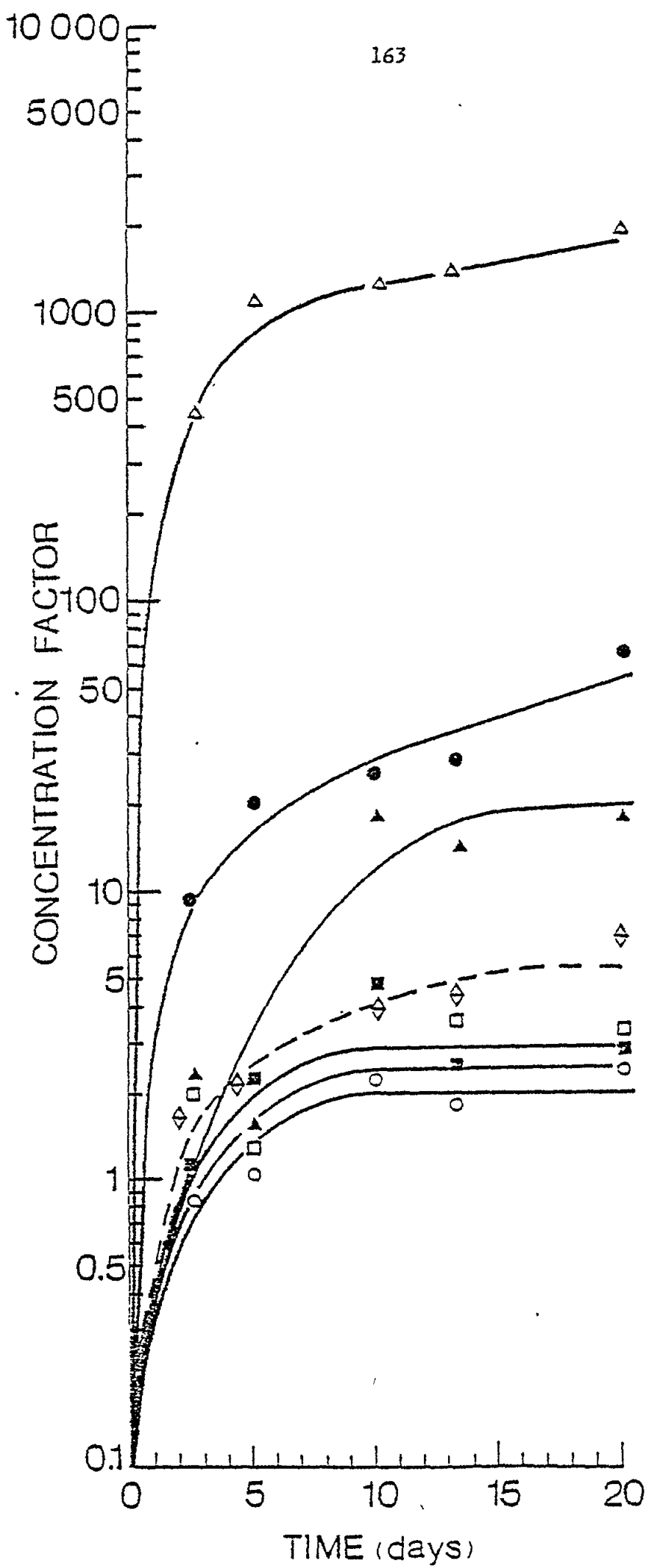


Fig. IV

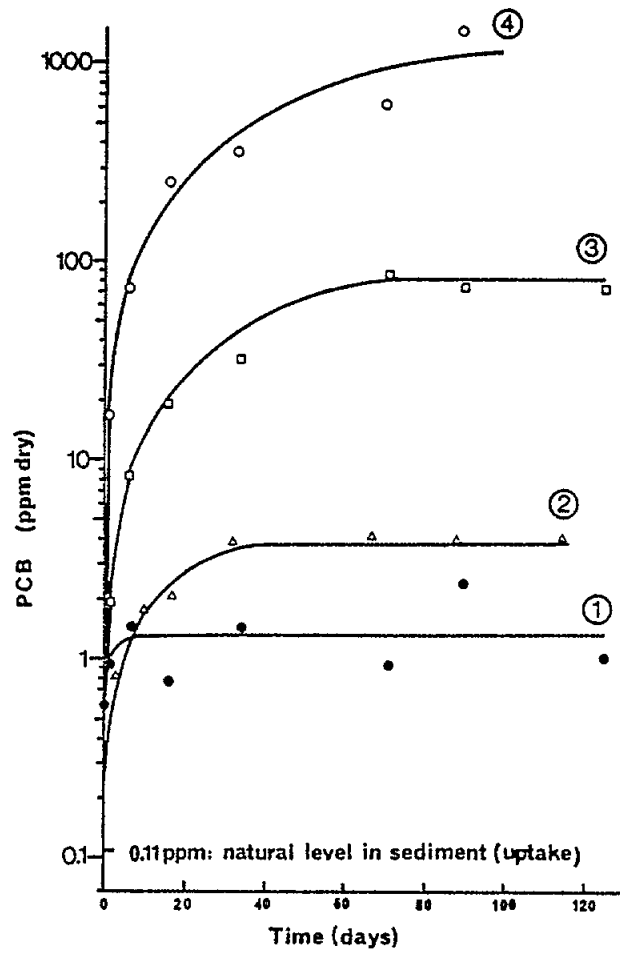


Fig. V

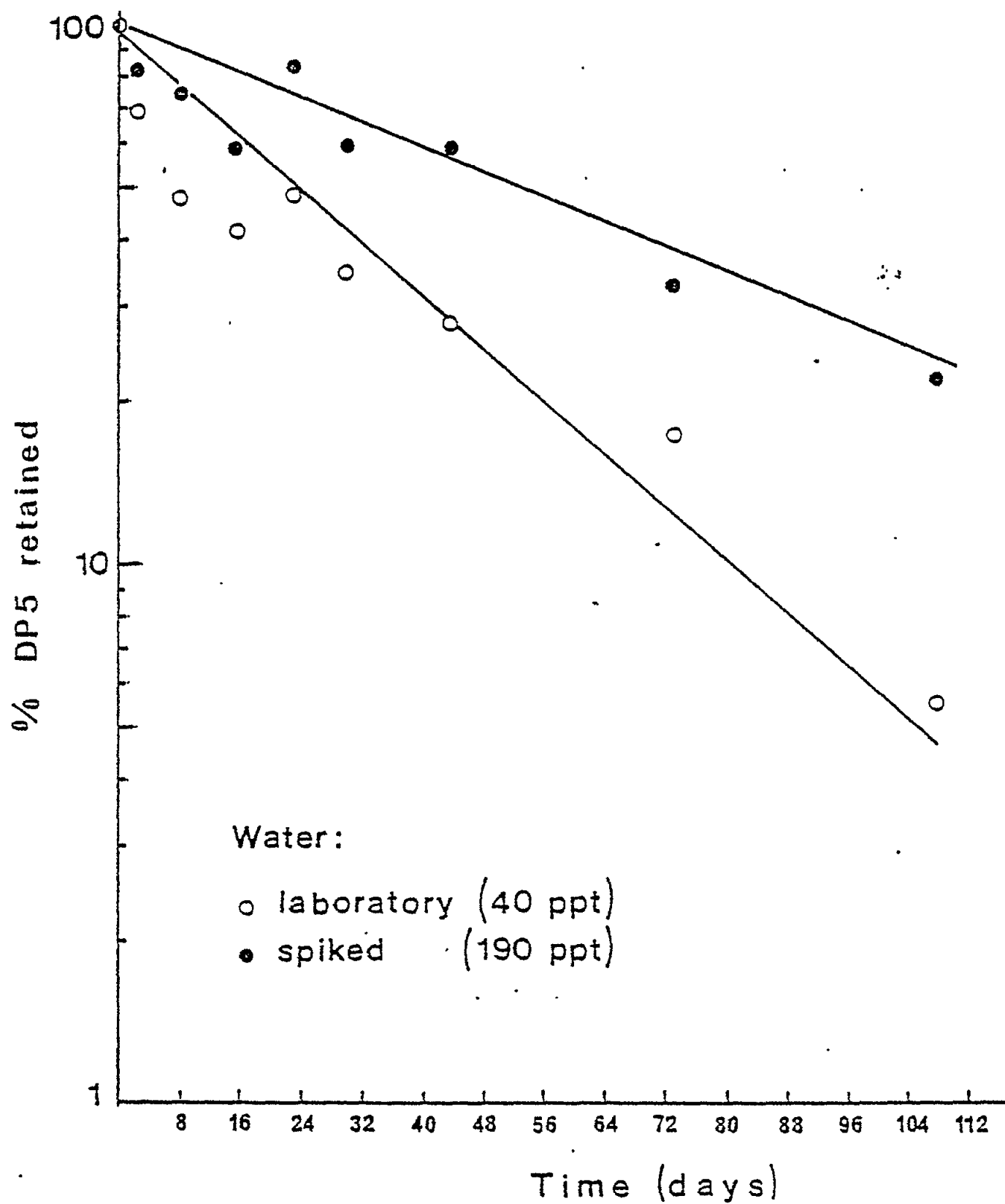


Fig. VI

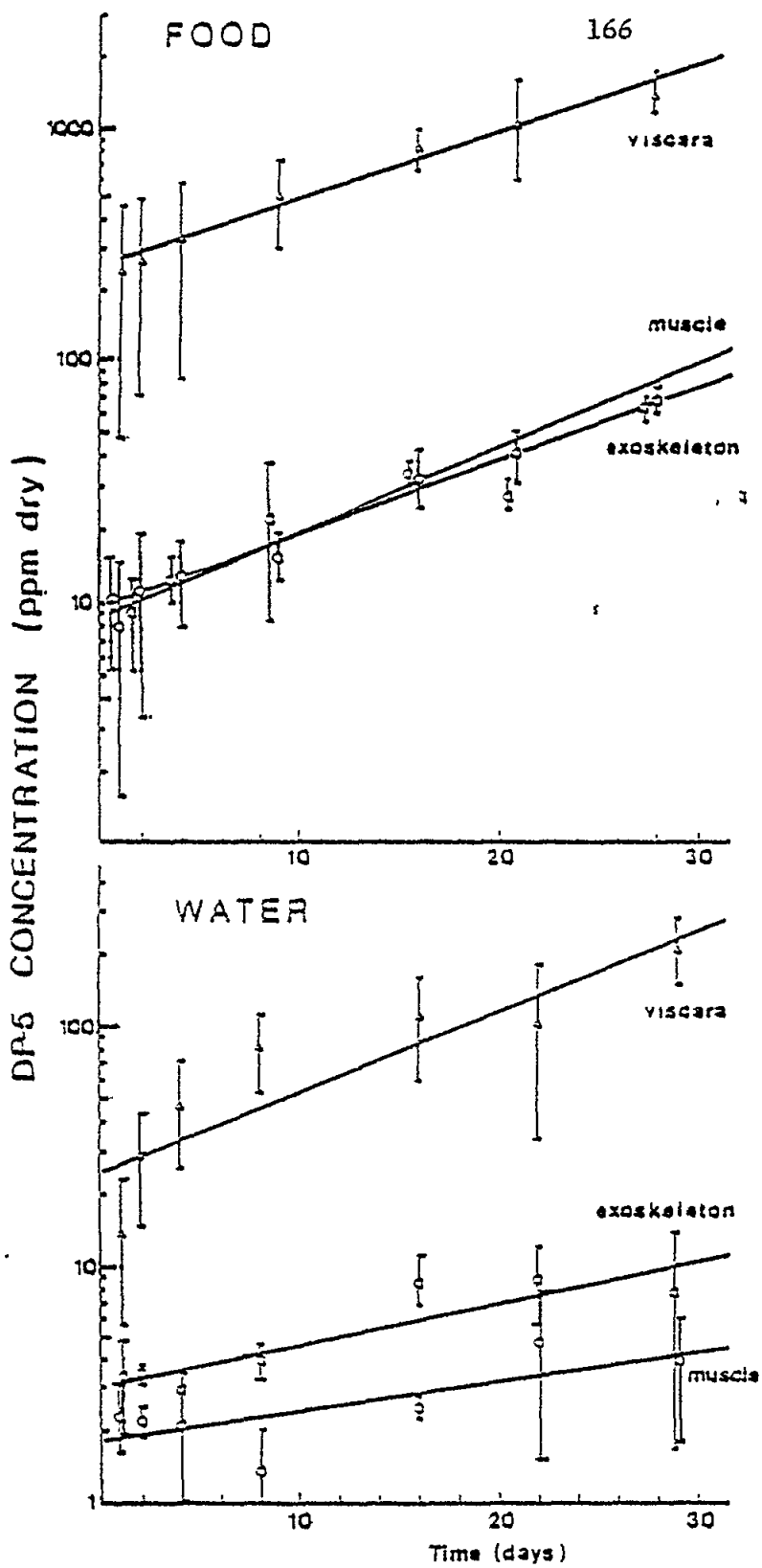


Fig. VII