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Assessment of the state of pollution of the Mediterranean Sea by mercury and mercury compounds and proposed measures

In co-operation with:

FAO WHO

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BACKGROUND

One of the primary aims of the Coordinated Mediterranean Pollution Monitoring and Research Programme (MED POL Phase I), launched in 1975 following its adoption by the Coastal States of the region as the scientific component of the Mediterranean Action Plan at the Intergovernmental Meeting on the Protection of the Mediterranean Sea against Pollution (Barcelona, 28 January - 4 February 1975), was to compile the maximum possible amount of data on the quality of the Mediterranean marine environment. Within this framework, the pilot project on baseline studies and monitoring of metals, particularly mercury and cadmium, in marine organisms (MED POL II), jointly coordinated by FAO and UNEP and implemented from 1975 to 1980, was designed to commence investigations on the concentrations of these metals in selected marine organisms on a regional basis. The eventual evaluation of data collected was also designed to provide an input on which to base the formulation of recommended control measures, including selected environmental quality criteria applicable to the Mediterranean Sea.

Article 5 of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources, adopted at the Conference of Plenipotentiaries of the Coastal States of the Mediterranean region for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources (Athens, 12-17 May 1980) stipulates (UNEP, 1980a) that:

a) The Parties undertake to eliminate pollution of the Protocol Area from land-based sources by substances listed in annex I to this Protocol.

b) To this end they shall elaborate and implement, jointly or individually, as appropriate, the necessary programmes and measures.

c) These programmes and measures shall include, in particular, common emission standards and standards for use.

d) The standards and the time-tables for the implementation of the programmes and measures aimed at eliminating pollution from land-based sources shall be fixed by the Parties and periodically reviewed, if necessary every two years, for each of the substances listed in annex I, in accordance with the provisions of article 15 of this Protocol.

Article 7 of the same Protocol stipulates that:

a) The Parties shall progressively formulate and adopt, in cooperation with the competent international organizations, common guidelines and, as appropriate, standards or criteria dealing in particular with:

the quality of seawater used for specific purposes that is necessary for the protection of human health, living resources and ecosystems

b) Without prejudice to the provisions of article 5 of this Protocol, such common guidelines, standards or criteria shall take into account local ecological, geographical and physical characteristics, the economic capacity of the Parties and their need for development, the level of existing pollution and the real absorptive capacity of the marine environment.

Even before final adoption and signature of the Protocol, the Intergovernmental Review Meeting of Mediterranean Coastal States and the First Meeting of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution and its related protocols (Geneva, 5-10 February 1979) recommended (UNEP, 1979) that:

> "Work should be continued on the development of the scientific rationale for the criteria applicable to the quality of recreational waters, shellfish-growing waters used for aquaculture, and seafood. Based on this rationale and taking into account existing agreements, the criteria should be formulated on a scientific basis and submitted to the Governments and the EEC for their consideration".

The Bureau of the Contracting Parties, at its first meeting in Geneva on 26 and 27 June 1979, also considered the matter and urged the Secretariat to develop environmental quality criteria for bathing waters and for mercury in seafood. Following this recommendation, interagency consultations were held in November/December 1979 on the design and implementation of a cooperation programme on health-related aspects of mercury levels in edible marine organisms. The problem of mercury was also comprehensively reviewed by WHO in a consultation meeting to re-examine the environmental health criteria for mercury, held in Geneva from 21 to 25 April 1980 (WHO, 1980). The UNEP/FAO/WHO Meeting of Experts on Environmental Quality Criteria for Mercury in Mediterranean Seafood, held in Geneva from 3 to 8 November 1980 (UNEP, 1980b), was also convened, in particular, to evaluate the hazards related to the intake of mercury from seafood by populations in the Mediterranean region and to develop recommendations on desirable environmental quality criteria for mercury in Mediterranean seafood.

During the course of MED POL Phase I, tentative environmental quality criteria for a selected number of parameters, including mercury in seafood, were proposed on a interim basis (UNEP, 1981a), pending the acquisition of more data on the situation regarding mercury concentrations in seafood, and, perhaps more important, the performance of epidemiological studies to correlate seafood quality with health effects.

In this context, the Second Meeting of the Contracting Parties, held in Cannes from 2 to 7 March 1981, approved the Long-term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL Phase II), including, under research and study topics, "Epidemiological studies related to the confirmation (or possible revision) of the proposed environmental quality criteria (standards of use) for bathing waters, shellfish-growing waters and edible marine organisms" as well as "Biogeochemical cycles of specific pollutants, particularly those relevant to human health" (including mercury) and "Development of sampling and analytical techniques for monitoring the sources and levels of pollutants" (UNEP, 1981b).

Within the framework of these activities, and as a natural continuation of the earlier studies, including the results and recommendations of the various expert meetings mentioned above, WHO, in cooperation with FAO and UNEP, developed a project on "Methylmercury in Mediterranean populations and related health hazards" as part of the appropriate activity within the research component of MED POL Phase II. This project was finalized at a consultation meeting held in Athens from 13 to 17 September 1982 (WHO/UNEP, 1982), and entered its initial operational phase in selected areas in Yugoslavia (1984), Greece (1985) and Italy (1985), following a second consultation meeting held in Zagreb from 17 to 21 September 1984 (WHO/FAO/UNEP, 1984), during which institutional participation and modalities were agreed upon. Results obtained were reviewed at a third consultation meeting held in Athens from 15 to 19 September 1986 (WHO/FAO/UNEP, 1986).

A document on "Assessment of the present state of pollution by mercury in the Mediterranean sea and proposed measures was prepared by FAO, WHO and UNEP in 1983 (UNEP/FAO/WHO, 1983). The scope of this document was to make a preliminary assessment of mercury pollution in the Mediterranean sea based on results obtained during the course of MED POL II, to outline the scientific rationale for criteria applicable to mercury in Mediterranean seafood based on the latest information available, both in general and within the region, and to propose measures for adoption by the Contracting Parties at their next meeting.

The main criterion recommended for adoption was the following:

"Seafood of Mediterranean origin is considered to present no hazard for consumption by the general population, provided that the Provisional Tolerable Weekly Intake (PTWI) established by the Joint FAO/WHO Expert Committee on Food Additives, of 300 ug of mercury, of which not more than 200 ug should be present as methyl mercury, for a person of 60 kg bodyweight is not exceeded. Compliance with this interim criterion shall be established on the basis of the concentration of mercury in relevant species of seafood sampled at quarterly (3-month) intervals and on seafood consumption patterns. The concentration of mercury should be determined by an agreed reference method, or by other methods yielding comparable results, proved by intercalibration with the relevant reference method. Consumption patterns shall be determined by agreed methods and protocols for those sectors of populations where either a high level of fish consumption is known or suspected, or where exposure to mercury from sources other than seafood is similarly known or suspected".

The recommendations were discussed by the Contracting Parties during their Extraordinary meeting in Athens from 10 to 13 april 1984 (UNEP, 1984) and their Fourth Ordinary meeting in Genoa from 9 to 13 September 1985 (UNEP, 1985a). The final recommendation approved by the Contracting Parties on interim environmental quality criteria for mercury at the latter meeting was as follows:

1) According to the available evidence to date, on the basis of present concentrations of mercury in Mediterranean seafood it appears that the consumption of seafood by the general population does not present any risk.

2) It is considered therefore that, at this stage, the adoption of upper limits for mercury concentrations in seafood on a common regional basis would not be a priori justified.

3) On the basis of the assessment of the quality of Mediterranean seafood with regard to its mercury content prepared by FAO/UNEP, the Contracting Parties:

   a) Take note of the interim criterion proposed by the joint FAO/WHO Committee of Experts on food additives. According to this criterion, the Provisional Tolerable Weekly Intake of 0.3 mg of mercury, of which not more than 0.2 mg is methyl mercury, for a person of 60 kg bodyweight, should not be exceeded;

   b) Take into consideration this criterion to establish, if national circumstances so require, standards for maximum concentrations of mercury in seafood;

c) Use for the determination of total mercury the Reference Method "Determination of Total Mercury in Selected Marine Organisms by Cold Vapour Atomic Absorption Spectrophotometry" (Reference Methods for Marine Pollution Studies No. 8/Rev. 1, UNEP/FAO/IAEA, 1984) and for the determination of methyl mercury in marine organisms, the Reference Method "Determination of Methylmercury in Selected Marine Organisms by Gas Chromatography" (Reference Methods No. 13, UNEP/FAO/IAEA, 1984). However, other methods giving comparable results could also be used;

d) Include, to the extent possible, in their National Monitoring Programmes, the sampling and analysis of species of seafood, known to accumulate mercury, in addition to those already monitored in the framework of MED POL - PHASE II;

e) Limit anthropogenic discharges of mercury into the Mediterranean Sea pending the eventual formulation of emission standards for mercury, as a result of the entry into force of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources, and in terms of article 5 of that Protocol, commence as early as possible, the elaboration of the necessary programmes and measures with respect to mercury;

f) Provide the Secretariat to the Convention with the fullest information possible on:

- present legislation and administrative measures on existing national criteria for levels of mercury in seafood;
- measures taken on b), c), d) and e);
- relevant monitoring data on d) above;

g) Continue to carry out the monitoring and research component of MED POL PHASE II relevant to the assessment of mercury content of Mediterranean seafood, and the risks affecting all sectors of the population arising from seafood consumption, in particular:

- identification of population groups at risk;
- surveys on seafood consumption patterns among such populations;
- surveys on mercury levels in affected population groups;
- epidemiological studies to obtain the necessary information on the relationship between mercury intake and health effects;
- studies of the relationship between total mercury and methylmercury content of seafood, and the effects of cooking on such content;
- studies on biogeochemical cycles of mercury in the Mediterranean;
- studies on the effects of selenium in decreasing mercury toxicity.

In compliance with the terms of sub-para 3 (e) above, and following approval of a programme of activities by a meeting of experts on the technical implementation of the Protocol for the Protection of the Mediterranean sea against Pollution from Land-based Sources, held in Athens from 9 to 13 September 1985 (UNEP, 1985 b), the present document has been prepared.

INTRODUCTION

The present document presents an updated picture of the state of pollution in the Mediterranean by mercury and mercury compounds, outlines the scientific rationale for establishing controls and measures and recommends measures to be adopted by the Contracting Parties.

Chapter I, which deals with the assessment of the state of pollution, provides information on the inputs in the Mediterranean and describes the nature and distribution of natural and anthropogenic sources. It also reviews the available data on levels in the various compartments of the environment (seawater, sediments, biota, etc), giving emphasis on those for marine organisms. In addition, it describes various processes taking place such as methylation of inorganic mercury, uptake and release of mercury, mercury/selenium relationship, etc. It also provides information on areas influenced by mercury sources. The chapter is concluded by the effects of mercury on marine organisms and communities as well as man.

Chapter II includes information on existing national and international controls and measures for the prevention of pollution by mercury. It also outlines the scientific rationale for the establishment of environmental quality criteria and controls and measures. As a consequence certain measures are recommended to the Contracting Parties for adoption.

I. ASSESSMENT OF MERCURY POLLUTION

1. General facts on mercury and mercury compounds relevant to the marine environment and human health

Mercury, atomic weight 200.61, belongs to group IIB of the Periodic Table together with zinc and cadmium. Air in equilibrium with metallic mercury contains 5.5 mg Hg m^{-3} at 10 ^{o}C and 13.2 mg Hg m^{-3} at 20 ^{o}C. Such high levels are never found in the atmosphere and, therefore, mercury in droplet form cannot occur in the environment (Matheson, 1979). Under equilibrium conditions the air over inorganic mercury salts can reach considerable concentrations. At equilibrium, mercuric sulphide reaches 100 ng Hg m^{-3} in dry air and 5000 ng Hg m^{-3} when the relative humidity is close to 100%. Over mercuric oxide, dry air contains 2000 ng Hg m^{-3}, and over methyl mercury chloride solutions (0.04 to 0.08%) the air concentrations range from 140,000 to 900,000 ng Hg m^{-3} (Matheson, 1979).

Knowledge of the chemical forms or species of inorganic mercury in natural waters is largely due to thermodynamic calculations which predict that in practical terms mercury (I) does not exist. Redox conditions determine the valency state. Mercuric (Hg(II)) species will predominate in well-aerated, oxygen-containing waters (Eh $\sim$ 0.5 V). Hg^{o} will be the main species under mildly oxidizing or reducing conditions, unless hydrosulfide or sulfide complexes of Hg(II) are stabilized by the presence of sulfide (Benes and Havlik, 1979). In sulfidic marine waters, in interstitial water of sediments and in waste waters, sulfidic complexes are to be expected. Mercury (II)sulphide, cinnabar, has a very low solubility (solubility product: 10^{-53} M, Hg(II) forms covalent bonds and is strongly coordinated with -SH ligands of biological molecules, especially proteins.

The emphasis on methyl mercury (MeHg) in the biogeochemical cycle has most probably distracted the attention from the fact that dissolved methyl mercury is not the dominant form of organic mercury in natural waters. CH_3Hg^+ occurs in aqueous solutions as an aquo complex $CH_3-Hg-OH_2^+$ with a covalent bond between mercury and oxygen. The cation behaves as a soft acid and has a strong preference for the addition of only one ligand. CH_3Hg^+ undergoes rapid coordination reactions with sulphur, phosphorus, oxygen, nitrogen, halogens, and carbon. The rate of the formation of Cl-, Br-, and OH- complexes is extremely fast and is diffusion-controlled (Stumm and Morgan, 1981). Methyl mercury, like Hg(II), forms strong bonds with sulfur, and it is very likely that all MeHg in biota is bound to the sulfhydryl groups of proteins. The organomercury-sulfide bond is, however, much less stable than the Hg-S bond and can be easily cleaved in acid solutions of pH 1. This is used to liberate methyl mercury from biological tissues prior to its analytical determination.

The CH_3Hg^+ unit itself is kinetically remarkably inert toward decomposition. Therefore, methyl mercury compounds once formed are not readily demethylated. The neutral species formed with CH_3Hg^+ are hydrophilic and lipophilic; thus they can readily pass through biological and non-biological boundaries. This, together with their broad tendency to form stable complexes quickly and the robustness of the CH_3Hg^+ unit characterizes some of the toxicological properties of methyl mercury (Stumm and Morgan, 1981).

The schemes proposed for the biogeochemical cycle of mercury show the dissolved inorganic and organic mercury as ions but in the actual environment the mercury species are associated with various ligands. In fact, Andren and Harriss (1975) observed that the dissolved mercury is associated with dissolved organic matter in water samples from the Mississippi Delta and the Florida Everglades. 46 to 82% of the total dissolved mercury was associated with fulvic matter type ligands of a molecular size fraction of less than 500 and about 8 to 16% was associated with four greater molecular size fractions. In less saline water (Salinity: S =4) of the Everglades, with a higher load of dissolved organic matter, 38% of the dissolved mercury was associated with molecular size fraction of less than 500. Also Wallace (1982) found that 4 to 50% of the total mercury in coastal seawater were associated with surface-active dissolved or colloidal organic matter isolated from the water column of a controlled experimental system. More recently Suzuki and Sugimura (1985) found that the mercury in seawater was associated with organic matter of a molecular size of 9000.

2. Sources and inputs into the Mediterranean

The mercury concentrations in various compartments of the Mediterranean are derived both from natural and anthropogenic sources. Both sources have not been covered comprehensively because only few sources have received scientific attention and others have been detected during surveys, which however, do not cover the entire Mediterranean but only certain parts. The data available are, therefore, only partial and their identification depend on more sporadic observations than systematic surveys. French rivers in the Rhone basin had water concentrations ranging from L1 ug Hg l^{-1} to 4 ug Hg l^{-1} (Agence de Bassin Rhone, 1983).

2.1. Natural sources and their geographical distribution

Natural sources are mercury ores, soils, degassing of the earth's crust and the oceans, and emissions from volcanoes.

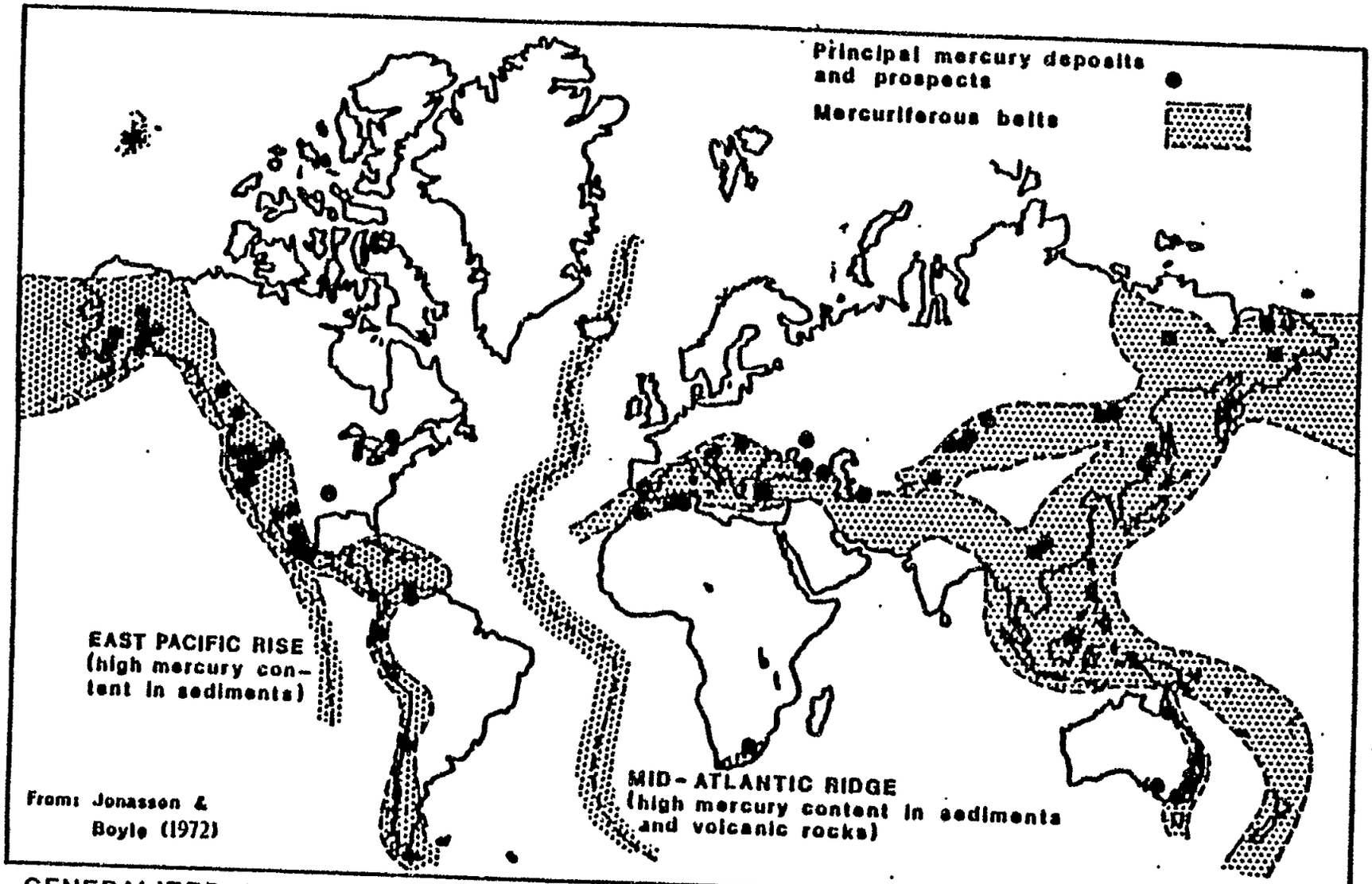
Mercury occurs naturally in the environment and is concentrated in geographic belts. Mercury deposits belong to one of the two Tertiary or Quaternary orogenic and volcanic belts: the Circumpacific and the Mediterranean-Himalayan belt (Fig.1). A more detailed figure of past and present mines of the Mediterranean shows the wide distribution of mercury in the Mediterranean basin (Fig.2). Published detailed surveys are rare but no doubt the mining companies possess extensive data from the prospecting for possible mercury mining sites. In addition, mercury concentrations higher than background, but too low for mining, may occur in many parts of the Mediterranean. Although a systematic survey of mercury levels in the Mediterranean has not been carried out, it is estimated that 65% of the world's mercury resources are located in the Mediterranean basin which occupies only 1% of the earth's surface (Table I).

A rough comparison of the watershed of the Mediterranean basin (Fig.3) and the locations of the mining areas (representing the mercury anomalies) shows that only the Almaden in Spain does not drain into the Mediterranean and the Konya in Turkey only partially (Fig.11). Their great influence on the mercury levels in sediments and biota for two areas (Mt. Amiata and Idrija) is discussed (section 3.8). For the other areas no data are as yet available, but an influence on the mercury concentrations in the adjacent marine environment can be foreseen and sediment concentrations should be checked.

The high volatility of many mercury species suggests that the atmospheric pathway is important in the biogeochemical cycle of mercury. Unfortunately no degassing rates over land or sea have been determined in the Mediterranean basin, and, therefore, to obtain at least some idea of the phenomenon, data from non-Mediterranean regions must be considered.

The major natural sources of atmospheric mercury are land and ocean degassing. Although a precise quantification is difficult, the following global values have been suggested by Matheson (1979): land degassing 17,800 t/year, open ocean degassing 7,600 t/year, coastal water degassing 1,400 t/year and volcanic activity 20 t/year. This estimate of emissions totals 26,820 t/year, which is higher than the 18,500 t/year quoted by Miller and Buchanan (1979). There is obviously considerable uncertainty attached to these estimates, particularly in accounting for recycling and in extrapolating to the global totals.

McCarthy *et al.* (1969) considered that mercury levels in soil concentrations were less important than in the underlying mineral deposits. He found degassing rates ranging from 0.64 ug Hg m^{-2} day^{-1} in areas



GENERALIZED MAP SHOWING THE MERCURIFEROUS BELTS OF THE EARTH.

Figure 1. The mercuriferous belts of the earth (Australian Working Group, 1980).

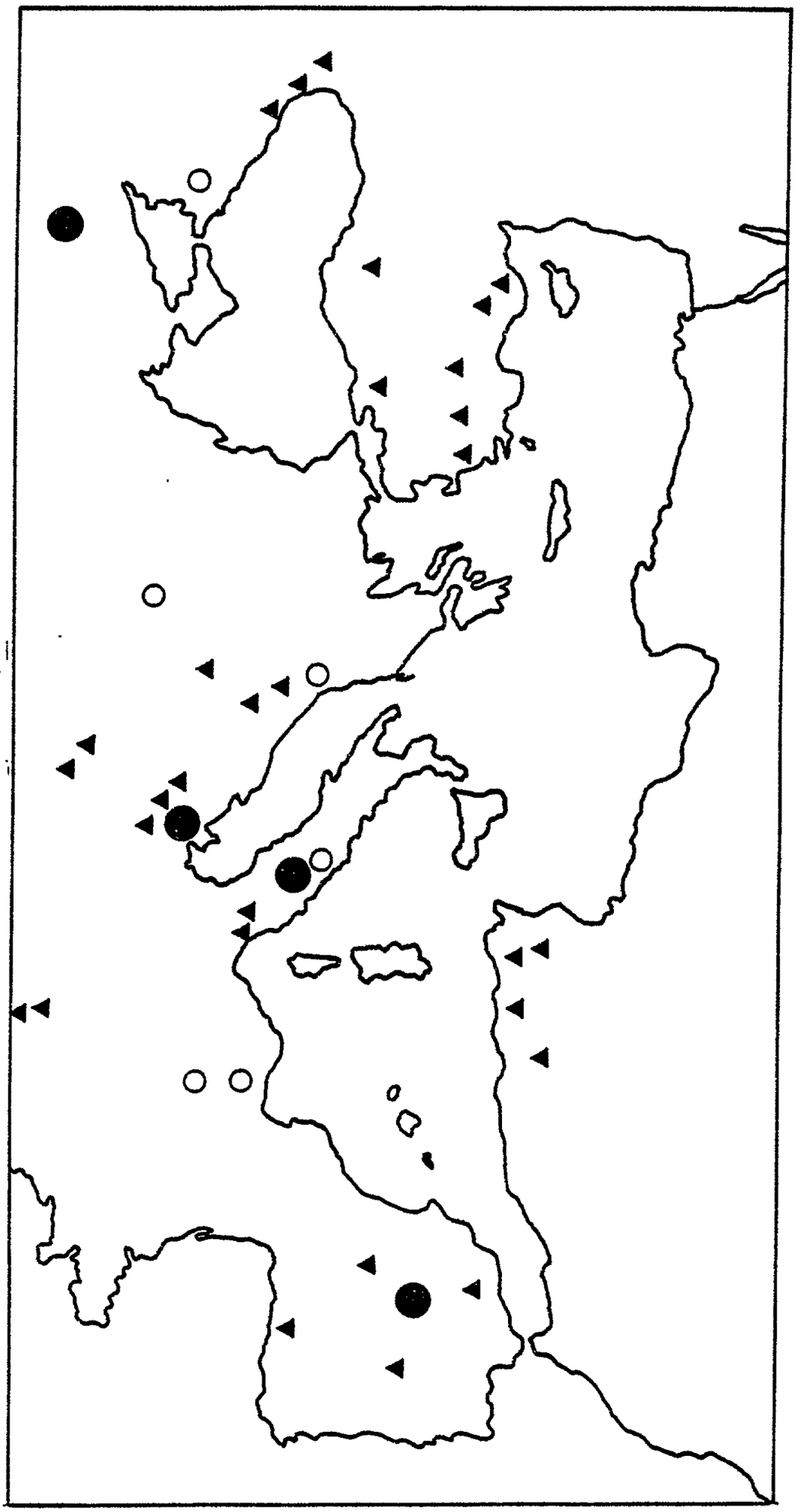


Figure 2. Locations of active and inactive mercury mines in the Mediterranean (courtesy Mt. Amiata Mining Company).
- ● very productive mines
- ▲ previously productive mines
- o presence of mercury

Table I
Reasonable assured mercury resources and yearly production of mercury in 1975
(Bernhard and Renzoni, 1977)

	Production (metric tons)	Reserves	ore grades (in %)
Mediterranean:			
Spain	1,622	87,000	1 -2
Italy	1,048 (*)	21,000	0.5-0.8
Yugoslavia	584	20,000	0.2-0.9
Algeria	458	?	?
Turkey	300	?	?
Tunisia	?	?	?
	>4,012	>128,000	
Total world	8,585	215,000	
Mediterranean in % of world	47	65	

(*) the Italian production was discontinued in 1978 because mining is no longer profitable.

without underlying mineral deposits to about 42 ug Hg m^{-2} day^{-1} over cinnabar veins. The author determined the mercury increase in oceanic air moving over 100 km of land and estimated the degassing rate of the soil around San Francisco to be about 4 ug Hg m^{-2} day^{-1}. Considering that this soil contained about 5 times more mercury than the average soil the degassing rate for the US continent was estimated at 0.8 ug Hg m^{-2} day^{-1}. Later this estimate was lowered to 0.3 ug m^{-2} day^{-1} (US EPA, 1975).

The natural mantle degassing processes emit elemental mercury vapour for the greater part. Methyl mercury is thought to have mainly biological origin (section 4.1).

Mercury emitted from volcanoes is a special source. Investigating with INAA (instrumental nuclear activitation analysis) the emission of atmospheric particulate matter collected on Whatman 41 filter paper from the Etna, Buat-Menard and Arnold (1978) found a geometric mean of 0.25 ug Hg-T m^{-3} for three samples in the main plume (about 5 ^{o}C) and a geometric mean of 0.5 ug Hg-T m^{-3} in three samples taken from hot vents (greater than 300 ^{o}C).

Lindqvist et al. (1984) estimated that the total global deposition of mercury lies between 4 and 30 ug Hg-T km^{-2} $year^{-1}$. Buat-Menard and Arnold (1978) and Arnold et al. (1983) made estimates for the Western Mediterranean: 50 ug Hg-T m^{-2} $year^{-1}$ (flux of particle deposition: 1 cm sec^{-1}). According to these authors the higher values from the Mediterranean are mainly due to higher introduction in the atmosphere from the industrial sources of Western Europe and, to a lesser extent, inputs into the atmosphere from volcanic activities. The possible higher degassing rates from the westerly situated geochemical anomalies (Almaden and surroundings) have not been considered by these authors.

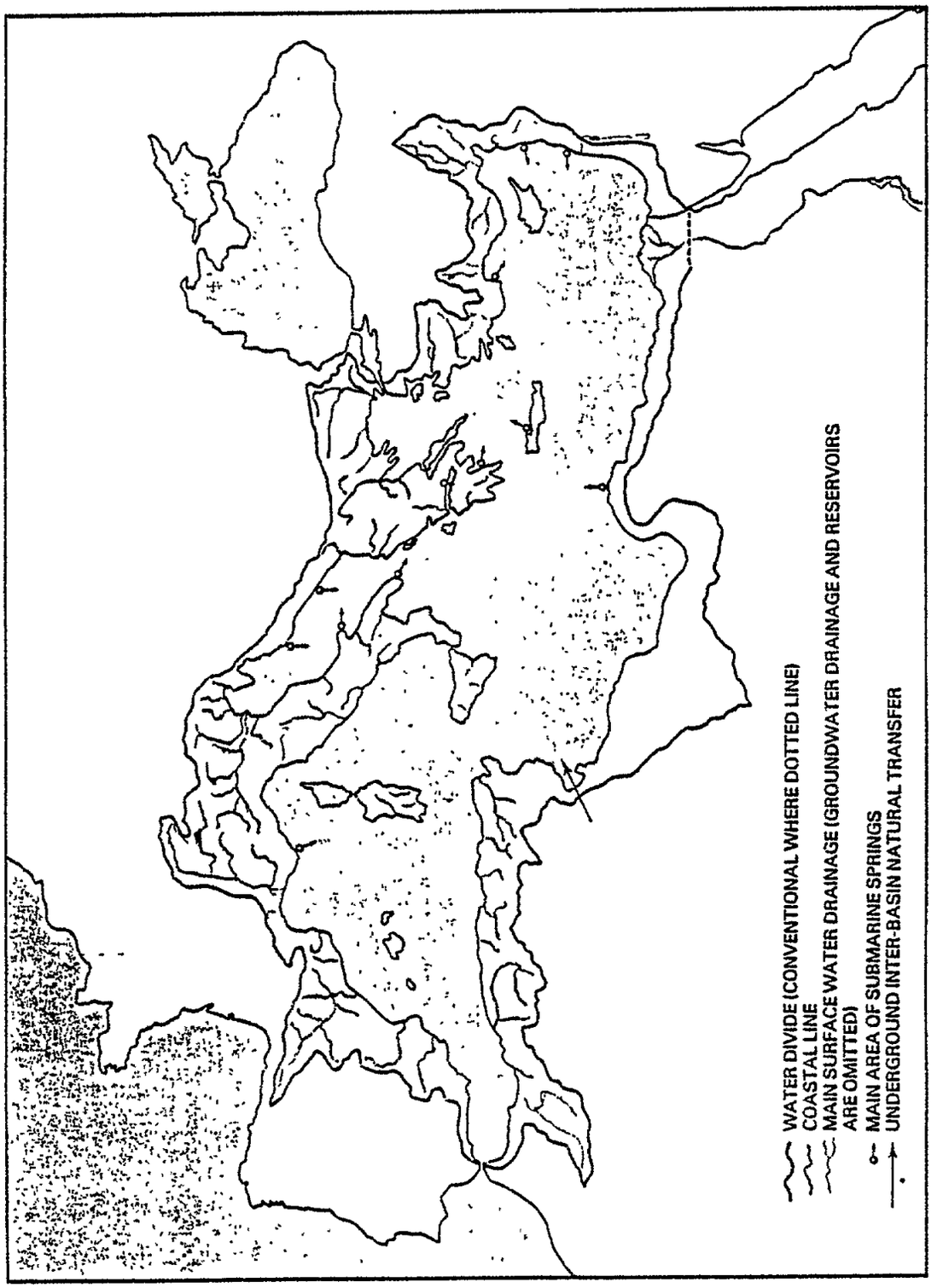


Figure 3. Conventional watershed of the Mediterranean (Ambroggi, 1977). The freshwater drainage area is about 1.8 million km^2 including only 30,000 km^2 of the Nile delta out of the 2.7 million km^2 of the Nile River basin.

The data on mercury levels in air over land and sea (section 3.2) are consistent with the hypothesis that the major source of atmospheric mercury is continental (Fitzgerald et al., 1983). The mercury is principally emitted into the air in the gas phase and probably mainly as elemental mercury and organo-mercury species, but perhaps also in other forms. Anthropogenic but also natural sources can considerably modify the relative abundance of different species, especially on a local scale. Over open ocean areas the air contains mainly inorganic mercury which most probably is mainly Hg^{o}. The particulate fraction is about 100 to 1000 times smaller than the gaseous mercury and lies in the range of 0.4 to 2 pg Hg m^{-3}.

Finally, it should be noted that Ferrara et al. (1982) concluded from their observations on mercury concentrations in air and rainwater that the Mt. Amiata mercury anomaly has only a very limited influence on the biogeochemical cycle of mercury in the Mediterranean (section 3.2). Clearly, more data are needed to enable us to estimate the contribution of natural degassing fluxes and industrial inputs.

2.2. Nature and geographic distribution of anthropogenic sources

Anthropogenic sources are numerous and have been reviewed by Nriagu (1979). The mining activities in the Mediterranean countries are shown in Table I. In 1970, Italy exported 35% of its production, Spain 95% and Yugoslavia 90% (Nriagu, 1979) showing that the mercury is not necessary dispersed in the country of production.

Mining wastes originate in the various mining areas (Fig.2) and the high mercury concentrations in some of the rivers in the Mt. Amiata area and in the Isonzo are caused by the discharge of these wastes. The high mercury levels in sediments in rivers not serving directly the mining outfalls must, however, be due to natural weathering processes.

The main anthropogenic sources of importance for the marine environment are:

a) river runoff carrying anthropogenic wastes discharge into the river system,

b) waste discharges directly into the marine environment, either as discharges as liquid effluents or through dumping (e.g. solid wastes, sewage sludge), and

c) atmospheric inputs of anthropogenic origin

In the framework of MED POL-Phase I, an assessment of the total pollution inputs from land-based sources was attempted (project MED POL X, UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984) which included also very approximate estimates on the mercury input from various sources (Table II). It must be pointed out however, that in many cases it was necessary, because of lack of data, to make extrapolations based on a very small and unevenly distributed data base. Therefore, the estimates may not even be correct in their orders of magnitude. More data are urgently needed and since it has been shown that even large anthropogenic sources have only a limited influence (section 3.9), future data should be presented on a local basis rather than for the whole Mediterranean or large areas. MED POL X is now repeated to collect more recent and accurate data.

Examples of anthropogenic releases from chlor-alkali plants, petrochemical plants and from sewage outfalls which raised sediment concentrations are discussed in section 3.4 and 3.9. Chlor-alkali plants have been studied in Italy, Yugoslavia, Israel and Egypt. Details on some discharges are discussed in section 3.9. Similar sources exist certainly in other areas and especially all major sewage outfalls are potential sources for mercury. The sewage outfall of Naples at Cuma, where no mercury build-up in the adjacent sediment was observed, can be considered an exception. Sewage sludge can contain high amounts of mercury (5 to 30 mg Hg-T kg^{-1} DW) with low amounts of methyl mercury; less than 1% (Van Faassen, 1975). The dumping of these sludges can, therefore, be easily responsible for high mercury levels in coastal sediments for which no apparent land-based source can be held responsible.

Atmospheric emissions from anthropogenic sources are less than those from natural sources; reported ratios vary between 1 to 4 and 1 to 30 (Miller and Buchanan, 1979). However, on a local basis anthropogenic emissions can certainly be of considerably greater significance than natural emissions (see Lindqvist et al., 1984).

The contribution of anthropogenic atmospheric inputs into the Western Mediterranean are discussed in section 2.1 and examples of atmospheric emissions in section 3.2.

Table II
Estimates on inputs of mercury in the Mediterranean
(UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984)

Region	Originating in coastal zones				carried by		
	domestic		industrial		rivers		total
	t/year	% total	t/year	% total	t/year	% total	t/year
I	0.04	2	0.6	24	1.8	74	2.5
II	0.28	1	2.7	8	30	91	33
III	0.04	1	0.2	7	2.5	92	2.7
IV	0.12	1	1.1	10	9.5	89	10.7
V	0.08	>0	0.5	1	40	99	41
VI	0.03	>0	0.16	2	9.6	98	9.8
VII	0.03	2	0.16	9	1.5	88	1.7
VIII	0.05	>0	0.2	2	14	98	14.3
IX	0.01	>0	0.05	1	7	99	7.1
X	0.07	1	1.2	17	5.6	82	6.9
Total	0.75	0.6	6.87	5.4	121.5*	94	129.7

* in this amount 32 metric tons were considered as "background"
The Mediterranean regions are shown in Fig.11

3. Levels in the Mediterranean

3.1. Data quality and intercalibration

One of the major problems encountered in the determination of mercury levels in air, sea water, sediment and biota is the uncertainty in the accuracy and precision of chemical measurements (quality control). While the uncertainty of precision can be overcome by analysing an adequate number of subsamples of the original sample, the determination of accuracy presents a formidable problem, especially since it is not sufficient to determine accurately the total amounts of mercury in samples of various matrices but, more important, the exact amount of different key species of mercury.

Recognizing that insufficient analytical quality control may jeopardize the success of the MED POL projects, FAO/UNEP accepted the recommendation of the 1975 Expert Consultation to sponsor an analytical quality control programme (MED POL XI "Intercalibration of analytical techniques and common maintenance service") in collaboration with the IAEA's International Laboratory for Marine Radioactivity at Monaco (FAO/UNEP, 1975). ILMR prepares and distributes sediment samples and samples prepared from various marine organisms for intercalibration exercises (e.g Fukai et al. 1978; IAEA, 1978, 1985). Certified reference standards (US National Bureau of Standards (NBS) and reference samples from the European Economic Community (EEC) were also used by workers from the Mediterranean area. Unfortunately, no standard or reference material exists for methyl mercury. Also there are no intercalibration standards which could be used for mercury analysis at the low levels found in sea water, rainwater and air. The two Canadian sea-water references (Marine Analytical Chemistry Standards Programme, National Research Council of Canada, Ottawa) do not report data for mercury. This is regrettable since, due to the extremely low mercury concentrations in sea water, rainwater and air, the uncertainty of the data available is very high (see also discussion in section 3.3).

Intercalibration has two important aspects: participation increases the confidence in the analytical data published and it also improves the analytical technique used, since very often errors in the analytical procedures can only be detected through a participation in an intercalibration or a comparison with a certified standard. Topping (1983) describes the experiences gained during several intercalibration exercises in the framework of the ICES monitoring programmes. The distribution of standard metal solutions revealed that some analysts used wrong working standards. Adjusting for these differences in standards reduced the range of submitted means of the intercalibration samples. Comparing the range of means submitted by laboratories which had participated in the first three exercises showed a decrease of the interlaboratory coefficient of variation (CV) from 35 to 5%. Lower levels of mercury in the two samples of the fourth intercalibration again increased, however, the CV to 33 and 50%. The International Laboratory of Marine Radioactivity (Monaco) distributed several biological intercalibrations samples in the framework of the MED POL programme. The CV in the different matrices ranged from 4 to 40% (Fukai et al., 1978; IAEA, 1978, 1980, 1985).

3.2. Air

When evaluating mercury concentrations in air, the different behaviour of the various mercury species must be taken into consideration. Although soluble and particulate mercury usually account for less than 1% of the total mercury (Fitzgerald et al., 1983) these two mercury species are mainly

responsible for the transport of mercury from the atmosphere to the earth's surface. Particles are easily washed out by rain or - to a lesser extent - scavenged by dry deposition. Often reference is made to "marine aerosol". This term is defined by Buat-Menard (1983) as: a variable mixture of all classes of particles (0.1 um to 50 um in diameter) found in the marine atmosphere consisting of modified marine and continental source materials.

The number of mercury determinations in Mediterranean air are limited and come mostly from Tuscany and the Ligurian coast. Breder et al. (1983) and Breder and Flucht (1984) (a smaller subset of the same data are also mentioned in Ferrara et al., 1983) compare mercury concentrations in air taken at ground level and on board a zeppelin a few hundred metres above the ground from different locations in Italy (Table III). They collected the mercury present in air on small-diameter gold wire eliminating particulate matter with a 0.45 um pore size filter. The "gaseous Hg" determined by these authors is, therefore, operationally defined. This procedure has shown good collecting efficiency for non-particulate mercury species such as gaseous elemental mercury, methyl mercury, dimethyl mercury, and mercuric chloride (Braman and Johnson, 1974; Seiler et al., 1980).

From Table III it is evident that near the Tuscan coast the air has lower mercury concentrations than in rural areas in Tuscany and much lower levels are observed in "normal rural areas" than in the rural areas of the Monte Amiata Hg anomaly. Examples of more detailed measurements are given in Breder and Flucht (1984). Anthropogenic influences are shown in urban areas and near the Solvay chlor-alkali plant. The extremely high value of 1244 ng Hg m^{-3} observed over Genoa during the 1980 airship cruise could not be Diano Marina to Genoa were repeated on 15 October 1980 during rain. This reduced the mean levels from 3.7 ng Hg m^{-3} to 2.4 ng Hg m^{-3}. In Table III the overall mean is given, but it was not possible to reconstruct the data, so, where possible, the means of Table III were calculated from the data given by Breder and Flucht (1984). The other means were cited directly from Breder and Flucht (1984). Breder et al. (1983) found, however, that the high levels of the Solvay plant were very localized. Background levels were already restored 4 to 5 km from the plant. Revisiting the site in 1981 showed the mercury distribution in more detail. Levels from Florence to the Solvay plant were significantly higher than levels from other areas. High levels (430 ng m^{-3}) were observed in air collected from the exhaust of the ventilation confirmed either on the ground or during the 1981 cruise (Breder and Flucht, 1984). The levels determined on 12 to 14 October 1980 over the sites from system of a cinnabar mine which had been closed two years prior to sampling. The authors were surprised to find that the mercury concentration in the air at a distance of only 200 metres from hot steam wells was reduced to one third of the concentration near the wells.

Also interesting are the levels found on Mont Blanc and Vesuvius. It may be worthwhile pointing out that two teams, Breder and collaborators and Ferrara and collaborators, have been collecting data in the Tuscan region, often on the same sites, hence there is some confirmation of the data obtained. Ferrara et al. (1982) also showed that the mercury concentration in urban areas may have a marked diurnal variation, not easily attributable to industrial activities. These authors also report 0.2 to 0.3 ng Hg m^{-3} in aerosol and rainwater (Table IV) from an urban area. Rainwater collected early in a storm had higher mercury levels than rainwater collected later in the storm because the early rain washes out particles and scavenges mercury.

Table III
"Gaseous mercury" (ng m^{-3}) in the atmosphere of different locations from NW Italy.
(Data from Breder et al., 1983 and Breder and Flucht, 1984)

	n	mean	range	
Tyrrhenian Sea (several km off coast)	200	2.1	0.9- 2.7	
Italian Riviera (more than 0.5 km off coast)	21	3.3	1.1- 9.9	STP
Ligurian beach (Fiascherino)	150	6.0		STP
Mont Blanc (3842 m)	5	5.9		STP
(2300 - 3400 m)	15	11		
Tuscany (rural area)	115	4.0	1.2- 6.3	
Mt. Amiata (Hg anomaly)	130	15.0	8.2-86.3	
Hg mine exhaust (Abbadia S. Salvatore)	5	480		
near hot steam wells	14	88		
200 m downwind of wells	?	15		
geothermal power plant (Larderello)	5	8.3		
Livorno (urban area)	300	10.1	2.2-31.5	
Genoa (urban area)	29	8.3	1.8-71.0	
Florence (urban area)	7	16.1	7.1-28.0	
La Spezia (urban area)	17	19.8		
Different sites, Tuscany	12	21.1		
Rosignano Solvay chlor-alkali plant				
ground level	67	22.1	12.1-35.5	
250 m above plant	6	22.5	20.0-26.5	
150 m above chimney	2	73.2		
Vesuvius	3	94		

STP: values corrected for standard pressure and temperature Note: a limited set of the same data is published in Ferrara et al. (1982). In Breder et al. (1983) and Breder and Flucht (1984) some data are the same, but it is not always possible to identify which are the identical ones.

Table IV
Mercury concentration (ng l^{-1}) in rainwater from an urban area (Ferrara et al., 1982)

	Particulate Hg-T		Dissolved Hg					
			Hg-T		reactive		organically assoc.	
	mean	range	mean	range	mean	range	mean	range
Early rain	41	(10 - 500)	25	(21 - 35)	11	(6 - 21)	14	(9 - 18)
Late rain	8	(4 - 12.5)	9.5	(6.6 - 14)	2.5	(1.5 - 4.5)	7.5	(3.5 - 11.5)

Shani and Haccoun (1976) compared air pollution in the city of Beer-Sheva (Israel) with an unpolluted desert area 40 km south of this city. The authors did not find any significant difference. The three measurements made ranged from 1.8 to 4 ng m^{-3}.

Particulate mercury levels are generally a few percent of the gaseous levels and, therefore, concentrations observed by Arnold et al. (1983) agree with the data from Ferrara et al. (1982), Breder et al. (1983) and Breder and Flucht (1984). In the course of two cruises Arnold et al. (1983) investigated the trace metal concentrations in marine aerosols. They found high enrichment factors (EF) similar to values observed in the North Atlantic (Table V). They attributed the high EF to anthropogenic inputs from countries bordering the northern Mediterranean. Natural degasing was not considered by these authors.

Table V

Mercury concentrations (ng m^{-3}) in aerosol in the Western Mediterranean (Phycemed 81), around Sicily (Etna 80) and in the North Atlantic (Arnold et al., 1983)
(EF: enrichment factor rel. to aluminium)

Etna 80		Phycemed 81		North Atlantic	
mean	EF	mean	EF	mean	EF
0.1	560	0.24	910	0.065	450

Note: $EF = \frac{\text{(element conc./Al conc.) in sample}}{\text{(element conc./Al conc.) in earth's crust}}$

3.3. Sea water

Total Hg (Hg-T) concentrations have been lowered continuously in recent years mainly because more attention has been given to sample contamination. Since methyl mercury predominates in marine organisms, it is the most important mercury species from the biological and health protection point of view. Unfortunately only very few methyl mercury data for sea water exist (Fujita and Iwashima, 1981; Egawa et al., 1982; Yamamoto et al., 1983). Their values range from 0.03 to 6% of the Hg-T present (Table VI). No methyl mercury data exist for the Mediterranean.

Several authors have determined "reactive mercury" i. e. the mercury which reacts with the reagents for flameless mercury determination (in general after the sea water sample has been acidified with HCl for conservation during storage). "Reactive Hg" represents those mercury species that are readily reducible with stannous chloride at the sample pH. These species include dissolved inorganic Hg species, labile organo-Hg associations and mercury that is readily leachable from any particulate matter present (Gill and Fitzgerald, 1985). Obviously, these data cannot be compared with the concentrations obtained with analytical procedures that determine Hg-T which include also stable organo-Hg associations and mercury in particulate matter. The mercury species in sea water are only operationally defined and more work on the actual species present in sea water are urgently needed.

Table VI

Selected mercury concentration (ng l^{-1}) in sea water from the Mediterranean and other regions

	n	mean	range	location	sampling depth	reference
Mediterranean						
open sea:						
Hg-T	3	92	62 - 110	Gibraltar	15 - 300	Robertson et al., 1972
Hg-T	47	10 M	5 - 17	NW Medit.	25 - 2500	Huynh-Ngoc & Fukai, 1979
Hg-Td	4	25	20 - 30	Tyrrhenian	0 - 5	Fukai & Huynh-Ngoc, 1976
Hg-Td	54	7.2	1.4 - 19.2	Tyrrhenian	0	Ferrara et al., 1986
Hg-T	2	120	90 - 140	Cyprus	15 - 300	Robertson et al., 1972
Hg-R	56		0.1 - 50	W-Mediter.	0 - 3000	Copin-Montegut et al., 1985
Hg-R	89	2	0.5 - 10	Ligurian	0 - 100	Copin-Montegut et al., 1986
Hg-Rd	46	2.9	0.5 - 5.9	Tyrrhenian	0	Ferrara et al., 1986
Hg-A	7	20	8 - 32	NW Medit.	0 - 5	Huynh-Ngoc & Fukai, 1979
Hg-A	46	10	3 - 23	NW Medit.	25 - 2500	Aston et al., 1986
Hg-A	10	26	10 - 40	Tyrrhenian	0 - 5	Huynh-Ngoc & Fukai, 1979
Hg-A	6	30	5 - 80	Ionian-Cent	0 - 5	Huynh-Ngoc & Fukai, 1979
Hg-A	3	40	15 - 80	Aegean	0 - 5	Huynh-Ngoc & Fukai, 1979
Hg-A	4	16	12 - 20	S. Levantine	0 - 5	Huynh-Ngoc & Fukai, 1979
Hg-P	41	2.3	0.3 - 8	Tyrrhenian	0	Ferrara et al., 1986
Hg-P	36	1.4	0.7 - 1.9	W-Ligurian	?	Buat-Menard et al., 1981
coastal areas:						
Hg-T	31	70	12 - 280(*)	Estuaries Tuscan riv.	0	Breder et al., 1981
Hg-T	19	2.25	1.4 - 5.6	N-Tyrr. coa.	0	Barghigiani et al., 1981
Hg-Td	24	6.3	1.4 - 8.0	Tyrrh. coast	0	Ferrara et al., 1986
Hg-Td		46		Tyrrh. coast		Alpha et al., 1982
Hg-Td		93		Ionian coast		Alpha et al., 1982
Hg-T		6.5		Ionian coast		Brondi et al., 1986
Hg-T	20	9.6	1.7 - 12.2	Tuscan coast	0	Seritti et al., 1982
Hg-R	46	1.5	0.5 - 9	Villefr. B.	?	Copin-Montegut et al., 1986
Hg-R	16	2.0	0.5 - 2.5	Tyrrh. coast	0	Ferrara et al., 1986
Hg-E	6	350 M	240 - 520	Thermaikos G.	0	Fytianos & Vasilikiotis, 1983
Hg-E	4	340 M	210 - 370	Kavala Gulf	0	
Hg-P	20	3	0.4 - 3.6	Tuscan coast	0	Seritti et al., 1982
Hg-P	13	3.4	1.5 - 8.0	Tyrrh. coast	0	Ferrara et al., 1986
Non-Mediterranean						
open sea:						
Hg-T	47	2.2	±1.0	N-Atlantic	0 - 1730	Olafson, 1983
Hg-T	?		2 - 8	Atlantic	0	Slemr et al., 1979
Hg-T	2		3.8 - 3.9	Japan Sea	0	Fujita and Iwashima, 1981
Hg-T	17	14	8 - 24	WN Pacific	0	Miyake and Suzuki, 1983
Hg-T	45		3.6 - 20.5	WN Pacific	0 - 6200	Miyake and Suzuki, 1983
Hg-T	56	5.8 ± 2.2		Bering Sea	0 - >500	Nishimura et al., 1983
Hg-T	139	5.6 ± 1.8		Pacific	0 - >500	Nishimura et al., 1983

Table VI (cont.)

	n	mean	range	location	sampling depth	reference
Hg-T	87	4.8 ± 1.6		Japan Sea	0 - >500	Nishimura et al., 1983
Hg-T	27	5.2 ± 1.9		E+S China S.	0 - >500	Nishimura et al., 1983
Hg-T	33	4.4 ± 2.2		Indian Ocean	0 - >500	Nishimura et al., 1983
Hg-R	73	1.5 ± 0.7		N-Atlantic	0 - 1730	Olafson, 1983
Hg-R	16	~ 1.0	0.4 - 2.0	NW-Atlantic	0 - 1000	Gill and Fitzgerald, 1985
Hg-R	81		0.9 - 6.2	North Sea	0	Baker, 1977
Hg-R		1.7 ± 0.7		S Iceland		Olafson, 1983
Hg-R	16	0.5	0.3 - 0.7	N-Atlan. st.	0 - 4750	Dalziel and Yeats, 1985
Hg-R	16	0.4	0.26- 0.7	Sargasso st.	0 - 2600	Dalziel and Yeats, 1985
Hg-R	24	4.1 ± 1.0		Gulf Stream	250- 4460	Mukherji and Kester, 1979
Hg-R		8 ± 4		Gulf Stream	0 - 750	Fitzgerald, 1975
Hg-R	13	~ 0.35	0.23- 0.4	N-Pacific	0 - 4000	Gill and Fitzgerald, 1985
Hg-R	?	0.5 ± 0.2		Hawai-Tahiti	0	Fitzgerald et al., 1983
Hg-R	52	5	3.9 - 5.6	Japan Sea	0 - 1200	Matsunaga et al., 1975
Hg-P	2		1.2 - 1.5	Japan Sea	0	Fujita and Iwashima, 1981
Hg-P	16	0.5 M	0.5 - 0.9	WN Pacific	0	Miyake and Suzuki, 1983
Hg-P	28		0.2 - 0.8	WN Pacific	0 - 6200	Miyake and Suzuki, 1983
Hg-Or	17	6.8 M	3.6 - 11	WN Pacific	0	Miyake and Suzuki, 1983
Hg-Or	45		1.7 - 9.1	WN Pacific	0 - 6200	Miyake and Suzuki, 1983
MeHg	5	0.3 M	0.1 - 0.9	Japan Sea	0	Fujita and Iwashima, 1981
MeHg-P	2		0.2 - 0.2	Japan Sea	0	Fujita and Iwashima, 1981
coastal areas:						
Hg-T	?	7.9	3.4 - 22	"UK seas"	0	Baker, 1977
Hg-T	15		0.07- 0.8	♯Puget Sound	0 - 5	Bloom and Crecelius, 1983
Hg-T	4	5.1	3.2 - 7.4	Suruga B.Jap	0	Fujita and Iwashima, 1981
Hg-T	3	12.4 M	6.3 - 16	Japan coast	0	Yamamoto et al., 1983
Hg-R	27		0.1 - 0.3	♯Puget Sound	0 - 5	Bloom and Creselius, 1983
Hg-P	5	2.3 M	1.8 - 11.4	Suruga B.Jap	0	Fujita and Iwashima, 1981
MeHg	5	0.2 M	0.2 - 0.4	Suruga B.Jap	0	Fujita and Iwashima, 1981
MeHg-P	5	0.3 M	0.2 - 0.3	Suruga B.Jap	0	Fujita and Iwashima, 1981
MeHg	3	0.1 M	0.04- 0.16	Japan coast	0	Yamamoto et al., 1983

Hg-T: total Hg
Hg-Td: total dissolved Hg (membrane filtered)
Hg-A: ASV, unfiltered at pH 2
Hg-E: ammonium pyrrolidine dithiocarbomate extracted with methyl-isobutyl-ketone
Hg-R: reactive Hg (in acidified sample ?)
Hg-P: particulate Hg (membrane filtered)
MeHg: methyl mercury
Hg-Or: organic mercury
M: median
(*) levels too high (Stoeppler 1984, pers. com.)
?: data unknown
♯: range of means
±: standard deviation

Data of mercury concentrations in sea water from the Mediterranean are few; the validity of many of the older data is doubtful and even for recent data it is not clear which mercury species or groups of mercury species have been determined. Furthermore, several different methods have been used for which it is not clear which fraction of the mercury species present in the sea water was determined. At present the fraction of the Hg-T determined by each analytical procedure can only be operationally defined. This makes it impossible to compare results obtained by different authors and it is also not clear if the same analytical procedure will determine the same fraction of mercury species in different water masses. Hence, the results are not comparable and the data published can only give an idea of the order of magnitude of the mercury concentrations determined. In Table VI an attempt has been made to characterize to some extent the "operational species" involved and to illustrate the analytical differences in the methods used.

It is now believed that the mercury concentrations in open sea will range from fractions of ng Hg-T l^{-1} to ng l^{-1} (Bruland, 1983). However, one should not be inclined to accept the lowest values as the more accurate. Not all "mercury methods" determine total amounts and mercury adsorbs easily to surfaces. In addition, many mercury species are highly volatile. Hence involuntary losses during sampling, storage (only in glass bottles) and analysis are just as likely to occur as additions caused by sample and reagent contamination, or during analysis in Hg-contaminated laboratories. The lack of a sea water standard at ng Hg l^{-1} levels allows no estimation on the accuracy of the data presented and makes a comparison of data from different authors practically impossible.

The seawater concentrations reported for the Mediterranean vary over a wide range (Table VI). The oldest data are from Robertson et al. (1972) and are much higher than the recent data. But also in recent data, the means for total mercury (Hg-T) of different authors range from 7 to 25 ng Hg-T l^{-1} with ranges from 1 to 30 ng Hg-T l^{-1}. For many areas, especially of the eastern and southern Mediterranean no data exist. The different operationally defined mercury species have also wide ranges. It may be worthwhile noting that it is general practice to acidify seawater samples for storage. This means that if unfiltered open-sea samples are analysed, the acidified samples most likely have concentrations near total mercury concentrations. Means of Hg-T from non-Mediterranean areas range from 2 to 14 ng l^{-1} with some values up to 24 ng Hg-T l^{-1}. Also the levels reported for other operationally defined mercury forms vary widely both in the Mediterranean and in other regions. So even if one is willing to accept the mercury levels, no differences between Mediterranean and non-Mediterranean mercury concentrations can be established from the data because the range of means for the Mediterranean vary by a factor of about four and the range of means from other areas by a factor of seven.

The vertical distributions of "reactive Hg" in the Strait of Gibraltar and other stations of the western Mediterranean are of interest (Fig.4). In the Strait of Gibraltar, the salinity wedge at about 90 m depth corresponds to a mercury maximum. Does this mean that high salinity Mediterranean sea water has a higher mercury concentration than low salinity Atlantic water? In all three figures, stations SRG1, SRG2, SRT and SRS1 have high surface mercury concentrations. The meaning of these high surface concentrations is not clear. The authors suggest that the mercury levels in the Atlantic are higher than in the Mediterranean because of these high surface levels. These observations do not fit with the lower mercury levels observed in pelagic fishes from the Strait of Gibraltar (section 3.5.5) which would indicate low mercury concentrations in sea water and food of these fishes.

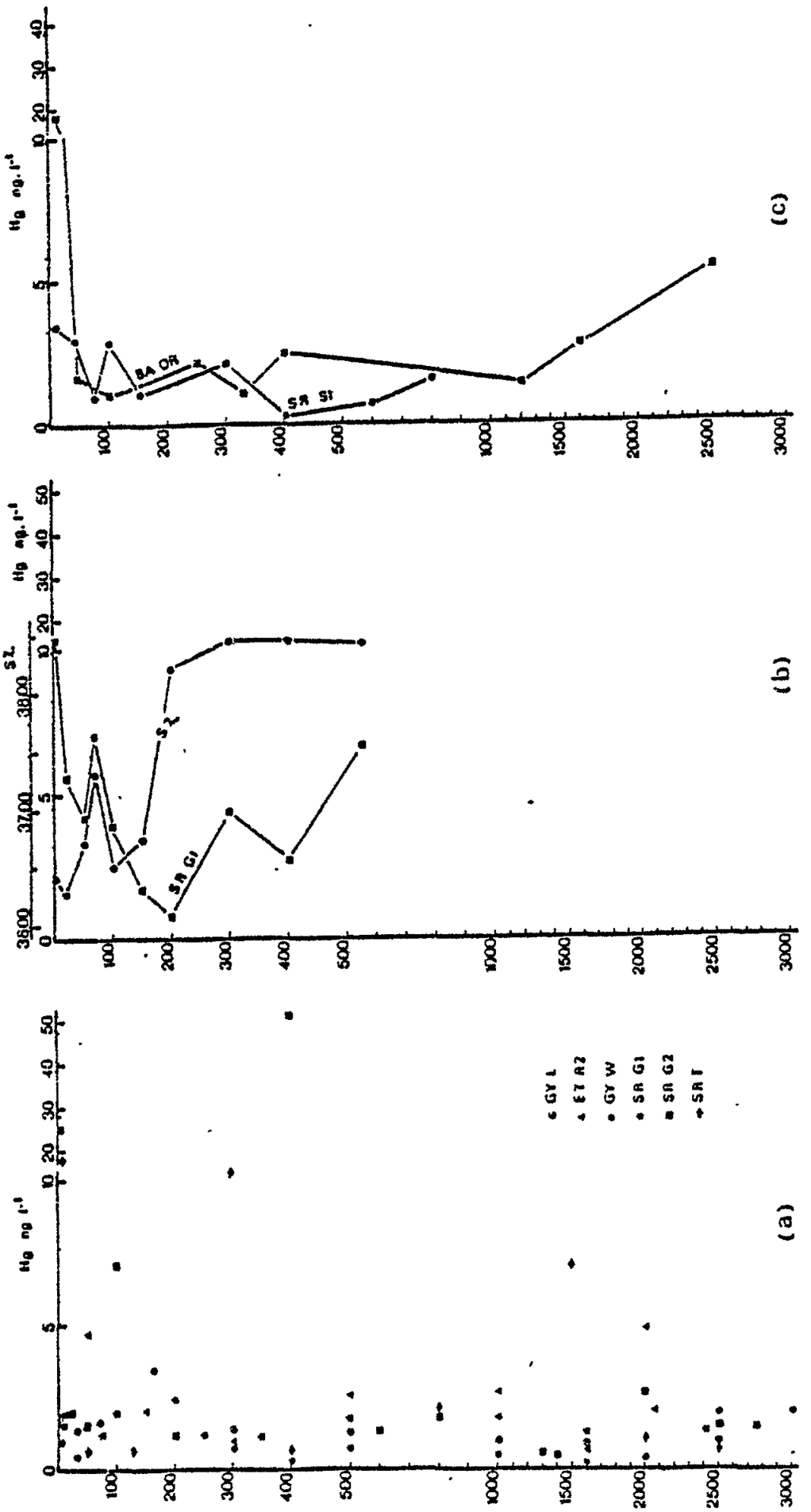


Figure 4. Vertical distribution of mercury. (a) in the western Mediterranean basin; (b) in the Straits of Gibraltar; (c) in the Strain of Sicily and eastern basin (Copin-Montegut et al., 1986).

Levels in coastal areas are strongly influenced by natural and anthropogenic sources (section 3.8 and 3.9). The data from Barghigiani et al. (1981) and Seritti et al. (1982) may give an idea of the possible (operationally defined) species of mercury (Table VII):

(i) in coastal zones without a strong influence of natural sources (north of the Arno River),

(ii) under the influence of natural sources (south of the Arno and south of Livorno, and the area under the influence of the Hg anomaly: stations 6 and 7,

(iii) under anthropogenic sources (around the Solvay chlor-alkali plant and the industrial area north of Livorno.

Except for the concentrations around the Solvay plant and the Orbetello Lagoon no exceptional high values are observed (Table VII). Also high mercury levels were not found in both sampling times. Clearly sea water concentrations are less indicative for pollution sources than sediments (section 3.8 and 3.9).

The input of mercury (among other trace elements) into the lagoon of Venice from 23 outlets was investigated by Bernardi et al. (1983). In two outlets on which data were presented the mercury concentrations ranged from not detected to 26 ug l^{-1} with a mean of 1.7 ug l^{-1} (the Dese river) and from 45 ug to 410 ug l^{-1} with a mean of 170 ug l^{-1} (Silone Canal). These are certainly high levels. The authors estimated the input into the lagoon through the Dese river as 0.17 MT/y (metric tonnes/year). For the Silone Canal no figures were given since the authors think that "the available data refer to extreme situations and are, therefore, not suitable when calculating the mean". Certainly, if the data on the water concentrations are correct, the input of mercury through the Silone Canal into the Venice lagoon must be enormous.

Table VII
Concentrations (ng l^{-1}) of different fractions of mercury in sea-water samples collected in May/August 1980 and May/June 1981 from the western Italian coast (Seritti et al., 1982)

No.	location	year	Hg-T	Hg-R	(Hg-T)-(Hg-R)	Hg-P
1	Gombo	1980	3.5	1.0	2.5	8.5
		1981	5.2	1.0	4.1	1.5
2	Arno, mouth	1980	1.7	0.5	1.2	36.4
		1981	6.8	1.9	4.9	79.6
3	Tirrenia, beach	1980	2.2	0.5	1.7	13.7
		1981	2.8	0.7	2.1	1.0
4	Livorno, harbour	1980	1.7	0.4	1.3	44.6
		1981	3.6	1.3	2.3	10
5	Solvay	1980	4.9	1.4	3.5	10.3
		1981	12.2	2.2	10.0	4.1
6	Albenga, mouth	1980	1.9	0.5	1.4	27
		1981	4.4	0.8	3.6	5.4
7	Orbetello Lagoon	1980	3.6	0.6	3.0	14.2

Table VII (cont.)

No.	location	year	Hg-T	Hg-R	(Hg-T)-(Hg-R)	Hg-P
		1981	10.5	1.3	9.2	4.5
8	Livorno,	1980	6.3	3.1	6.2	0.95
	off-shore	1981	6.5	1.9	4.6	1.2
9	Gorgona Island	1980	8.1	3.6	4.5	0.5
	off-shore	1981	3.2	1.0	2.2	0.5
10	Capraia Island	1980	6.1	2.9	3.2	0.3
	off-shore	1981	3.8	1.3	2.5	0.4
11	Corsica,	1980	6.6	3.4	3.2	1.1
	off-shore	1981	4.7	1.9	2.8	0.9

Hg-T = total
Hg-R = reactive
Hg-P = particulate

3.4. Sediments

Not many data on open-sea sediment concentrations have been collected in the Mediterranean Sea (Table VIII). In considering these data one has to bear in mind that the analytical procedures differ between authors. In addition, even authors of recent papers have not reported whether they have checked their analytical procedures against sediment reference standards now available from IAEA, National Bureau of Standards and others. The use of different pretreatments (extraction methods) by the various authors make the results not strictly comparable, but the order of magnitude can be assumed to be right. The few data available today show that 0.05 to 0.1 mg Hg-T kg^{-1} DW may be considered a typical background value for the Mediterranean. Industrial sources (see section 3.9) and the frequent natural geochemical anomalies in the Mediterranean (see section 3.8) influence the mercury distribution in the marine sediments adjacent to these sources. Near river mouths, due either to anthropogenic or natural sources, sediments show higher levels. Where distribution patterns emerged the data have been discussed individually anticlockwise around the Mediterranean coasts.

Obiols and Peiro (1981) investigated the mercury levels in sediments off the Ebro delta. Later Peiro *et al.* (1983) studied, among other elements, the distribution of mercury in more than 70 sediment samples between Barcelona and the Gulf of San Jorge. Off the Ebro mouth and off Tarragona high mercury levels were observed showing concentations higher than 1 mg Hg kg^{-1} DW offshore of Tarragona. Between the Ebro delta and Tarragona, concentrations vary between background levels and 1 mg Hg kg^{-1} DW. Where investigated, a gradient decreasing versus northeast was observed in front of the Ebro delta and one decreasing from Tarragona southeastwards. The mercury content in sediments north of Barcelona, near the mouth of the river Besos and near the Barcelona sewage outfall, showed high levels of mercury only in the surface layers near the sewage outfall (Cros Miguel and Garcia Rey, 1980). This high concentration decreases both in deeper sediments and away from the coast.

Table VIII
Selected mercury concentrations (mg kg^{-1} DW) in "open-sea" sediments

depth	n	mean	range	location	reference
2720	1	0.26		Alboran	Robertson et al., 1972
?	51	0.23	0.01 - 0.64	E-Gulf Lions	Arnoux et al., 1983
?	43	0.11	0.01 - 0.27	W-Gulf Lions	Arnoux et al., 1983
?	14	0.38	0.07 - 0.23	NW Mediterranean	Arnoux et al., 1983
?	17	0.13	0.16 - 0.57	NW Mediterranean	Arnoux et al., 1983
93 - 1715	9	0.1 M	0.05 - 0.24	Tyrrhenian	Selli et al., 1973
390 - 3520	4	0.1 M	0.05 - 0.16	Tyrrhenian	Selli et al., 1973
5 - 1195	20	0.1 M	0.07 - 0.97	Adriatic	Selli et al., 1973
64 - 888	2		0.05 - 0.1	Adriatic	Selli et al., 1973
12 - 1200	38	0.05	0.01 - 0.16	Adriatic	Kosta et al., 1976
2360	1	0.3		S off Crete	Robertson et al., 1972

M = median

The French Mediterranean coast has received considerable attention. Mercury concentrations were studied in the Marseille area (Fig.5) and in the adjacent open-sea region (Arnoux et al. 1981, 1983a, 1983b). The Etang de Berre, especially in the southern part where most industrial plants are located showed high mercury concentrations (Fig.6). The highest levels were detected in 1981 in the north (up to 3.8 mg Hg kg^{-1} DW). In the Gulf of Fos the 63 u fraction of the sediments contained concentrations of up to 6 mg Hg kg^{-1} DW, but the highest levels were observed near the sewage outfall of Marseille at Cortiou where concentrations up to 16 mg Hg kg^{-1} DW have been recorded. These concentrations, however, level off to less than 1 mg Hg kg^{-1} DW at about 3 km from the outfall. The mercury gradient from the mouth of the Rhone to the ports north of Marseille shows a considerable increase in mercury concentrations towards Marseille. These high sediment levels are probably caused in part by wastes discharged into the Rhone and in part by pollution caused by the industries located in and around Marseille. For comparison, the highest levels observed in the Gulf of Lions had 0.63 mg Hg kg^{-1} DW (mean 0.175 mg Hg kg^{-1} DW) and the BIOMEDE cruises in the Western Mediterranean showed that the maximum concentration was 0.57 mg Hg kg^{-1} DW with a mean of 0.18 mg Hg kg^{-1} DW (Fig.7).

Rapin et al., (1979) investigated the mercury levels in the 63 u fraction of coastal sediments from St. Tropez to Cap Ferrat. High levels up to 12.6 mg Hg kg^{-1} DW were observed in the ports of Cannes and Villefranche, while offshore levels approached background values. Flatau et al., (1983), determining the mercury levels in unfractionated sediments between 10 and 100 m depth found values ranging from 0.01 to 0.052 mg Hg kg^{-1} DW with a median of 0.014 mg Hg kg^{-1} DW. These levels are background levels. The very high levels found by Rapin et al. (1979) in the ports of Cannes and Villefranche are certainly unusual and the sources causing such high concentrations need to be identified.

The investigations on the sediment concentrations along the western Italian coast will be discussed together with their sources in sections 3.8 and 3.9.

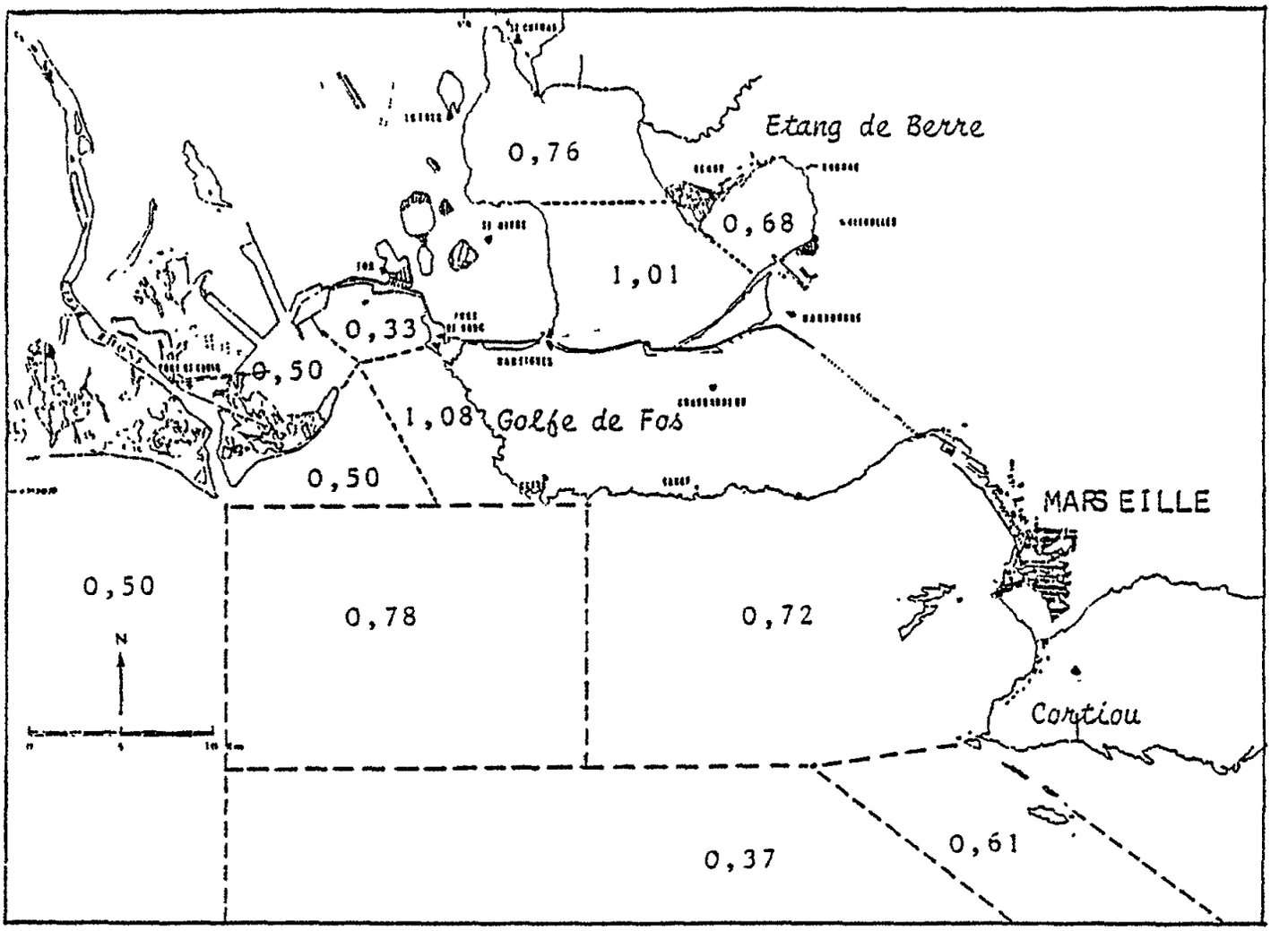


Figure 5. Mean mercury concentrations (mg kg^{-1} DW) in sediments near Marseille (Arnoux et al., 1983).

The mercury distribution in sediments of the Gulf of Naples has been studied by Baldi et al. (1983). They found high levels near Naples and other towns in the gulf (Fig.8). The vertical mercury distribution in the cores showed higher mercury levels in the surface layers of the sediments (Fig.9) indicating continuous releases of mercury into the marine environment. It is noteworthy that near Cuma where the main sewage outfall of Naples is located the mercury levels in the sediments are near background. This is certainly a

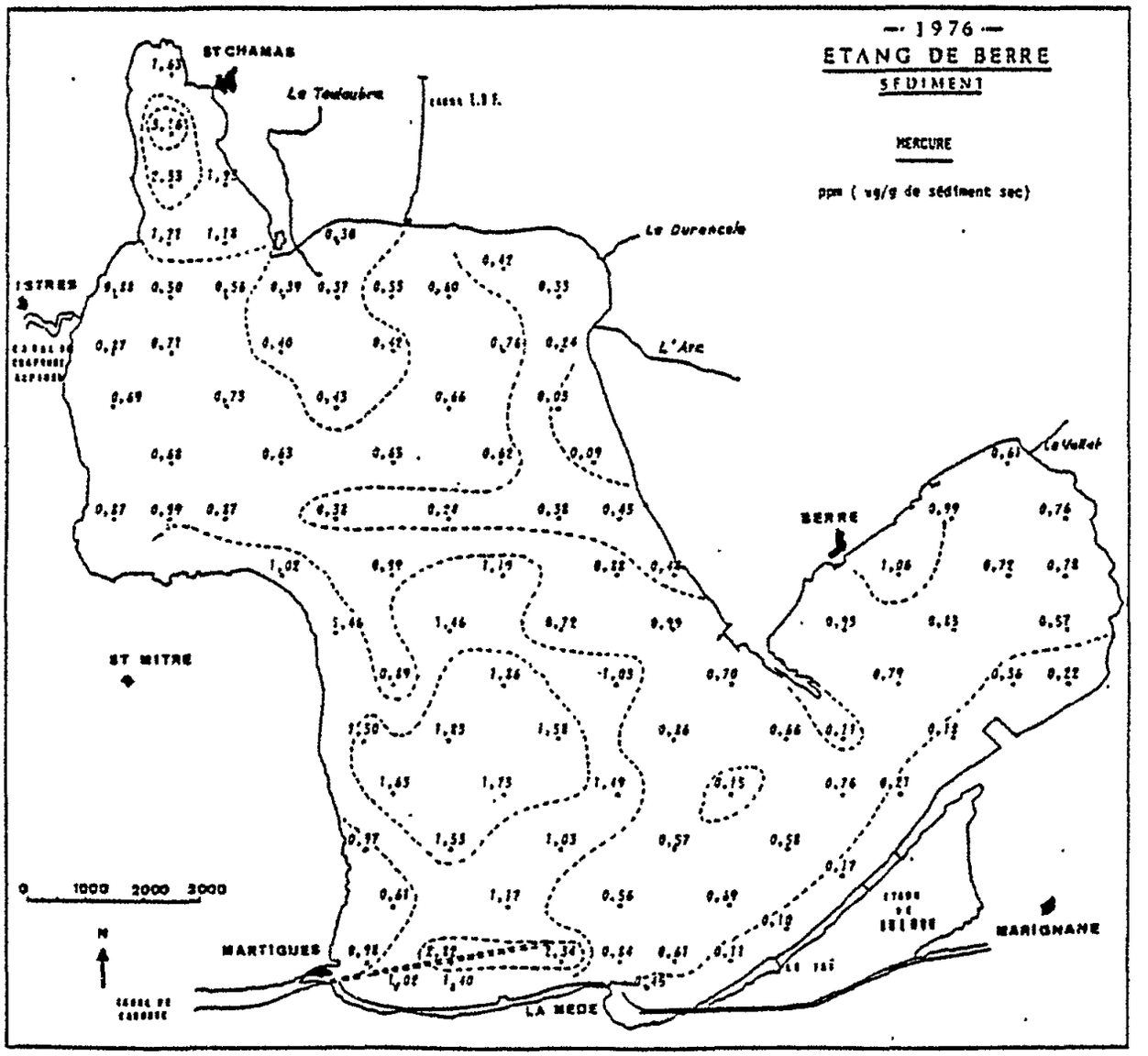


Figure 6. Mercury concentrations (mg kg^{-1} DW) in the Etang de Berre (Arnoux et al., 1981).

remarkable difference to the high mercury concentrations observed near Tarragona, Barcelona, Marseille, Athens and Tel-Aviv (see below) and the reasons for this difference are not clear.

Angela et al. (1981) and Donazzolo et al. (1984) studied the mercury levels in sediments from the Gulf of Venice (Fig.10). The authors state that the high levels at some distance from the port entrances and the granulometric composition of the sediments strongly indicate that the high concentrations are caused by direct dumping of wastes.

The situation in the Gulf of Trieste and in the Kastela Bay (Split) is discussed in section 3.8.

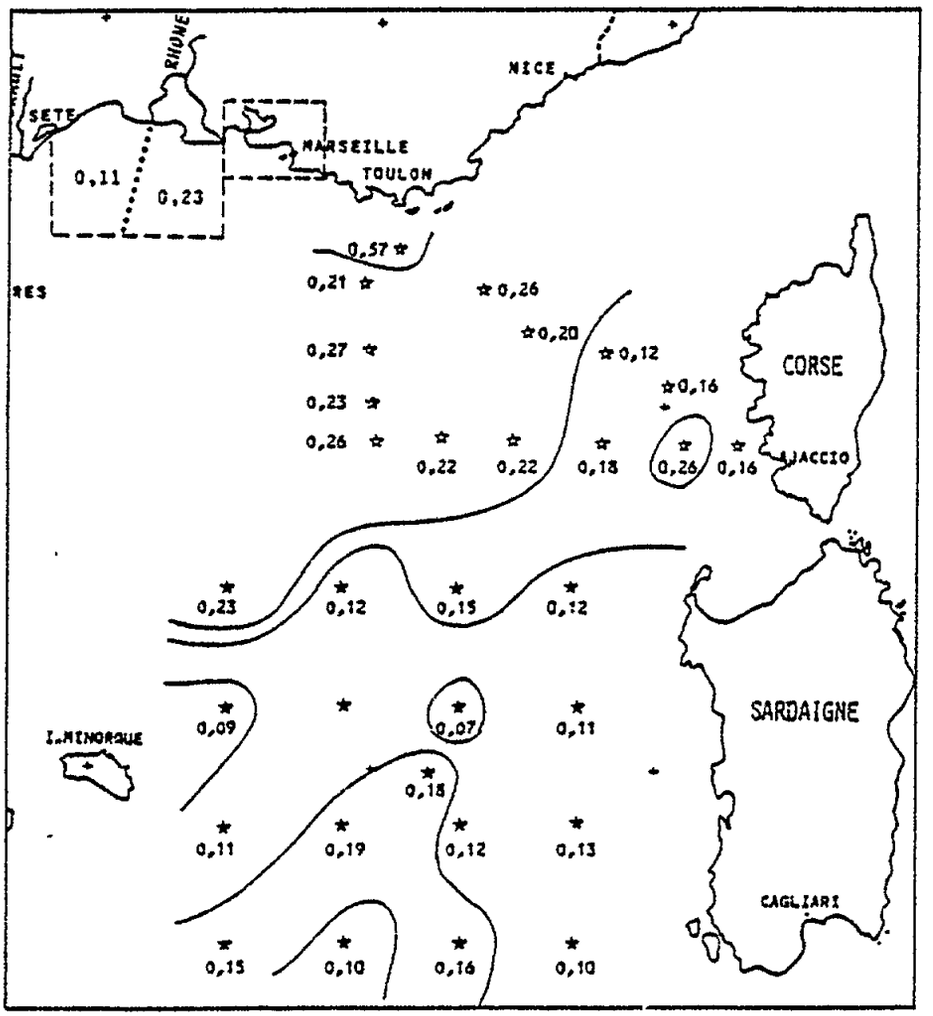


Figure 7. Mercury levels in sediments (mg kg^{-1} DW) in the Western Mediterranean (Arnoux et al., 1983).

The sewage of Athens is discharged into the Saronikos Gulf. Investigating the distribution of mercury and other trace elements in sediment samples from this outfall area, Grimanis et al., (1977) found 9 to 10 mg Hg kg^{-1} DW at the entrance of the Piraeus Harbour and 2 to 3 mg Hg kg^{-1} DW at the sewage outfall. The dominant dispersal path was directed south-eastwards and southwards. At about 10 km distance from the outfall the mercury levels in the sediments were again at about background levels.

Salihoglu and Yemenicioglu (1986) determined mercury and methyl mercury in river deltas and harbours along the Turkish Levantine coast. The mercury concentrations in samples collected near Mersin and in the harbour of Mersin were at background levels. Five to 20 % of the Hg-T was methyl mercury.

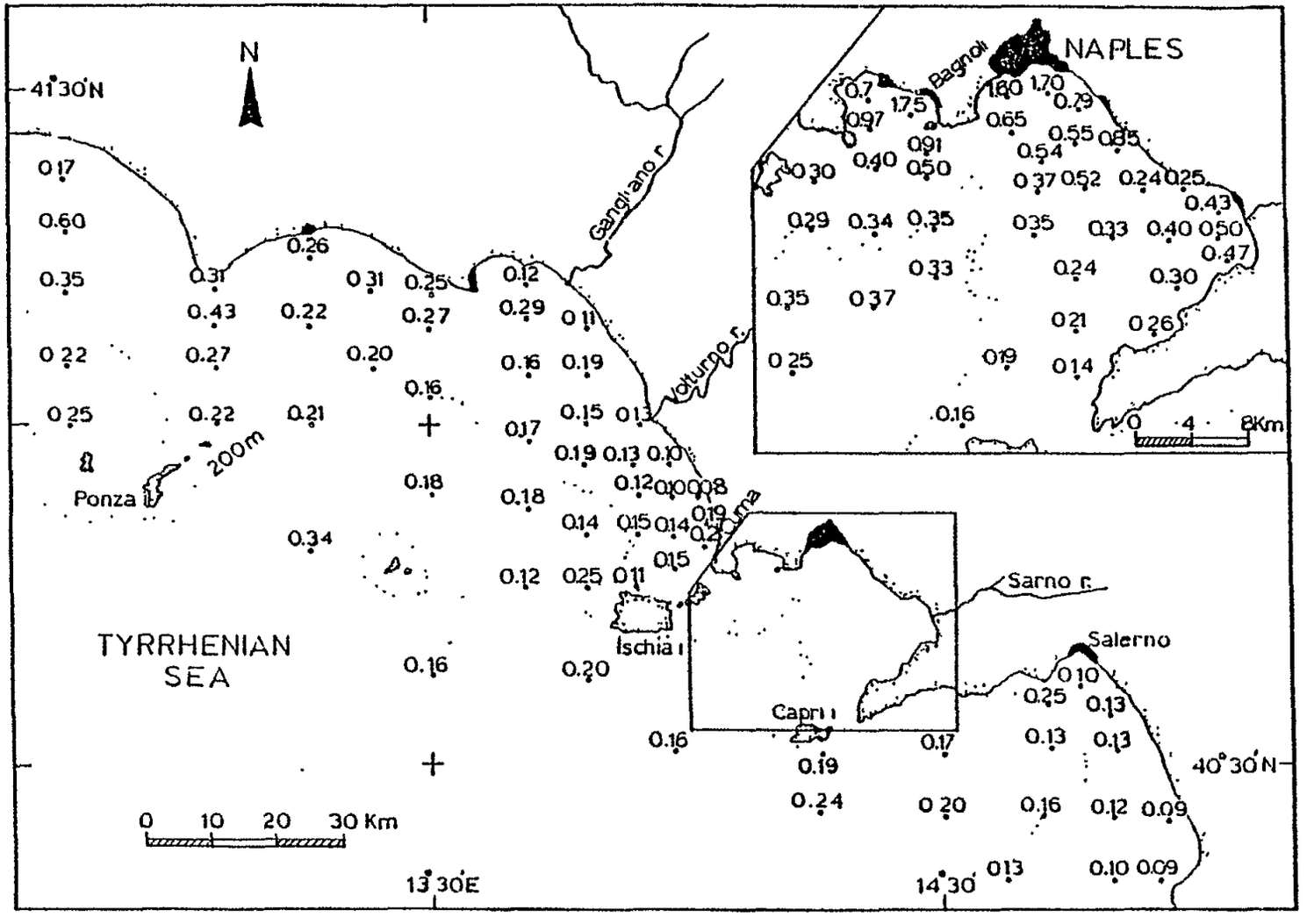


Figure 8. Mercury concentrations (mg kg^{-1} DW) in the top 3 cm of sediments in the Gulf of Naples (Baldi et al., 1983).

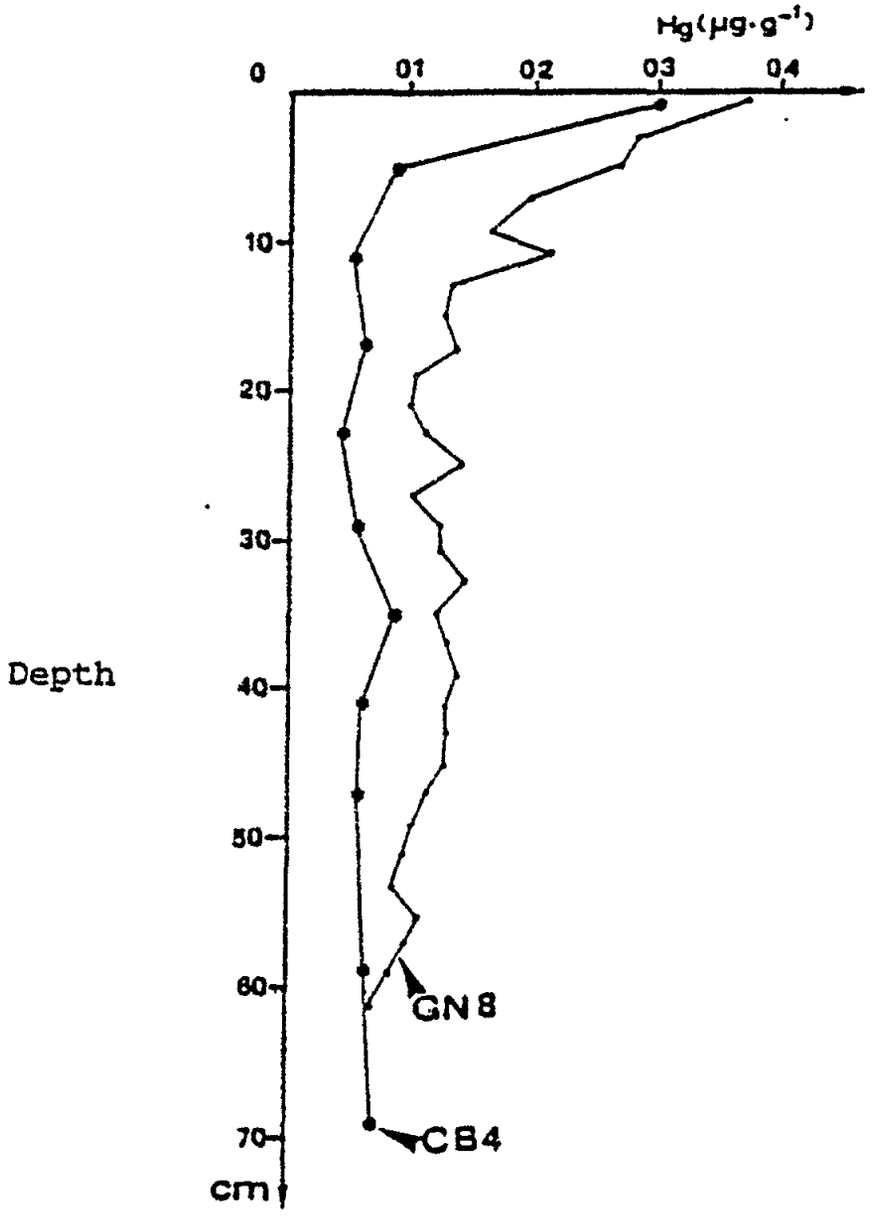


Figure 9. Mercury in the cores from the Gulf of Naples (GN8) and the Tuscan coast (CB4) (Baldi, 1986).

Amiel and Navrot (1976) investigated the mercury distribution adjacent to the sewage outfall of Tel-Aviv-Yafo. Significant quantities of trace elements (Ag, Co, Cr, Cu, Ni, Pb and Zn) together with mercury were found in the sediments. Mercury concentrations decreased from about 0.5 mg Hg kg^{-1} DW to background levels ($\sim$0.1 mg Hg kg^{-1} DW) at a distance of about 1700 m. Hornung and collaborators studied the influence of mercury releases from a chlor-alkali plant situated in the Bay of Haifa. These data and the influence of mercury sources near Alexandria are discussed in section 3.9.

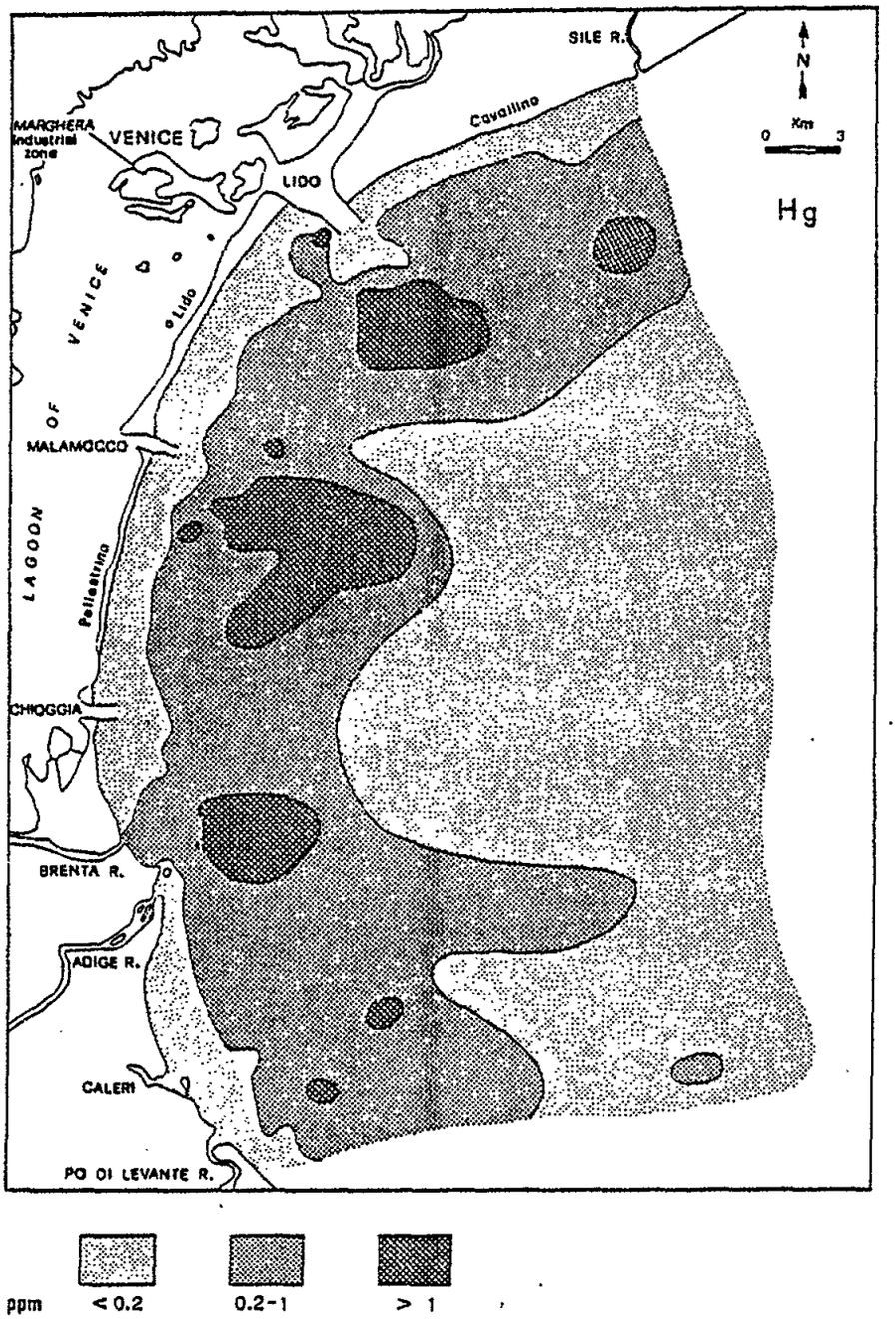


Figure 10. Mercury concentrations in sediments along the coastline of Venice (Donazzolo et al., 1981).

3.5. Biota

It is well known that mercury is an accumulative trace element, i. e. the body concentrations of mercury increase with age of the specimen. Mercury concentrations in an organism depend on environmental factors such as the concentration of mercury in sea water and its food-chain position and, in particular, on the chemical species of mercury to which the organism is exposed (see section 4.2). Various biological species may have different mercury concentrations and also different biological tissues have different mercury concentrations. In addition, the relative distribution of various chemical species of mercury differ between biological species and their tissues and organs. This means that it is difficult to compare the mercury concentration of different biological species, and for a comparison of mercury concentrations in marine organisms the relation between mercury concentration and size (age) in the specimens of the same biological species and the same tissues must be known. Data on the mercury concentration in marine organisms without age or size data have very limited use. If the sample selected is representative of the size distribution of the species in a catch or on the fish market it may still be useful for an estimate of the frequency distribution (abundance) of mercury concentration in the seafood consumed; but rarely have samples been selected with this purpose in mind (e.g. Paccagnella et al., 1973).

Due to the difficulties in determining exact mercury concentrations in biological tissues the Hg/size relationship is statistically more significant at higher Hg body and tissue concentrations. The best correlation is exhibited by tuna (Fig.12), but also other marine organisms of different taxonomic groups show similar size/Hg concentration relationships (Fig.13-20). Further examples can be seen in other figures (see section 3.8 and 3.9). The only exceptions so far reported concern mussels (see section 3.5.4). In general, only total Hg (Hg-T) concentrations are reported. However, recently a few data on methyl mercury concentrations in Mediterranean marine organisms have been published (see below). Because the physiological behaviour of various mercury species is very different (see section 4.2), detailed information on the chemical species of mercury in marine organisms is urgently needed for a more precise prediction of the mercury levels in marine foods.

The largest uniform data base on Hg-T concentrations in the Mediterranean were collected in the framework of the UNEP/FAO pilot project on baseline studies and monitoring of metals, particularly mercury and cadmium, in marine organisms (MED POL II) (MAP Tech.Rep.Ser. No 2). The participants in this project were aware that certain criteria had to be established in order to make the survey efficient. First of all, all participants had to intercalibrate with the reference materials distributed by IAEA (see section 3.1). Since different species and specimens of the same species of different size cannot be compared and also different tissues of the same specimen may have different mercury concentrations, the results of the monitoring exercise could only be comparable if the size range and the tissues to be analysed were specified. Wide distribution in the Mediterranean of the species to be monitored was one of the criteria for selecting the species to be monitored:

Mussels (Mytilus galloprovincialis): shell length 4-5 cm; soft parts of individual or a composite sample of 10 mussels without palleal fluid and

Striped mullet (Mullus barbatus): fork length 10-15 cm; fillets of individual specimens or a composite sample of the fillets of 6 specimens.

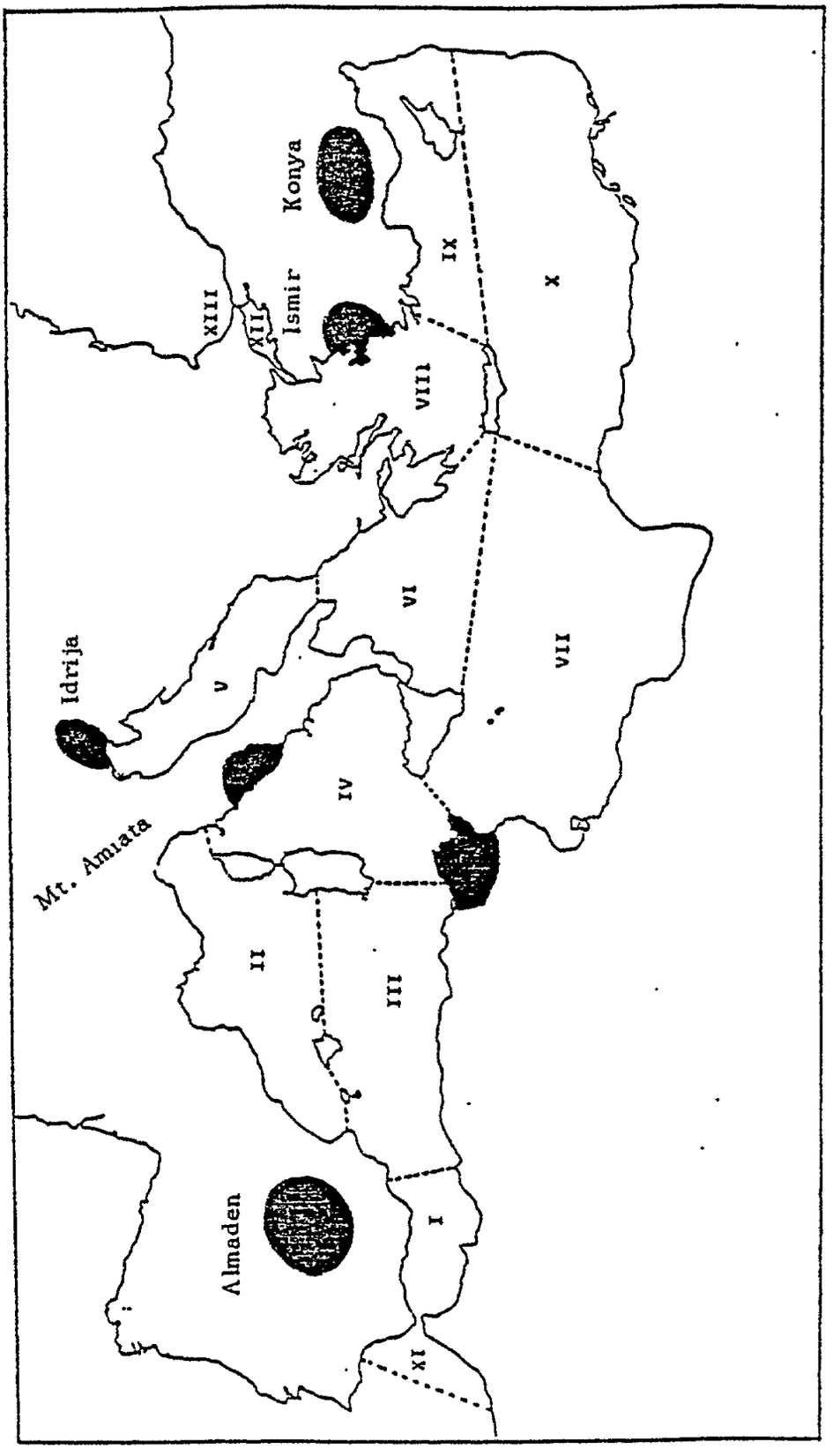


Figure 11. MED-POL areas and mercury mining areas (data from UNEP, 1980).

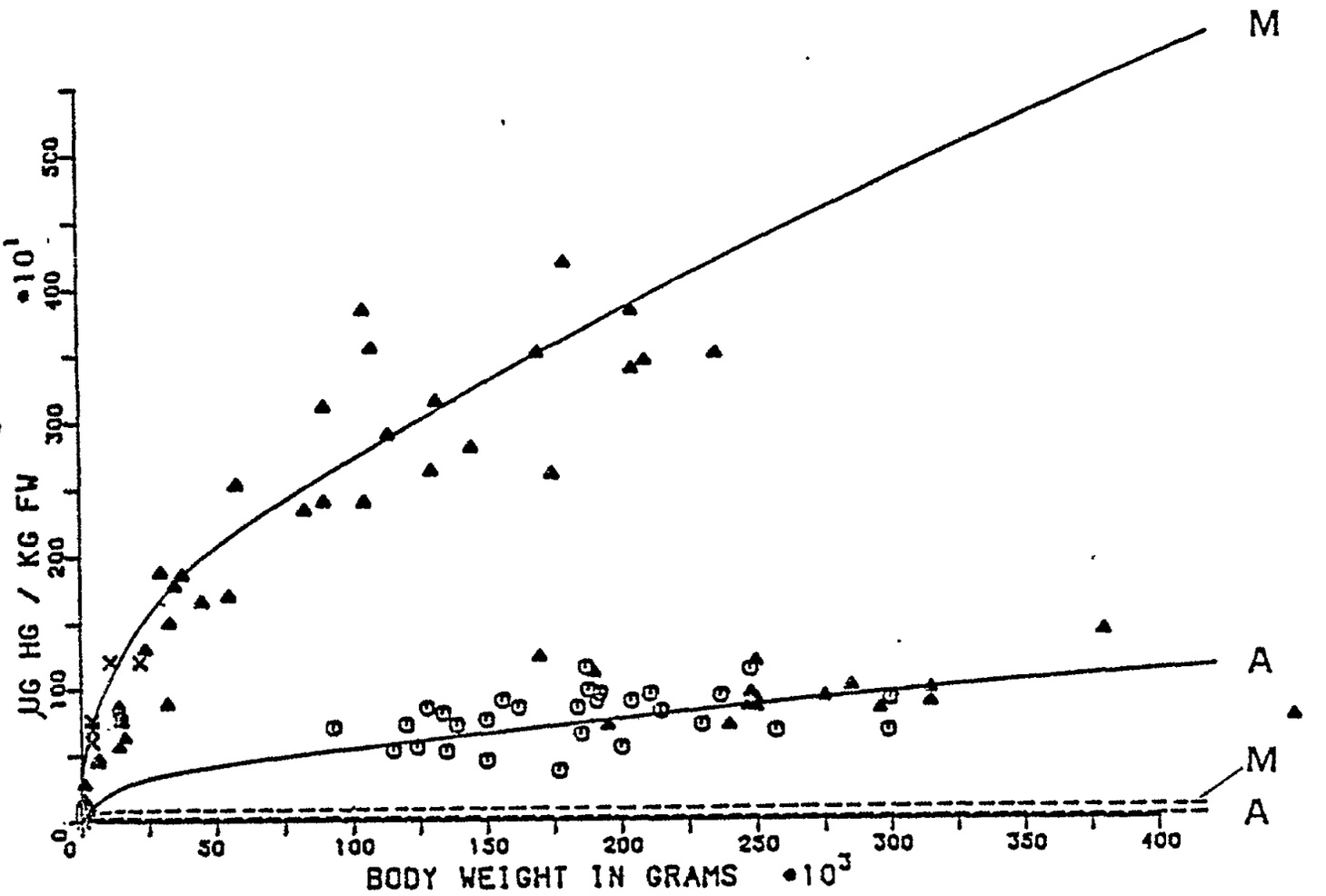


Figure 12. Total mercury concentrations in Thunnus thynnus from the Strait of Gibraltar (⊙), Tyrrhenian Sea (▲) and Spanish coast (x). The continuous line shows total Hg concentrations calculated by a model; intermittent line shows inorganic Hg concentration calculated by a model. M: prediction for Mediterranean tuna, A: prediction for Atlantic tuna. (Bernhard, 1985).

Since high mercury concentrations had been reported for tuna and swordfish it was recommended to analyse specimens of the bluefin tuna (Thunnus thynnus) whenever available and regardless of size.

In retrospect, the data collected would have been more informative, if the participants had been asked to establish "mercury concentrations versus size" relationships, because, the differences in mercury levels are much easier to establish if their "Hg concentration/size" relationship is compared rather than the levels in specimens of the same size.

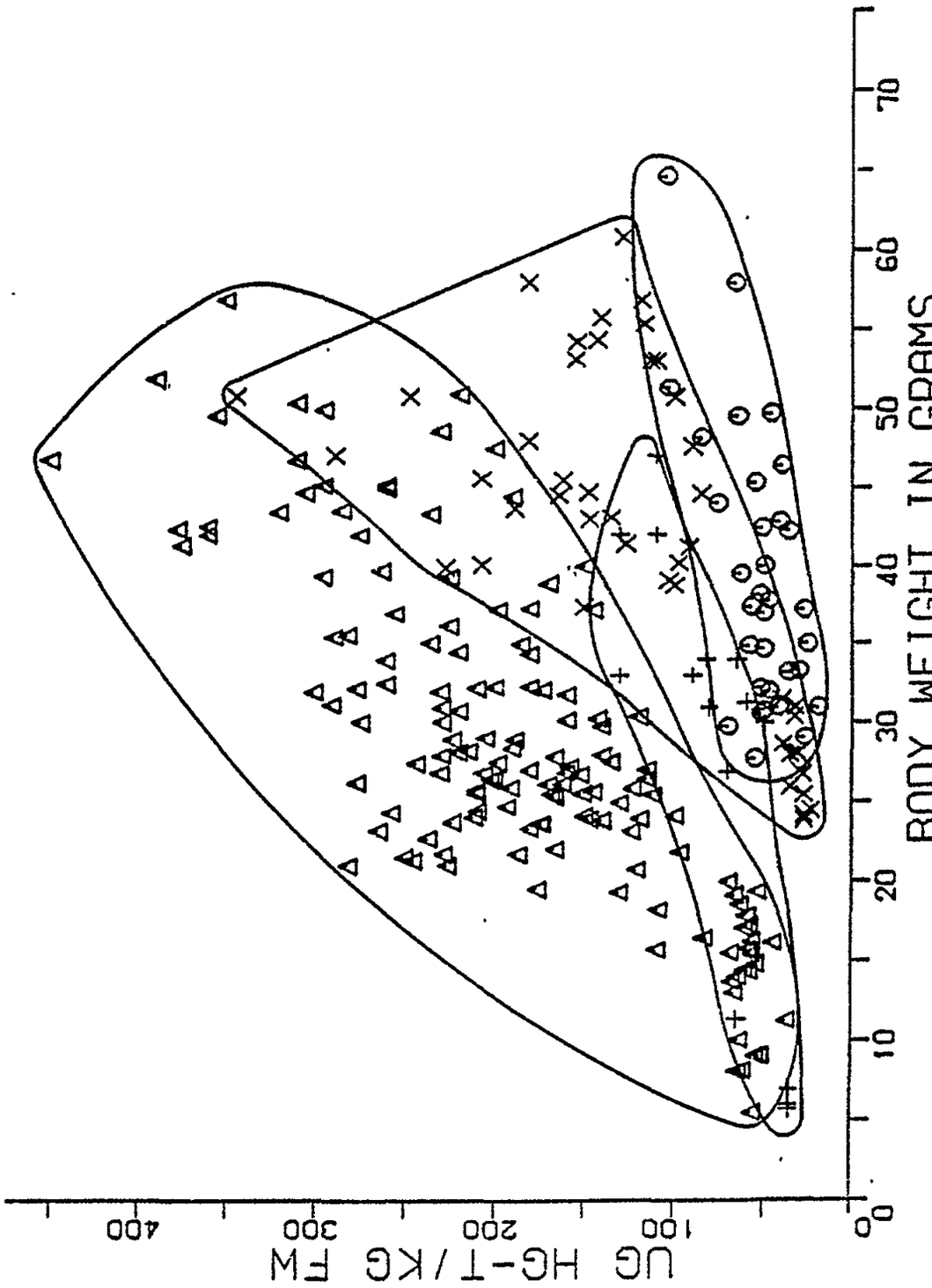


Figure 13. Total mercury concentrations in Sardina pilchardus from the Strait of Gibraltar (⊙), Tyrrhenian Sea (Δ), Sanremo (+) and Fano (x). (Data from Stoeppler et al., 1979, Baldi et al., 1979).

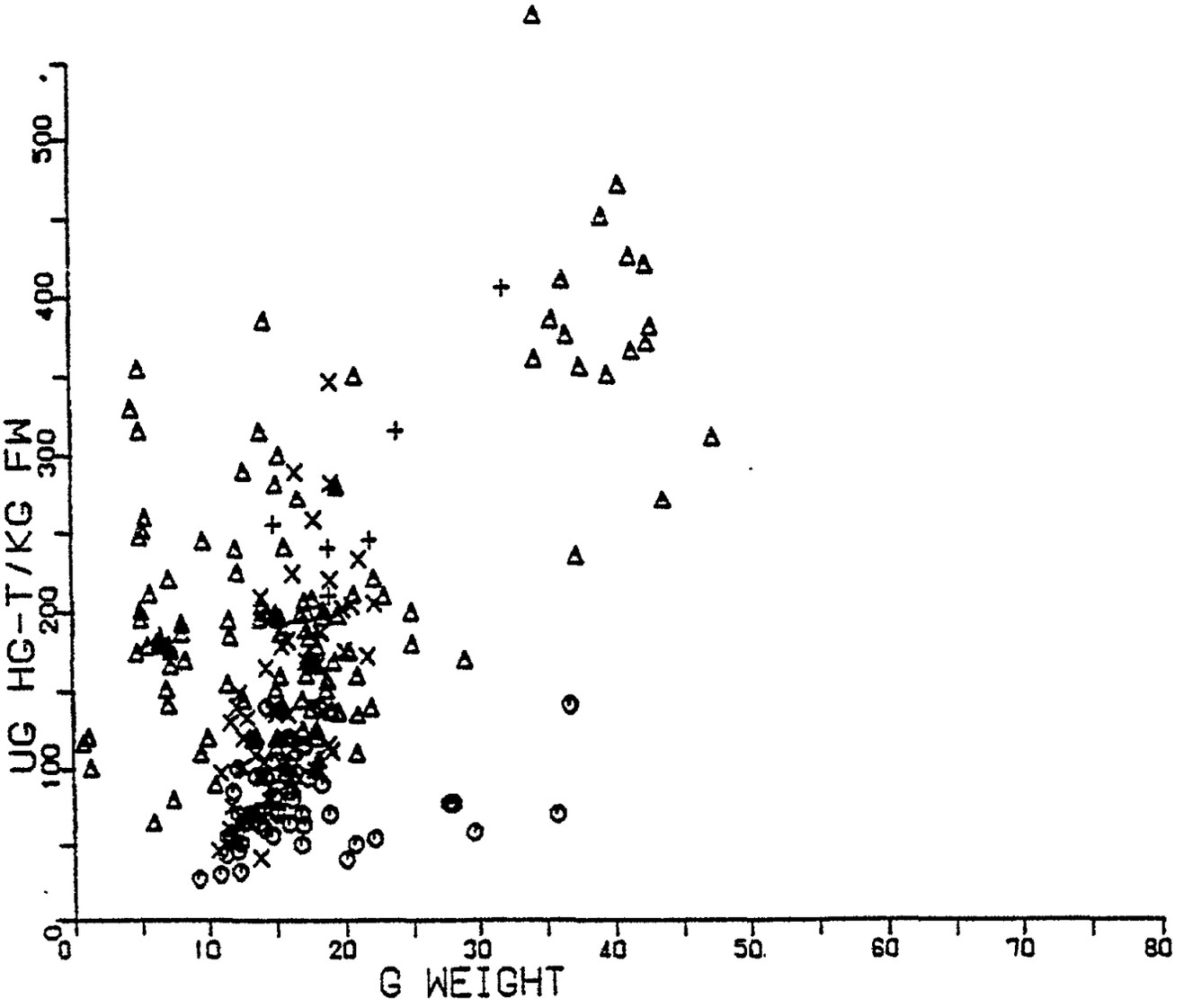


Figure 14. Total mercury concentrations in Engraulis encrasicholus from the Strait of Gibraltar (ϕ), Tyrrhenian Sea (△), Sanremo (+) and Fano (x). (Data from Stoeppler et al., 1979, Baldi et al., 1979).

Stimulated by the MED POL pilot project many other species of marine organisms have also been analysed for mercury (Table IX) and in many cases their "Hg concentration/size" relationship was established. The data of these analyses were transmitted to FAO and are preliminarily summarized in UNEP/FAO/WHO, (1983) and in MAP Technical Reports No. 9. Subsequently individual workers have published their results in the open scientific literature. Since it is very difficult to identify the single data in the individual publications after they have been summarized in the UNEP documents and since, on the other hand, data limited to only mercury concentrations

Table IX

Mercury levels in various Mediterranean marine organisms (Nauen et al., 1980)

Besides the number of different single data sets ('number of data'), the number of samples they represent is given in brackets. Mean concentration of mercury and standard deviation (s) refer to single unweighted data. Numbers after a species name represent different Mediterranean areas based on GFCM classification

Name	Number of data (Number of samples analysed)		Average Hg concentration (ug kg^{-1} FW)	s	Range
Anguilla anguilla	4	(11)	184	141	20 - 304
Aporrhais pes pelecani	2	(11)	125	120	40 - 210
Arnoglossus laterna	1	(10)	170		
Argyrosoma regium	1		340		
Atherina hepsetus	10		86	37	23 - 130
Boops boops	26	(60)	126	93	12 - 432
Boops salpa	5	(8)	61	97	3 - (230)
Callinectes sapidus	1		170		
Carcinus mediterraneus	15	(50)	223	124	(50) - 500
Conger conger	10	(16)	278	199	(74) - 650
Dentex dentex	6		385	100	220 - 480
Dentex gibbosus	11		138	21	99 - 178
Dicentrarchus labrax	3	(15)	313	64	(240) - (360)
Diplodus sargus 37.4	2	(11)	90	28	(70) - (110)
Diplodus sargus 37.3	22		265	205	35 - 697
Donax trunculus	45	(383)	226	237	35 - 909
Eledone moschata	13	(19)	486	392	(80) - 1330
Engraulis encrasicolus	105	(952)	150	65	(21) - 320
Epinephelus guaza	1		450		
Epinephelus aeneus	8	(9)	257	95	99 - 397
Euthunnus alletteratus	3	(4)	3670	3208	50 - 6160
Flatfish	9	(17)	252	197	13 - 642
Gobius niger	1		120		
Gobius sp.	97	(121)	131	140	17 - 1148
Hexanchus griseus	6	(256)	1075	721	(250) - (2000)
Homarus gammarus	1	(10)	290		
Lithognathus mormyrus	7	(18)	209	142	34 - 466
Loligo vulgaris	8	(20)	258	219	12 - 606
Lophius pescatorius	26	(32)	502	805	23 - 3941
Lysmata semicaudata	6	(42)	264	353	16 - 935
Maena sp.	14	(18)	153	101	30 - 390
Merlangius merlangus	4		172	53	100 - 220
Merluccius merluccius	60	(167)	232	229	25 - 850
Micromesistius poutassou	5	(14)	258	118	(100) - 400
Mugil cephalus	17	(32)	135	85	50 - 319
Mugil auratus	57	(74)	216	806	1 - 5600
Mullus barbatus	768	(2143)	635	887	2 - 7050
Mullus barbatus 37.3	26		139	142	40 - 260
Mullus barbatus 37.4	32		115	126	6 - 668
Mullus surmuletus	229	(259)	95	62	15 - 510
Mullus surmuletus 37.4	6		123	142	4 - 380
Mustelus mustelus	3	(10)	430	286	200 - 750
Myliobatis aquila	1	(5)	100		

Table IX (cont.)

Name	Number of data (Number of samples analysed)		Average Hg concentration (ug kg^{-1} FW)	s	Range
Mytilus galloprovincialis					
37.4	184	(≫ 184)	92	108	16 - 919
37.3	7		93	111	20 - 342
37	441	(> 441)	153	534	4 - 7000
Nephrops norvegicus	238		1024	576	40 - 3000
Oblada melanura	1	(7)	150		
Octopus vulgaris	12	(18)	182	144	86 - 600
Orcynopsis unicolor	2		1900	28	1880 - 1920
Pagellus acarne	12		170	88	32 - 337
Pagellus erythrinus	119	(236)	204	112	53 - 805
Pagellus bogaraveo	1	(12)	320		
Pagrus pagrus	5		212	329	40 - 800
Palaemon serratus	22		431	383	62 - 1625
Pandalus borealis	3	(64)	123	60	60 - 180
Parapenaeus longirostris	51	(511)	415	410	110 - 2500
Pecten jacobaeus	1	(8)	40		
Penaeus kerathurus	18	(67)	108	113	8 - 477
Platichthys flesus	5		115	91	31 - 250
Portunus pelagicus	1		11		
Raja alba	1	(7)	60		
Raja asterias	1	(5)	290		
Sarda sarda	41		837	621	228 - 2300
Sardina pilchardus	16	(54)	159	99	70 - 380
Sardinella aurita	22		66	39	10 - 144
Saurida undosquamis	156	(263)	152	109	42 - 649
Scomber sp.	26	(45)	198	119	73 - 700
Scorpaena sp.	22	(42)	295	480	10 - 2175
Scyliorhinus canicula	3	(12)	473	168	290 - 620
Scyllarus arctus	6		204	202	67 - 600
Sepia officinalis	31	(45)	150	156	24 - 800
Serranids	2	(32)	190	71	140 - 240
Solea vulgaris	9	(34)	118	151	40 - 510
Sparus auratus	3	(18)	147	32	110 - 170
Sphaeronassa mutabilis	1	(7)	50		
Sphyraena sphyraena	10	(24)	257	181	81 - 700
Sprattus sprattus	7	(14)	142	76	40 - 242
Squalus acanthias	6		1455	344	890 - 1900
Squilla mantis	8	(19)	362	211	100 - 654
Thunnus alalunga	16	(24)	245	114	60 - 399
Thunnus thynnus (canned)	13	(65)	248	178	80 - 320
Thunnus thynnus (fresh)	228	(1085)	924	903	20 - 6290
Todarodes sagittatus	12		96	75	12 - 240
Trachinus sp.	6	(17)	206	224	90 - 660
Trachurus mediterraneus	74	(153)	149	165	8 - 955
Trachurus trachurus	4	(15)	360	341	80 - 848
Trigla sp.	7	(26)	139	54	80 - 240
Upeneus moluccensis	130	(> 130)	426	288	38 - 1122
Uranoscopus scaber	16	(20)	195	88	71 - 363
Venus gallina	5	(15)	74	36	15 - 114
Xiphias gladius	14	(39)	613	650	45 - (2000)
Zeus faber	5	(10)	117	198	11 - 470

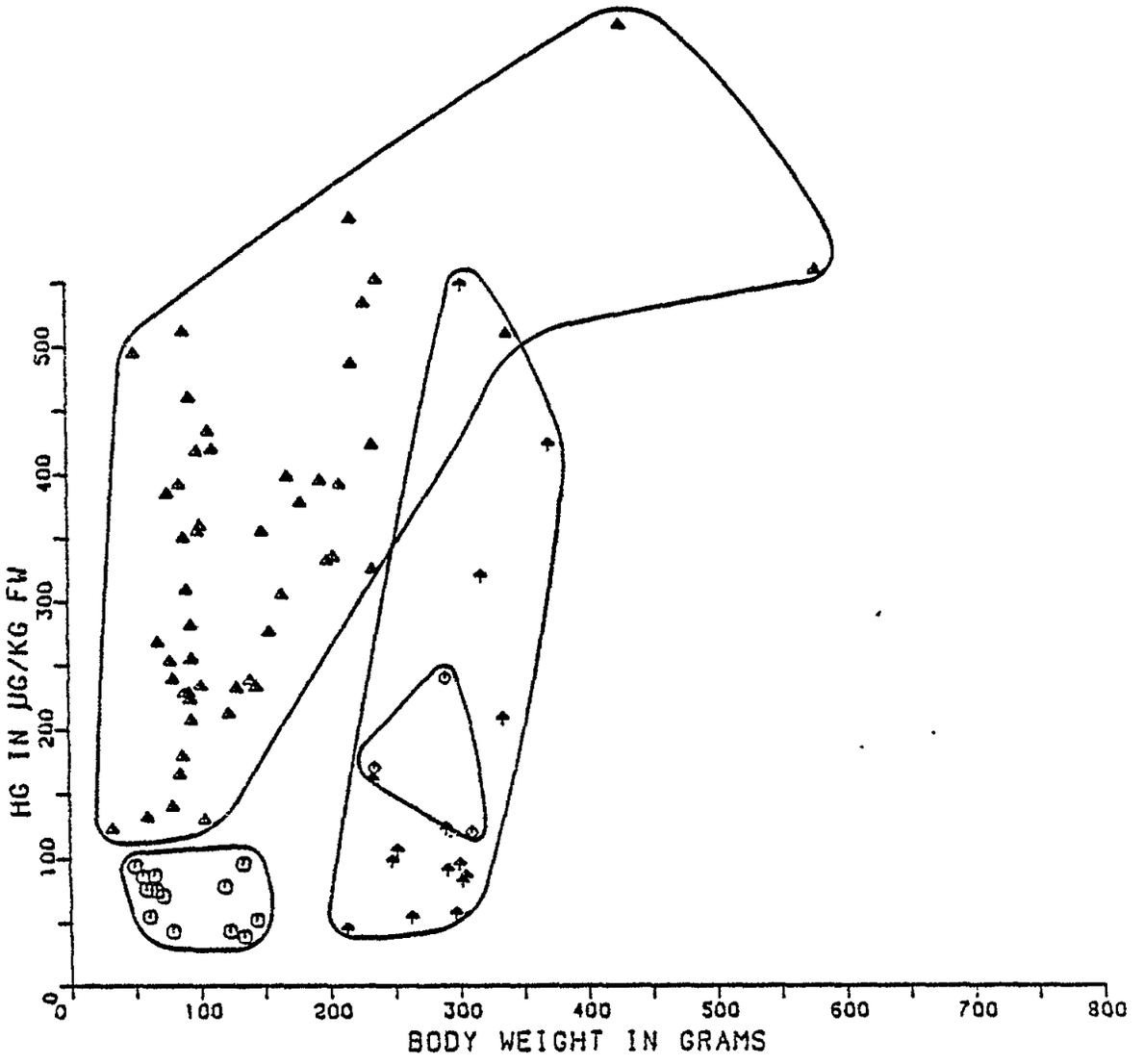


Figure 15. Total mercury concentrations in Scomber scomber and S. japonicus from the Strait of Gibraltar (▲), Tyrrhenian Sea (△), Helgoland (○) and Schevingen (♣). (Data from Stoeppler et al., 1979).

without data on size can only give a very approximate idea of the mercury levels present in the marine organisms, it was preferred to use the table which appears in UNEP/FAO/WHO, (1983) and to treat individual data published in scientific journals only if they contain collateral biological or ecological data which can explain phenomena of the mercury accumulation, retention and release.

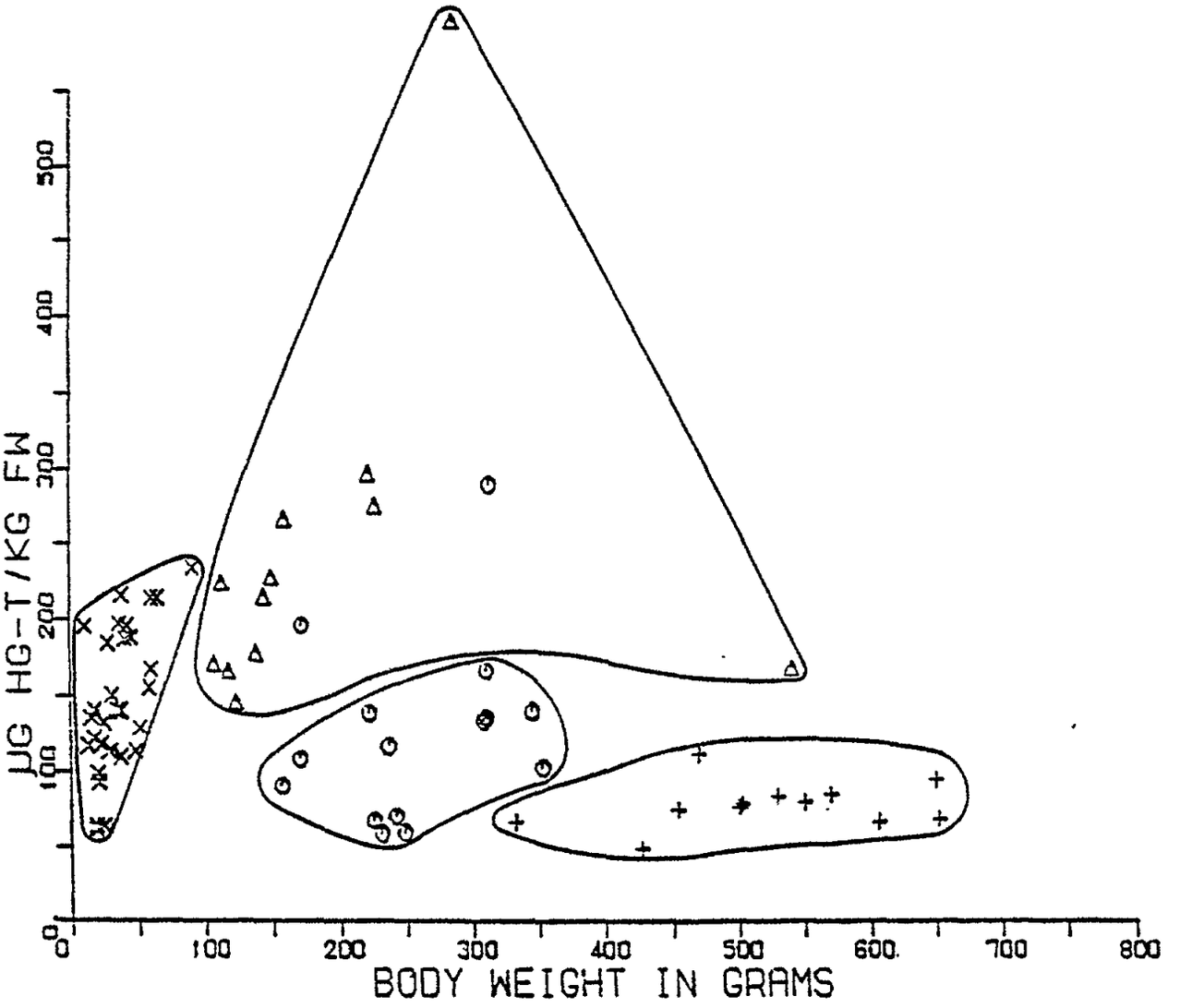


Figure 16. Total mercury concentrations in Sepia vulgaris from the Ostend (♂), Chioggia (x), Tyrrhenian Sea (Δ) and Schevingen (+) (Data from Stoeppler et al., 1979).

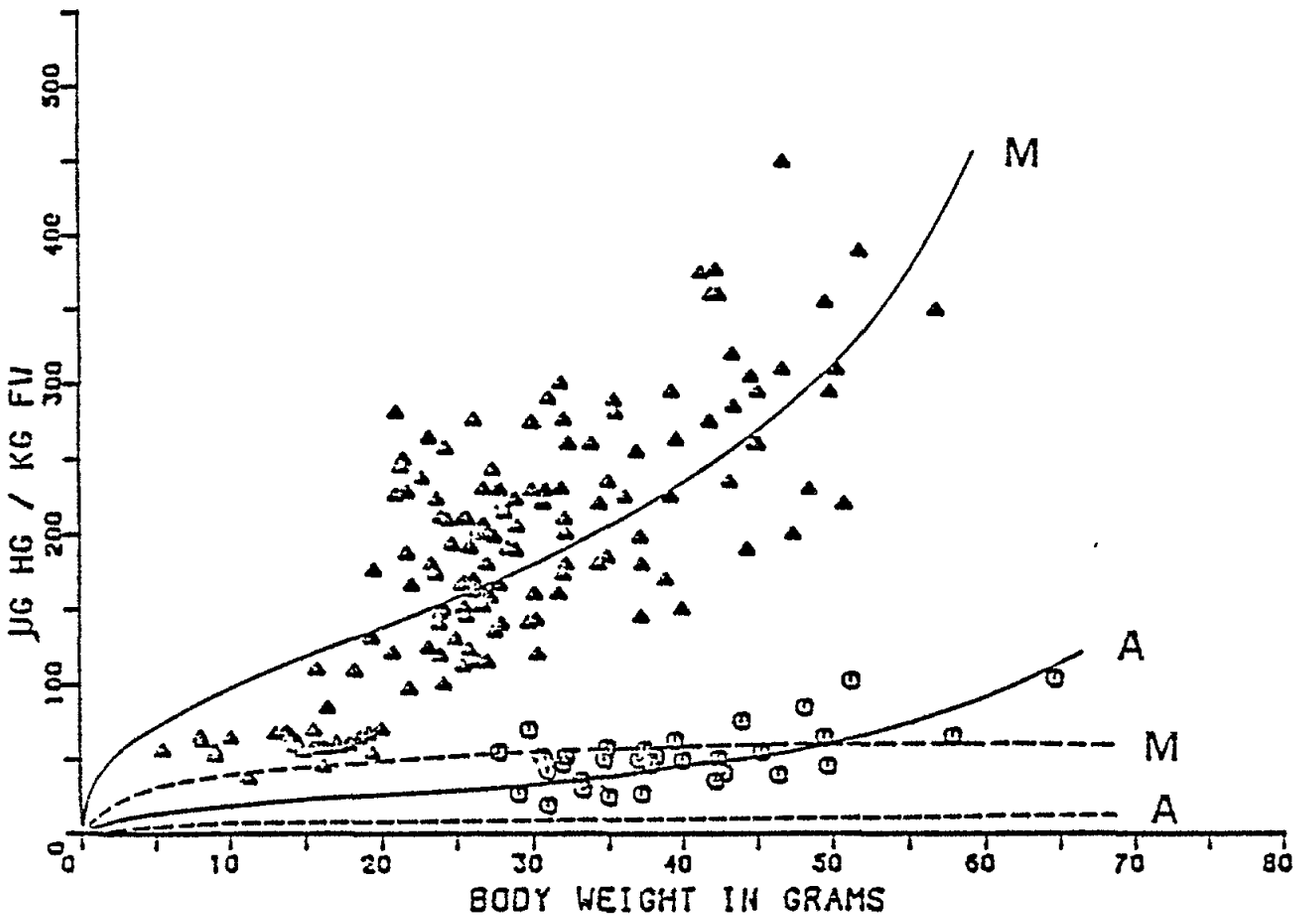


Figure 17. Total mercury concentrations in Sardina pilchardus from the Strait of Gibraltar (⏻) and Tyrrhenian Sea (◭). The continuous line shows total Hg concentrations calculated by a model; intermittent line shows inorganic Hg concentration calculated by a model. M: prediction for Mediterranean tuna, A: prediction for Atlantic tuna. (Bernhard, 1985).

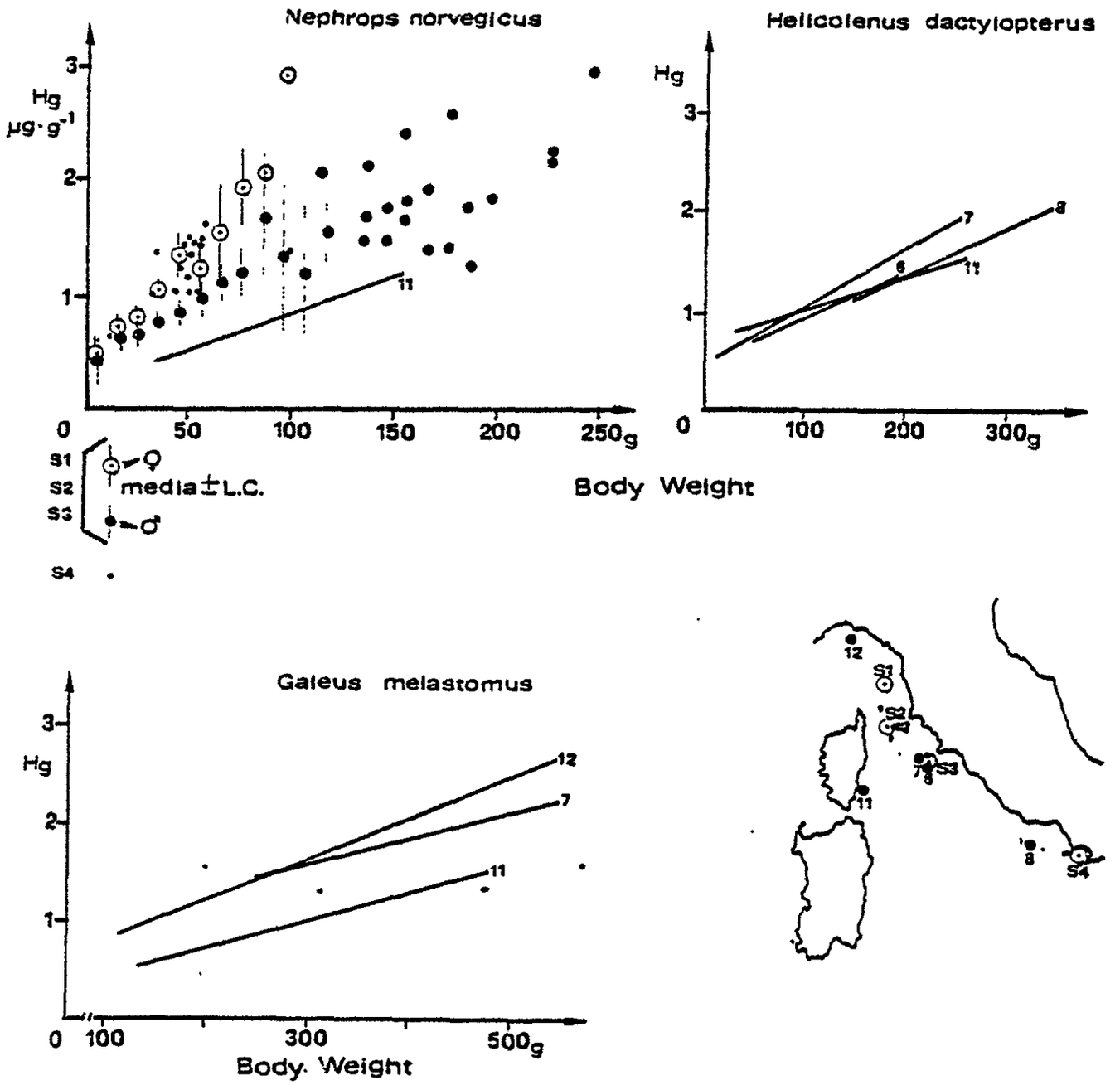


Figure 18. Mercury concentration vs. size in benthic crustaceans from remote sampling areas in the Ligurian and Tyrrhenian Seas (Baldi, 1986). Numbers in the graphs indicate sampling stations in the map. The data points in the figure for N. norvegicus refer to sample location S1 to S3. Full circle = male; open circle with dot = female.

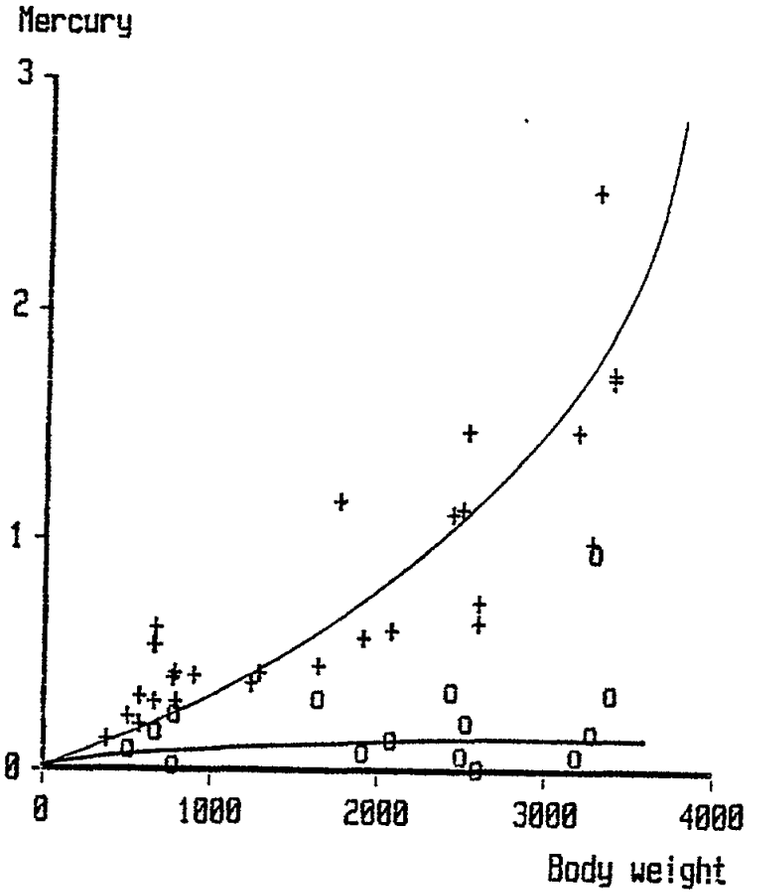


Figure 19. Total (+) and inorganic (o) mercury (mg kg^{-1} FW) in dark muscle of Sarda sarda versus weight (9) (Capelli et al., 1986). Curves fitted by eye.

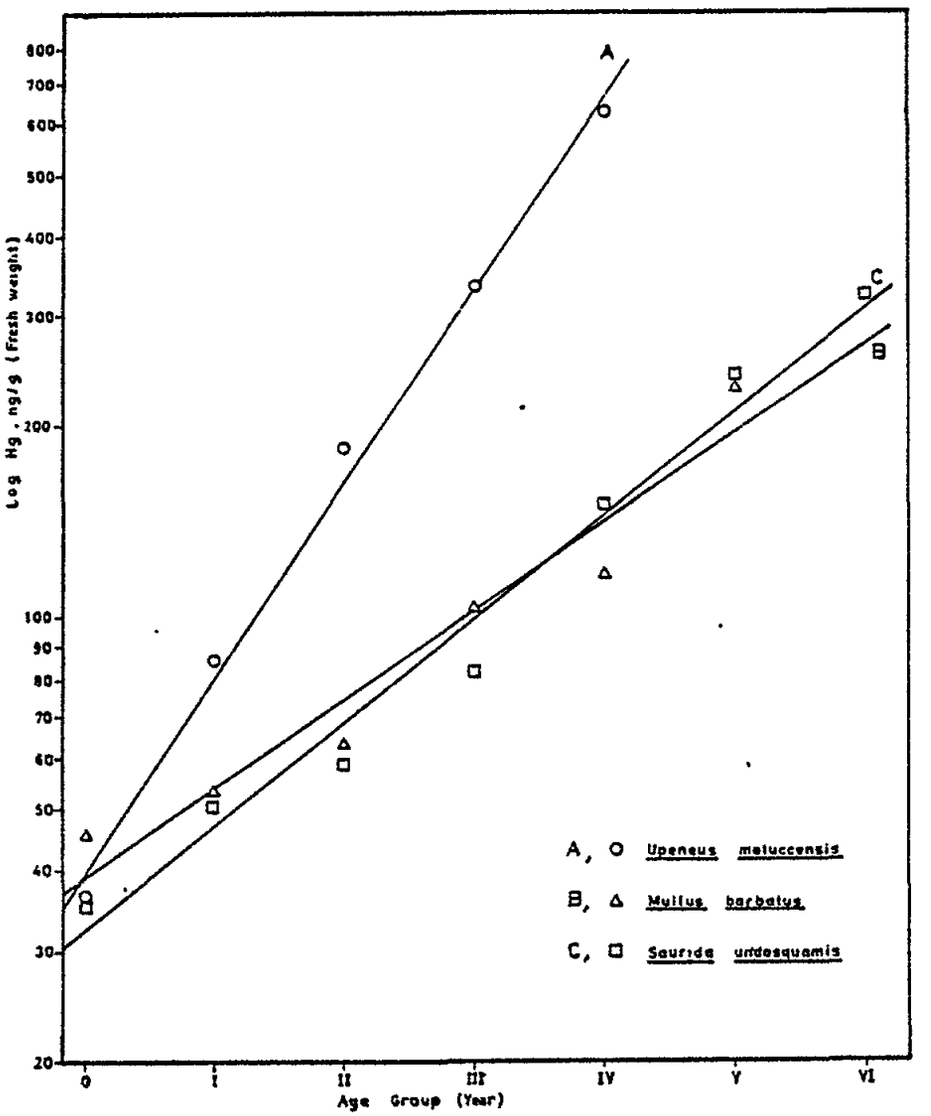


Figure 20. Mercury concentration vs age in Upeneus moluccensis, Mullus barbatus and Saurida undosquamis (Aydogdu et al., 1983).

3.5.1 Plankton

Few data have been published on mercury concentrations in plankton organisms (Tables X and XI). The samples in Table X are all plankton net samples containing mixed species of phytoplankton and zooplankton i.e. a mixture of algae, herbivorous, omnivorous and carnivorous species and, therefore, their value is very limited. The most extensive data are from Fowler (1985a) with 19 samples from the Aegean sea to Gibraltar collected with a mesh size net of 60 um and 13 samples over the same distance collected with a mesh size net of 132 um. In other areas nets with other mesh sizes have been used (60 to 500 um). All mercury concentrations are given without data on the taxonomic species composition. Depending on the mesh size of the net, samples contain a varying mixture of phytoplankton and zooplankton species. In general, nets with smaller mesh size contain phytoplankton species larger than copepods. In addition, many factors, (e.g. clogging, towing speed, net avoidance) not controllable in hauls with normal plankton nets, determine how much and what plankton species present in the sea water are actually collected. Therefore, samples taken with the commonly used plankton nets will not be representative of the actual plankton population present. Phytoplankton organisms are underestimated because many smaller organisms pass through the meshes of the nets, not to mention bacteria- and microphytoplankton which can be smaller than 1 um in diameter. But also zooplankton is misrepresented because nauplies and copepodits will pass through the 180 um mesh size nets and many species can avoid the slowly towed nets (Bernhard , 1973). Obviously the species composition of net samples taken with different mesh size nets will vary widely and therefore, mercury concentrations in samples taken with nets of different mesh size are not comparable. This great variability is reflected in the wide variation of the mercury concentrations which range from 15 to 560 ug Hg-T kg^{-1} DW in the samples from the Mediterranean and from about 100 to 1100 ug Hg-T kg^{-1} DW in selected samples from other areas, excluding the high levels from the Adriatic and the Minamata Bay. This means that Hg-T means vary by a factor of more than 40 in the Mediterranean and by a factor of 10 in the data from other areas. Even comparing plankton samples taken with nets having the same mesh size show ranges varying by a factor of 4 to 9.

It is unfortunate that so little attention has been given to the mercury concentration in individual phytoplankton and zooplankton species. Plankton serves as food for the higher trophic levels and therefore, it is of great importance to obtain information on the concentrations of different chemical mercury species in phytoplankton and zooplankton, but these must be measurements on single plankton species. Since the life span of zooplankton ranges from weeks to years, data on mercury concentration versus developmental stages are needed to evaluate the dynamics of the accumulation and release of mercury species by these organisms which present the first levels of the marine foodchain. Some species like Euphausids have a life span of four to five years (Mauchline, 1980) which are comparable to that of sardines and anchovy and data on the relative distribution between inorganic mercury and methyl mercury are needed to understand their role in the dynamics of the accumulation and release of mercury species in the marine foodchain of which they form part (see section 4.2).

The very few data, some with information on the size of the specimens, available on individual plankton species are shown in Table XI. The data in this and the previous Table X show that mercury concentrations in plankton are enriched as compared to sea water (Table VI) by a factor of 1000 to 5000, showing that the enrichment from sea water to plankton (zooplankton and phytoplankton) is the highest among all trophic levels examined.

Table X
Selected mercury concentrations (ug Hg-T kg^{-1} FW) in mixed plankton samples from the Mediterranean

Mesh size (in um)	n	dry weight mean	min	max	location	ref.
60	19	100	30	260	Aegean-Gibraltar	a
132	13	130	60	265	Aegean-Gibraltar	a
60	2		36	180	SE-Mediterranean	a
280	3	180 M	160	560	SE-Mediterranean	a
280	4	25	18	34	E-Mediterranean	a
80	2		63	115	Ionian	a
280	2		39	40	Ionian	a
60	2		50	65	Tyrrhenian	a
280	2		36	41	Tyrrhenian	a
500	5	33	15	78	NW-Mediterranean	a
220	38	105	20	130	Adriatic	b
250	7	290	160	440	Aegaean, coasts	c
333	3	2860	1860	4230	Adriatic, open	d

M = median

Table XI
Mercury concentration ug Hg-T kg^{-1} DW in plankton species

Species	length cm	sample n	mean	min	max	location	ref.
Acartia clausi	?	8	290	30	240	Elefsis Bay (Greece)	a
Euphausia spp.	?	8	140	30	240	Mediterranean	b
	1	3	80	55	100	East-Ionian-Tyrrh.	c
	1.5-2	3	175	150	190	East-Ionian-Tyrrh.	c
	>2	1	240			East-Ionian-Tyrrh	c

a: Zafiropoulos and Grimanis, 1977
b: Fowler et al., 1976
c: Fowler, 1985a
d: Kosta et al., 1978

Fowler and his colleagues (Fowler 1985a, 1985b, Aston and Fowler 1985, Aston et al., 1986) have recently maintained that no difference exists between plankton from the Mediterranean and plankton from other oceans. In fact the published data on plankton do not show any differences between Mediterranean plankton and plankton from other oceans. This is mainly due to the fact that net plankton is a mixture of organisms belonging to the first and higher trophic levels of the foodchain and that the composition of the species in a sample can be quite different to each other. In order to compare plankton organisms it is not sufficient to compare mixed plankton samples but, like in larger marine organisms, size versus mercury concentration relationships must be compared. In fact, Fowler (1985a) has shown with some very limited data that the mercury concentration of euphausids, as expected, increases with size (Table XI). Euphausids of one cm length contain on the average 80 ug Hg-T kg^{-1} DW, those of 1.5 - 2 cm length 175 and euphausids longer than 2 cm, 240 ug Hg-T kg^{-1} DW.

The only data on organic mercury in plankton are from Aboul-Dahab et al., (1986). They found in 32 mixed plankton samples that about 20% of the Hg-T was organic Hg: range 13 to 42%.

3.5.2 Seaweeds

Only a few data exist for seaweeds. In a polluted site Capone et al. (1986) determined Hg-T ranging from 22 to 550 ug Hg-T kg^{-1} FW. In the green alga Cladophora 40% of the Hg-T was methyl mercury. Salihoglu and Yemenicioglu (1986) determined Hg-T and methyl mercury in the macro-algae Caulerpa prolifera. They found a mean (n = 17) of 67 ug Hg-T kg^{-1} DW (FW/DW $\sim$ 10) with a standard deviation of about 17. Methyl mercury made up about 10 % of Hg-T.

3.5.3 Crustaceans

The mercury levels observed in crustaceans from the Mediterranean (Table XII) are surprisingly high when compared with other crustacean species from the ICES area which mainly covers the North Sea (Table XIII). In the Mediterranean area II and IV mean levels of about 1100 ug Hg-T Kg^{-1} FW have been observed in Nephrops norvegicus (Norway lobster). In the other areas for which data exist, the means are already much reduced. The uneven distribution of samples over the Mediterranean, most samples having been taken near the mercury anomaly of Mt. Amiata (area IV) and in the Gulf of Genoa (area II), gives the impression that in all Mediterranean areas such high levels should be expected. More data, especially on Hg concentration/size relationships from all areas are needed for a realistic comparison.

Baldi (1986), summarizing the results obtained by the scientists working in the Istituto di Biologia Ambientale (Siena) showed that, similarly to other marine organisms, N. norvegicus also exhibits the typical "Hg concentration/size" relationship (Fig.18). Females have higher mercury levels than males of the same weight. These crustaceans are caught at depths of between 300 and 700 m. Also Capelli and Minganti (1986) found in the Gulf of Genoa that in N. norvegicus mercury levels increase with length. It is interesting that high mercury levels are found in benthic crustaceans from areas away from industrial sources (Table XIV). Very similar "Hg concentration/size" relationships to those of N. norvegicus were observed in some of these species (H. dactylopterus and G. melastomus).

Table XII
Mean levels (ug Hg-T kg^{-1} FW) in samples (n) of crustaceans from the Mediterranean. Data from MED POL II pilot project. (Nauen et al., 1980)

area	species	n	mean	range
II	Nephrops norvegicus	129	1080 (!)	350 - 3000
IV	Nephrops norvegicus	86	1110 (!)	60 - 2900
VI	Nephrops norvegicus	7	290	190 - 360
VIII	Penaeus kerathurus	10	175	75 - 475
	Carcinus mediterraneus	13	215	115 - 345
IX	Penaeus kerathurus	7	20	10 - 50
XII	Parapenaeus longirostris	3	300	270 - 350

(!): value above 500 ug Hg-T kg^{-1} FW
Sampling areas are shown in Fig.11

Table XIII
Mercury (ug kg^{-1} FW) in crustaceans (whole body) from the Atlantic. (median of means and ranges of means)

	mean	range	location	references
brown shrimp	110	50 - 230	North Sea	ICES, 1974
brown shrimp	140	70 - 390	North Sea	ICES, 1977b
brown shrimp	80	30 - 300	North Sea	ICES, 1977c
deep sea shrimp	25	20 - 30	W. Greenland	ICES, 1977a

Table XIV
Mercury concentrations (ug Hg-T kg^{-1} FW) in benthic organisms from remote areas at about 500 m depth (Renzoni and Baldi, 1973)

sampling area / species	n	body weight in grams mean	body weight in grams range	ug Hg-T kg^{-1} FW mean	ug Hg-T kg^{-1} FW range	Hg/weight correlat.
35 km west of Isle Giglio						
Aristeus antennatus	12	5.1	2.5 - 5.1	750	400 - 800	+
Helicolenus dactylop.	15	130	20 - 280	1100	500 - 1180	+
Hoplostestus medit.	14	80	48 - 110	1800	1100 - 2600	+
Lophius budegassa	2		360 - 9000		1350 - 2750	+
SW of Isle St. Peter (SW Sardinia)						
Aristeus antennatus	28	35	20 - 60	1200	450 - 2100	+
Centrophorus granil.	3	980M	460 - 1150	1100	800 - 2100	
Lophius budegassa	3	660M	580 - 740	930M	670 - 1000	

Table XIV (cont.)

sampling area species	n	body weight in grams mean	range	ug Hg-T kg^{-1} FW mean	range	Hg/weight correlat.
NW Isle Asinara (NW Sardinia)						
Aristeus antennatus	10	27M	12 - 80	560	190 - 1200	
Galeus melastomus	4	300M	155 - 450	800M	570 - 2200	
Helicolenus dactylop.	8	100	45 - 2200	650	370 - 1200	
20 km north off Solenzara (Corsica)						
Galeus melastomus	13	320	120 - 480	1000	480 - 1300	+
Nephrops norvegicus	15	110	35 - 160	350	250 - 1250	+

M = median

3.5.4 Molluscs

Mytilus galloprovincialis or, in the few locations where not available, other mussels of the same genera, was one of the "obligatory monitoring species" in the MED POL II pilot project. As can be seen from Table XV Hg-T concentrations vary widely. This is due to the fact that sessile filter-feeder mussels are exposed to local environmental mercury concentrations which are easily influenced by natural or anthropogenic sources. In fact, the great variation in mercury concentrations within a distance of only 92 meters from a source (Fig.21) shows how the mercury concentrations in a sessile organism can change within very small distances (Leonzio et al., 1981). In using mussels for monitoring of trace elements this must be taken into consideration and the composite sample taken from various sites located at some distance from each other. Even greater variability would probably be observed if the concentration of single mussels and not those of composite samples had been reported. The mercury level determined in a homogeneous composite sample is equal to the mean value of individual specimens. Therefore, in Table XV the mean value represents the mean of "composite means" of the entire monitoring period and "min" and "max" are the minimum and maximum of "composite means" observed during the monitoring period in composite samples of more than 10 individual mussels of a standard size range.

Not all molluscs accumulate mercury (or other trace metals) to the same extent. As can be seen from Table XVI molluscs collected in the same area can reach very different levels. Food-chain relationships could be the main cause. But the reasons for the differences are not easy to identify. All molluscs in this table are filter-feeders consuming inorganic and organic particles. Venus and Tapes inhabit sandy bottoms and have low mercury levels, while Mytilus and Ostrea, living in the infralittoral zone attached to hard substrates or on hard gravel or rocky bottoms, have higher levels. The highest level is reached by Ensis which lives deeply burrowed in low-depth muddy sand beaches in the infralittoral zone. It would be interesting to analyse gastropods which prey on other molluscs. They should have higher levels than the filter-feeder they prey on. Unfortunately no size measurements are supplied with the chemical data so differences may also be due to different age.

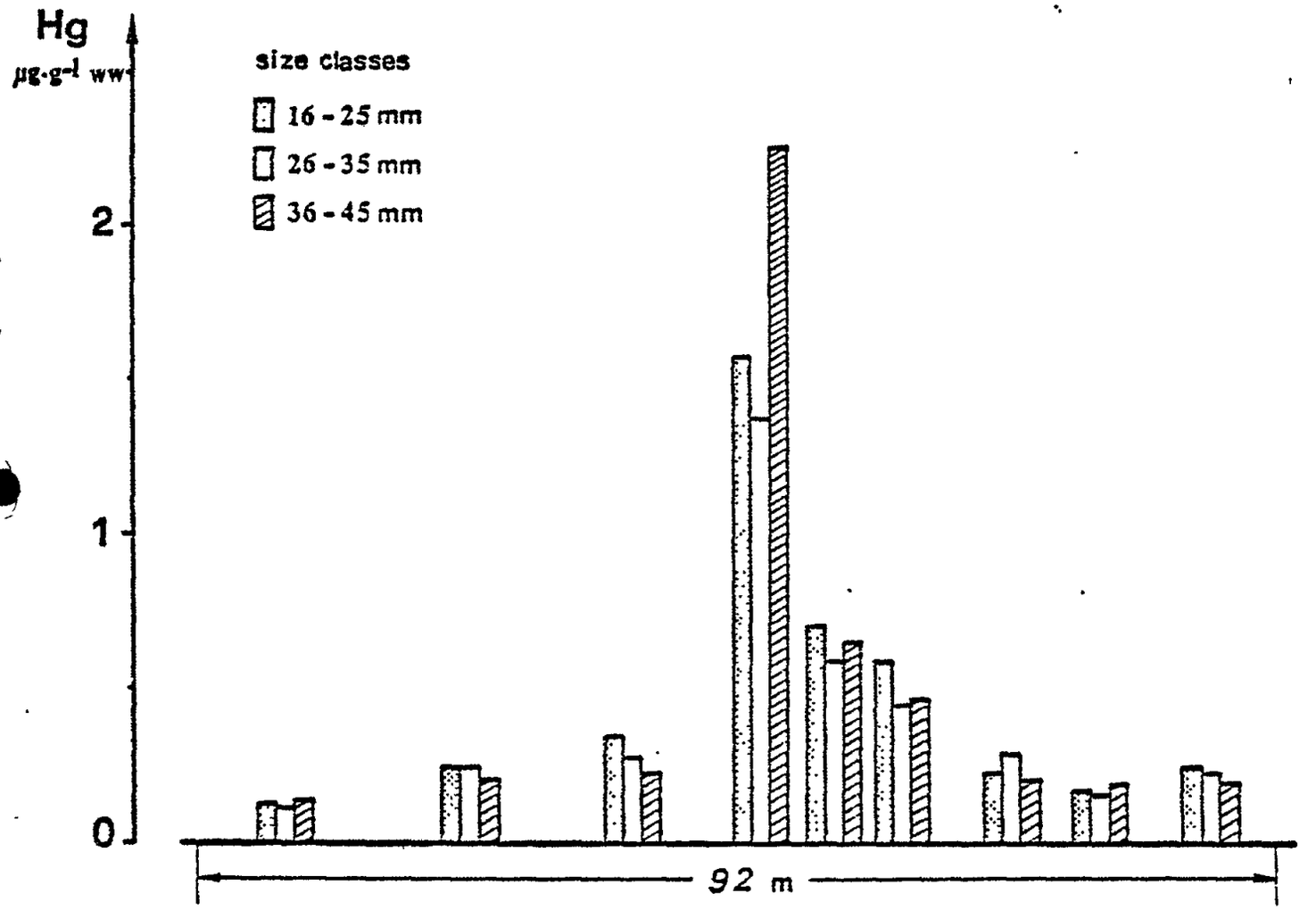


Figure 21. Variation of Hg concentrations in Mytilus galloprovincialis collected within a distance of 92 m from a source of mercury.

The Hg-T values shown in Table XV can be compared with the Mytilus edulis mercury determinations carried out in the framework of the ICES monitoring exercises (Table XVII). Examining the data in these two tables shows that the ranges of mercury levels for mussels from the Mediterranean are much wider than those from the ICES area. In one area, the Adriatic Sea (area V), the mean of 26 composite samples is 870 ug Hg-T kg^{-1} FW and the maximum is 7000 ug Hg-T kg^{-1} FW.

Recent data on mussels (M. galloprovincialis) are interesting showing that the methyl mercury (Najdek and Bazulic, 1986) and total mercury (Tusnik and Planinc, 1986) in mussels from the Yugoslav coasts decreased with increasing dry weight of the specimens. These observations are different from those made in other marine organisms where generally the mercury concentrations increase with weight. Also Hornung and Oren (1980/81) found a negative correlation between Hg-T and shell length in Donax trunculus from Haifa Bay. So far no explanation has been given.

Table XV
Overall averages of levels of mercury in composite samples (n) of molluscs. Data from MED POL II pilot project, (Nauen et al., 1980)

area	species	n	mean	range
II	Mytilus galloprovin.	37	70	15 - 400
III	Perna perna	192	76	20 - 370
IV	M. galloprovincialis	59	240	25 - 1260 (!)
V	M. galloprovincialis	26	870 (!)	25 - 7000 (!)
VI	M. galloprovincialis	12	75	35 - 145
VII	Lithophaga lithophaga	5	165	80 - 290
VIII	M. galloprovincialis	175	105	5 - 920 (!)
IX	M. galloprovincialis	4	37	20 - 50
	Donax trunculus	42	210	35 - 910 (!)
XI	M. galloprovincialis	3	190	20 - 290
XII	M. galloprovincialis	3	160	140 - 170

(!): value above 500 ug Hg-T kg^{-1} FW
Sampling areas are shown in Fig.11

Table XVI
Mercury concentrations (ug kg^{-1} DW) of the soft part of molluscs from the coastal waters of the western part of the Saronikos Gulf between Megara and Salamis Island. All samples were collected between 0 and 12 m depth. (Papadopoulou and Kanias, 1976)

species	Hg conc.
M. galloprovincialis	210
Venus verricosa	22
Glycymeris glycymeris	15
Ensis ensis	2350
Meretrix chionae	73
Ostrea edulis	320
Tapes decussatus	290

Coefficient of variance 10%, values in the lower part of the table were calculated from ash weight/dry weight ratios (Papadopoulou, pers. comm.)

For Sepia officinalis Hg-T concentrations increase with size and the concentrations in specimens from the Tyrrhenian Sea are higher than concentrations in specimens from Gibraltar and Schevingen. Comparable levels of sepias from the Chioggia (Adriatic Sea) are higher than the ones from the Tyrrhenian (Fig.16).

Table XVII
Mercury concentrations (ug Hg-T kg^{-1} FW) in Mytilus edulis from the ICES areas

mean	range	location	reference
50M	20 - 130	Norway/Netherl./England France, coast (1975)	ICES, 1977c
50M	<20 - 70	UK/Netherl./France, coast (1976)	ICES, 1977c
50	10 - 100	Canadian coast	ICES, 1980

M = median,

3.5.5 Fish

Due to its nearly ubiquitous distribution in the Mediterranean, the striped mullet (Mullus barbatus) was chosen as the species to be monitored for mercury. Since its mercury concentration is related to size (see below), the length of the specimens was prescribed. However, in this preliminary summary of the data obtained in the MED POL II pilot project, not all participants reported on M. barbatus of the prescribed size and hence the data shown in Table XVIII are not strictly comparable. From these data it appears that the M. barbatus of areas II and IV have higher mercury levels than those of other areas. The same results have been already observed for N. norvegicus. Data published before MED POL II and summarized by Bernhard and Renzoni (1977) have already shown that M. barbatus can have high mercury levels (Table XIX).

The first data, showing that mercury concentrations were higher in pelagic fishes from the Mediterranean than in the same species from the Atlantic, were published in the early seventies (Thibaud, 1971; Cumont et al. 1972). These data were later confirmed by data obtained in a collaboration between the Istituto di Biologia Ambientale (Siena), Institut fuer Angewandte Physikalische Chemie (Juelich, RFT) and ENEA, La Spezia (Baldi et al., 1979; Renzoni et al., 1979; Stoeppler et al., 1979) (Table XX). The three groups intercalibrated with each other and in addition made extensive use of reference materials supplied by NBS and IAEA (e.g. Stoeppler et al., 1979). Comparing general data from the North Atlantic with those from the Mediterranean show that in general Mediterranean fishes have higher mercury levels (Tables XVIII to XXI). In fact only the means of the mercury levels in plaice from the Atlantic are higher than 500 ug Hg-T kg^{-1} FW, while several of the Mediterranean species do exceed this level. Table XXI reports on median and range of means while the other tables give means and ranges of individual values (individual specimens and composite samples).

There exist now data for several species which allow the comparison of mercury concentrations versus weight of specimens. The clearest evidence comes from the mercury concentrations in bluefin tunas. Fig.12 shows two distinct populations: a "high-mercury" and a "low-mercury" population. The small tunas collected north of Sicily, medium size tunas from the Adriatic and from the Ligurian Sea as well as part of the large tunas caught in the tuna traps situated in Sicily and Sardinia belonged also to the "high-mercury" population. Another group of tunas belong to the "low-mercury" population. Note that these tunas were caught partly in the Strait of Gibraltar and partly off Sicily and Sardinia. The migration pattern of bluefin tuna can explain

the origin of these two tuna populations. Fisheries biologists studying these migration patterns have maintained for some time that Atlantic tunas enter the Mediterranean for spawning and leave again through the Strait of Gibraltar (e.g. Sara, 1973). "Tonnare" set to trap tunas entering the Mediterranean at Gibraltar catch these fishes from April to the beginning of May. The "tonnare" of Sicily and Sardinia catch tunas in May to June and the "tonnare" set to catch outgoing tunas in the Strait of Gibraltar catch tunas from July to August. Records kept for more than one and a half century illustrate the regularity of this migration. Tunas trapped in "tonnare" in Sicily and Sardinia caught both "low Hg" tunas and "high Hg" tunas. But samples obtained in the Strait of Gibraltar showed that the tunas caught in "tonnare" set to trap tunas entering the Mediterranean belonged only to the "low-mercury" population (Renzoni et al., 1979). Likewise, tuna caught in traps set to catch outgoing tunas belong exclusively to the "low-mercury" population. This confirms that only "low Hg" tunas enter and leave the Mediterranean. Also additional data published in the literature confirmed this observation. Establier's (1972) tunas caught in Barbate (Strait of Gibraltar) belong only to the "low-mercury" population while tunas caught in March along the north-east coast of Spain belong only to the "high-mercury" population (Ballester et al., 1978). Recently Thibaud (1979) has analysed several hundred tunas from the French Mediterranean coast and found that, with two exceptions, all belonged to the "high Hg population".

Table XVIII

Averages of mercury concentrations in fishes (ug Hg-T kg^{-1} FW) according to UNEP sampling areas (Nauen et al., 1980, modified)

area	species	n	mean	range	
II	Engraulis encrasicholus	37	140	20 - 300	
	Mullus barbatus	262	590 (!)	15 - 5600	(!)
	M. surmuletus	5	260	70 - 510	(!)
	Sarda sarda	14	1000 (!)	290 - 2300	(!)
	Thunnus thynnus	176	1100 (!)	20 - 6290	(!)
	Xiphias gladius	1	150		
III	M. surmuletus	204	90	30 - 230	
IV	E. encrasicholus	44	157	65 - 380	
	M. barbatus	195	1440 (!)	60 - 7050	(!)
	Thunnus alalunga	8	215	90 - 336	
V	M. barbatus	6	190	100 - 390	
VI	E. encrasicholus	11	145	55 - 270	
	M. barbatus	13	190	45 - 330	
	T. alalunga	8	275	60 - 400	
VII	M. barbatus	11	165	30 - 280	
	Trachurus mediterraneus	5	345	80 - 955	(!)
VIII	Merluccius merluccius	10	315	60 - 840	(!)
	Mugil auratus	16	350	85 - 2500	(!)
	M. cephalus	3	165	70 - 300	
	M. barbatus	127	175	15 - 1400	(!)
	T. thynnus	7	370	70 - 890	(!)
	Tr. mediterraneus	3	340	320 - 365	
	X. gladius	8	280	85 - 755	(!)
IX	Boops salpa	3	10	5 - 15	
	Boops boops	5	135	40 - 430	
	Mugil auratus	39	170	1 - 5600	(!)

Table XVIII (cont.)

area	species	n	mean	range	
	M. barbatus	6	55	2 - 90	
	M. barbatus	168	140	30 - 475	
	M. surmuletus	13	35	1 - 80	
	Upenaeus moluccensis	7	200	100 - 430	
	Dentex dentex	6	385	220 - 480	
	D. gibbosus	12	140	100 - 180	
	Epinephelus aeneus	4	250	100 - 400	
	M. merluccius	6	150	31 - 260	
	Pagellus acarne	7	190	70 - 340	
	Pagellus erythrinus	112	205	55 - 805	(!)
X	Saurida undosquamis	143	135	40 - 650	(!)
	Sphyraena sphyraena	7	165	80 - 245	
	Tr. mediterraneus	48	95	10 - 415	
	U. moluccensis	120	440	40 - 1120	(!)
XI	M. surmuletus	5	150	15 - 380	
	T. thynnus	1	550 (!)		
XII	M. merluccius	3	815 (!)	780 - 850	(!)
	M. barbatus	3	215	210 - 230	
	P. erythrinus	3	220	210 - 225	
	Tr. mediterraneus	3	345	340 - 350	

(!) = levels above 500 ug Hg-T kg^{-1} FW
Sampling areas are shown in Fig.11

Similar, but not so clear cut, differences in mercury levels have been observed in anchovy, mackerel and sardines (Fig.14, 15 and 13). These species are also pelagic. In all three species the specimens from Gibraltar, but also mackerel from the North Sea (from Schevingen and Helgoland), have lower concentrations than the specimens from the Mediterranean. In the Adriatic Sea, near Fano, lower mercury concentrations than in the Tyrrhenian Sea have been observed. The levels in specimens from Sanremo - Monaco lie between the Fano and the Tyrrhenian Sea ones. Similar differences were observed for the mollusc Sepia officinalis (Fig.16).

As already mentioned above, this review limits the discussion of mercury levels to the lists compiled by FAO(GFCM)/UNEP, because it is impossible to identify single mercury concentrations in scientific publications and separate them from the FAO(GFCM)/UNEP lists. Therefore, only a few data which have some significance for the general understanding of the biogeochemical cycle of mercury will be discussed below.

Studying the concentrations of total and organic mercury, Capelli et al. (1983, 1986) found that in the fish S. sarda, total mercury correlates significantly with weight and length; organic mercury ranged from 65 to 97% (median: 85%). In a more recent publication the predictions on the distribution between inorganic and methyl mercury made for the tuna model (Buffoni et al., 1982; Bernhard, 1985) could be confirmed with the data on S. sarda (Capelli et al., 1986), i. e. that the accumulation of inorganic mercury increase in the S. sarda until the fish reaches a certain length and then remains constant while methyl mercury continues to increase with specimen size (Fig.19).

Table XIX

Mercury concentrations (ug Hg-T kg^{-1} FW) and length (cm) in *Mullus barbatus* and *M. surmuletus* from the Mediterranean (Bernhard and Renzoni, 1977)

sample location	Hg concentration n	mean	range	fork length mean	range	ref.
Mullus barbatus						
Strait of Gibraltar	10n	280	50 - 615 (!)	16	12.5 - 21.5	a
Ebro - Blanes	18H	190 M	110 - 3450 (!)		9 - 20	b
La Spezia - Carrara	66n	130	20 - 760 (!)	12	8.5 - 16.5	a
Off river Arno	51n	220	60 - 900 (!)	12.2	10.5 - 18	c
North of Isle Elba	41n	1450 (!)	500 - 3700 (!)	13.2	11 - 16.5	c
Piombino, market	1H	3000 (!)		20		d
Orbetello, market	1H	1300 (!)		19		d
Isle Monte Cristo	22n	500 (!)	180 - 1750 (!)	17.4	14 - 23	c
Talamone coast	19n	200	55 - 335	14.1	13.5 - 16	c
South of Isle Giglio	61n	775 (!)	100 - 2500 (!)	13.5	9.5 - 18	c
Off North Sardina	15n	230	80 - 405	15.1	13.2 - 20.5	a
Civitamecchia to Reggio Cal. markets	6H	310 M	120 - 680 (!)	17 M	14 - 22	d
Trieste, market	1H	160				d
Chioggia - Pescara, markets	6H	250	140 - 1050(!)			d
Off Pescara	2n		55 - 145		9 - 14	f
Coast of Israel	3H	220 M	50 - 290	14 M	11 - 16	g
Isle Pilau, Tunis	10n	240	90 - 560 (!)	13.4	10.5 - 17	a
Mullus surmuletus						
Golf of Cadiz	2n		80 - 80		18 - 21	e
Strait of Gibraltar	4n	280	190 - 390	18.4	16.5 - 21.5	a
Ebro - Blanes	3H	180 M	160 - 500		10 - 20	b
Vada (Livorno)	6n	630 (!)	+ - 600			c
Off North Sardina	6n	150	60 - 320	~12		a
Trapani, market	8n	90	70 - 110	14.8	14 - 15.5	c

sample size: H = composite sample, n = individually analysed samples, M = median, (!) = levels above 500 ug Hg-T kg^{-1} FW

References: a: Stoeppler *et al.*, 1979 b: Ballester *et al.*, 1978, c: Renzoni and Baldi, 1973 d: Ciusa *et al.*, 1973, e: Establier, 1973 f: Caracciolo *et al.*, 1972,

Aydogdu *et al.* (1983) investigated mercury concentrations in the fishes *Upeneus moluccensis*, *Saurida undosquamis* and *M. barbatus*. No difference in mercury content between males and females of the same size were detected. For all three species a significant correlation of mercury level with size was observed (Fig.20). The authors point out that the mercury levels increased more with size in *U. moluccensis* than in *S. undosquamis*, although *S. undosquamis* feeds on *U. moluccensis*. Certainly the food-chain of *S. undosquamis* needs checking. According to FAO species identification sheets *S. undosquamis* "is a carnivorous species feeding mostly on fish such as anchovy and red mullets (Fischer, 1973). Hornung *et al.* (1984), citing unpublished data from Zismann, state that in the stomach of *S. undosquamis*, residues of *E. encrasicholus* (anchovy), *Sardinella aurita* and *Macrura* species (decapods) have been found. *U. moluccensis* is not mentioned, although the areas investigated

Table XX
Mercury concentrations (ug kg^{-1} FW) in some pelagic fishes from the Mediterranean and the Atlantic (Bernhard and Renzoni, 1977)

Species	n	Hg concentration mean	Hg concentration range	size in cm mean	size in cm range	sample location
Engraulis encrasicholus	(1H)	50			(12 -13)	NW African coast
	(1H)	110			(13.7-15)	NW African coast
	(1H)	60			(11 -12.5)	Gulf of Cadiz
	(3H)	400 M	(130- 660)		(15 -16)	Tyrrhenian
	(2H)		(280- 480)		?	R. Calabria
	(2H)		(160- 300)		?	Trieste (?)
	(1H)	240			?	St. Benedetto
	(2n)		(160- 160)		(13 -14)	Off Pescara
	(6n)	310	(100- 400)		(11 -15)	Off Bisceglie
	(9H)	140	(70- 215)	14.7	(12.2-16.5)	Off Rovinj
Sardina pilchardus	(2H)		(50- 70)		(11.5-15.5)	NW Africa
	(5H)	50 M	(50- 70)		(14 -16.5)	NW Africa
	(7H+5n)		(20- 760)		(10 -20)	NE Spain
	(4n)	175 M	(110- 315)	14 M	(9 -18)	Off Pescara
	(13n)	160 M	(36- 400)		(11 -19)	SW Adriatic
	(10H)	430 M	(200- 870)		?	W Adriatic
	(11H)	100	(40- 135)	15.5	(12.9-17.7)	Off Rovinj
Sardinella aurita	(5-7H)	80 M	(30- 120)		(11.2-17.2)	Israeli coast
Scomber colias S. scomber	(1H)	80			(31 -31.5)	NW Africa
	(3n)	100			(25 -28)	Cadia
	(4n)	360 M	(100- 500)		(25 -30)	NE Spain
	(3H)	580 M	(250- 680)		(28 -32)	Tyrrhenian
Thunnus thynnus	(6n)	720 M	(460- 910)	205 M	(200-270)	Cadiz
	(3n)	1700 M	(1650-2650)	150 M	(140-200)	Ebro delta
	(25n)	850 M	(>10-1750)		(160-220)	SW Sardinia
	(155n)	1650 M	(>10-3250)		(80-220)	SW Sardinia
	(2n)		(480- 560)		?	R. Calabria
Xiphias gladius	(5n)	1300 M	(1000-2000)	large		Off Cadiz
	(4n)		(1200-2450)		?	Off R. Calabria

M = median; H = composite sample; n = number of individual analysed in homogenate sample or individual sample; FW = fresh weight

Table XXI

Mercury concentrations (ug Hg-T kg^{-1} FW) in some fish (muscle)
Selected data from ICES areas and Mediterranean.
Median of means and range of means

	median	range	location	references
plankton feeder				
herring	40	20-240	N.Sea	ICES, 1974
herring	20	10- 35	N.Atl.	ICES, 1977a
herring	40	10- 23	Irish coast	ICES, 1980
"typical"	40			
sardine	60	6- 80	N.Atl.	ICES, 1977a
sardine	250	150-390	Medit.	UNEP, 1980
sprat	65	60-140	Irish c.	ICES, 1980
capelin	10	10- 30	N.Atl.	ICES, 1977a
feed on invertebrates				
cod	100	30-480	N.Sea	ICES, 1974
cod	100	60-300	N.Sea	ICES, 1977a
cod	40	40- 50	N.Atlantic	ICES, 1977a
cod	260		Irish Sea	ICES, 1980
cod	140	70-370	Irish Coast	ICES, 1980
cod	70	50-140	NW-Atlantic	ICES, 1977a
cod	80	70- 90	NW Atlantic	ICES, 1980
"typical"	100			
feed on crustaceans and fish				
hake	90	30-130	N.Atlantic	ICES, 1977a
hake	30-850		Mediter.	UNEP, 1980
haddock	50	20- 60	Irish coast	ICES, 1980
haddock	50		NW Atlantic	ICES, 1980
whiting	80	30- 90	Irish coast	ICES, 1980
Greenl.halibut	40	30- 50	N.Atlantic	ICES, 1977a
plaice	90	20-260	N.Sea	ICES, 1974
plaice	120	20-500	N.Atlantic	ICES, 1977a
plaice	25	10- 80	Irish coast	ICES, 1980
"typical"	90			
sole	150	50-320	N.Atlantic	ICES, 1977a

by Aydogdu et al. (1983) and Zismann are relatively near to each other. A seasonal fluctuation of the mercury levels was observed in U. moluccensis which is brought into association with mercury inputs from rainfall and the application of mercurial pesticides. It would be interesting to model this pathway in order to see if the amounts introduced into the sea from these two sources are sufficient to increase seasonally the mercury level in this fish.

3.5.6 Marine birds

The data on mercury levels in marine birds are still very few and very unevenly distributed over the Mediterranean area. The mercury levels determined in tissues of sea-birds from different sites in the Mediterranean are shown in Tables XXII, XXIII and XXV. Additional mercury levels are shown together with selenium levels in Table XXVIII. The birds caught in the highly polluted Lagoon of St. Gilla near Cagliari (Fig.22) had much higher concentrations than those from the remote lagoon Corru-e'-s'-ittiri further north in Sardinia. Birds from the Lagoon of Marano in the northern Adriatic had intermediate levels. The highest levels were observed in the liver and kidney. The fish-feeding Phalacrocorax carbo (cormorant) had higher mercury levels only in the St. Gilla Lagoon but in the Lagoon of Marano the mercury concentrations in the diversified feeder P. nigricollis (black-necked grebe) were higher (see below the influence of food-chain position on mercury levels). The different ages of the birds may be one reason. Also, the time of sampling has an influence on the mercury concentrations observed.

Table XXII
Mercury concentrations (ug Hg-T kg^{-1} FW) in eggs of marine birds (Larus and Anas) (Bijleveld et al., 1979)

species	n	mean	range	sampling location
L. audouinii	3	760	630 - 950	Chafarinas I.
L. audouinii	4	1120	879 - 1390	Balearics
L. audouinii	1	1200		Balearics
A. monachus	1	150		Balearics

Table XXIII
Mercury concentrations (ug Hg-T kg^{-} FW in different tissues of Larus (marine bird) (Vannucci et al., 1978)

species	n	mean	range	sampling location
L. ridibundus				
muscle	5		950 - 1800	Tyrrhenian coast
liver	5		1320 - 2300	Tyrrhenian coast
kidney	5		620 - 1400	Tyrrhenian coast
brain	1	650		Tyrrhenian coast

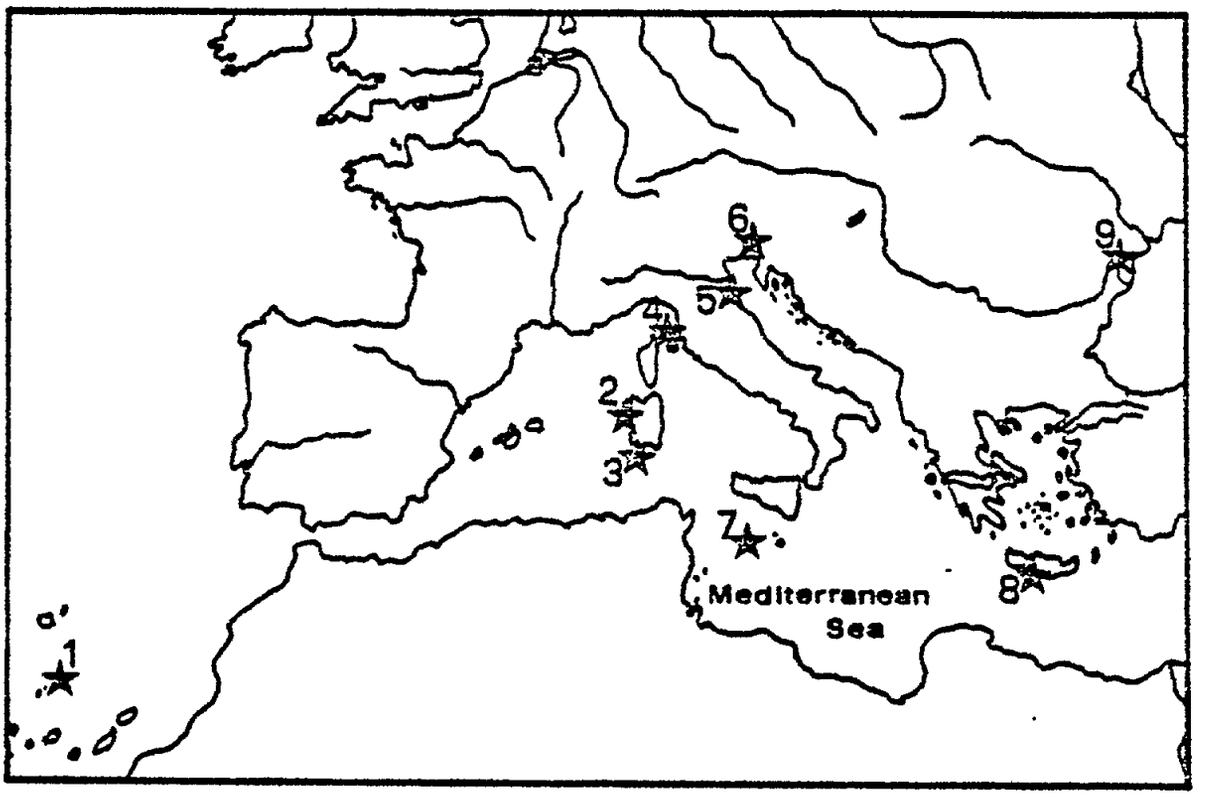


Figure 22. Sampling locations of marine birds collected by Renzoni's group (Leonzio et al., 1986) 1 Selvagens Island (Madeira) 2=S. Gilla Lagoon (Cagliari) 3=Mistras Lagoon 4=Isle Elba 5=Comacchio 6=Marano Lagoon (Grado) 7=Linosa Island 8=Dagonada (Crete) 9=Danube delta.

Table XXIV
Bird species monitored for mercury according to their feeding habits (Leonzio et al., 1986)

Primary consumers (almost no fish in their diet)	Anas platyrhynchos
	Fulica atra
	Himantopus himantopus
Secondary consumers (low fish content in their diet)	Podiceps migaricollis
	Egretta garzetta
	Larus ridibundus
	L. genei
	L. argentatus
	Gelochelidon nilotica
Tertiary consumers (high fish content in their diet)	Procellaria diomedea
	Phalocrocorax carbo
	P. pygmeus
	Pelecanus onocrotalus
	L. audouinii
	Sterna hirundo
	S. albifrons

Table XXV
Mercury concentrations (ug Hg-T kg^{-1} FW) in eggs and liver of Mediterranean birds (Leonzio et al., 1986)

	primary consumer			secondary consumer			tertiary consumer		
	n	mean	SD	n	mean	SD	n	mean	SD
Selvagens, Madeira									
eggs							24	400	± 185
liver							3	2440	± 460
Mistras									
eggs							6	1580	± 1000
liver							3	2180	± 2000
S. Gilla									
eggs				7	610	± 365	6	7760	± 4740
liver	2	5760		14	18800	± 13080	7	39420	± 19680
Elba									
eggs				25	585	± 345	16	2140	± 680
liver				4	1340	± 160			
Comacchio									
eggs	3	160	± 20	32	295	± 110	29	770	± 630
liver				4	2320	± 1680			
Marano									
eggs	10	150	± 150	21	440	± 110	22	2040	± 700
liver				8	1880	± 440	3	8480	± 8580
Linosa									
eggs							5	1300	± 380
liver							5	17240	± 19840
Dagonada									
eggs							2	1060	
liver							5	14960	± 10180
Danube, delta									
eggs	4	60	± 20	21	155	± 80	29	820	± 400

Note: the data have been converted into fresh weight by dividing dry weight by a factor of 5. Some of these summarized data are shown individually in Table XXVIII. The sample locations are shown in Fig.22

Birds collected shortly before their departure (April) from the Lagoon of Marano to their breeding areas in northern and central Europe had higher mercury levels (and chlorinated hydrocarbon levels) in their liver than birds collected shortly after their return from the north (October) in the lagoon. During the six months of their absence from the lagoon they had lost about 75% of the mercury previously accumulated in the liver and then regained about 85% of the original levels during the next six months of their presence in the lagoon. The data are not strictly comparable because the birds were not

tagged. This is also illustrated by the fact that the April 1983 levels are not equal to the ones of April 1984, but the data show nevertheless that the biological half-time of mercury in the liver of these birds must be relatively short.

Renzoni and his collaborators have grouped all their previous data according to the birds' foodchain relationships (Leonzio et al., 1986). The authors distinguished between primary consumers which have almost no fish in their diet, secondary consumers with a low content of fish and tertiary consumers with a high percentage of fish in their diet (Table XXIV). The results show that both in eggs and liver tertiary consumers have higher mercury levels than secondary consumers which in turn have higher levels than primary consumers (Table XXV). The lowest levels are observed in birds from a non-Mediterranean area (Madeira). The highest levels are found in eggs and livers of birds feeding in the highly polluted S. Gilla Lagoon (section 3.9). The mercury anomaly of Mt. Amiata influenced the levels, as it does those of fishes, in the birds from Elba. The birds from Marano (Grado) could be influenced by the Idrija mercury anomaly, but, in the other locations too, high mercury levels have been observed. A comparison of the mercury levels in the muscle tissue of the birds would probably have been more indicative than in liver and eggs since both these tissues are more subject to fluctuations in the mercury intake. Furthermore, it would be advantageous that data on birds could be compared with the mercury levels in the muscle of other marine organisms. When data of the same species and tissues are available the specimens from non-Mediterranean sites had much lower concentrations than the Mediterranean specimens (Fig.23).

3.5.7 Marine mammals

Remarkably high mercury concentrations were observed in dolphins, porpoises and whales from the Mediterranean and the Atlantic (Table XXVI). The concentrations in the liver are especially impressive (maximum value: circa 1 g Hg kg^{-1} FW). Here again smaller animals of the same species have lower concentrations. Mercury concentrations in muscle tissue are higher than in lipids. Organs such as the liver, heart, spleen and kidney have the highest concentrations. The limited data on specimens of the same species seem to indicate that also here the mercury concentrations in Mediterranean specimens are higher than in the specimens from the Atlantic. In the liver of marine mammals low methyl mercury percentages (2 to 10% of Hg-T) are found. This may indicate a demethylation in the liver.

Table XXVI

Mercury concentrations (ug Hg-T kg^{-1} FW) in pelagic mammals from the Mediterranean and the Atlantic (Bernhard and Renzoni, 1977)

sample location Species	sex age	size cm	concentration in muscle	fat	liver	sample location and date
Atlantic:						
Phoncena phocoena	M adult	172	6750	770	61000	Rochelle (V/1972)
Delphinus delphis	F young	125	890	710	900	Ile de Re (VII/1972)
	F adult	140	600	20	980	Pyrenees Atl. (VII/1973)
	F adult	165	910	27	1430	Pyrenees Atl. (IV/1973)
	M adult	185	1840	220	220	Landes (VII/1973)
	F adult	210	6250	2650	4850	Gironde (V/1972)
	M >15 y	220	2180	2780	66700	Tropic Atl. 1975

Table XXVI (cont.)

Mediterranean:						
D. delphis	M >12 y	205	1450	3900	604000	Mediterranean 1973
Stenella coeruleo.	F adult	168	1950	1800	39850	Iles d'Hyeres (II/1973)
	M adult	210	23800	6000	344900	Lavandou (Var) (IV/1973)
Grapus priseus	F adult	300	16000	1700	905000	Cacalastre (Var)
Tursiops truncata	?	140*	41000	-	-	Pescara (1971)
	M 6-18m	160	2200	310	14600	Mediterranean (1973)
	M >25 y	330	24000	4400	293000	Mediterranean (1973)
Atlantic:						
Globicephala	F young	300	640	50	900	Gironde (IV/1972)
melaena	M adult	490	5300	860	860	Charente (VIII/1972)
Mediterranean:						
G. melaena	F adult	390	13100	1290	670000	Cros de Cagne (Alp. Mar.) (VII/1973)
Physeter catodan	M ?	800	4050	3150	-	Bonifacio (Cors.) (XII/1972)

*) size in kg
M = male; F = female; y = year; m = month
(Data compiled from Thibaud and Duguy (1973), Martoja and Viale (1977) and Caracciolo et al., (1972)

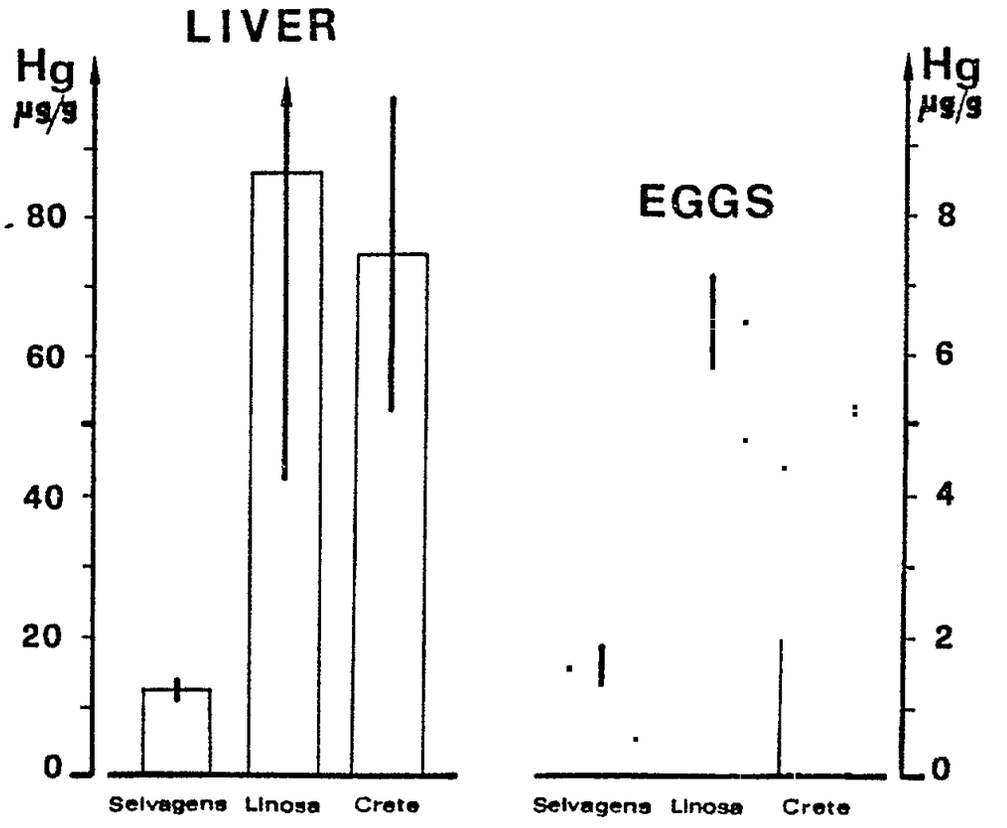


Figure 23. Mercury concentrations in liver and eggs of C. diomedia from Madeira (Selvagens), the Isle of Linosa (Sicilian Channel) and Crete (Leonzio et al., 1986). For locations see Fig.22 .

3.6 Organic mercury

Despite its great importance not many data exist on organic mercury in Mediterranean biota. Aboul-Dahab et al. (1986) found in 32 mixed plankton samples that about 20% of the Hg-T was in the organic form (range 13 to 42 ug Hg-T kg^{-1} FW). Capone et al. (1986) determined that in the green alga Cladophora from a contaminated site 40% of the Hg-T was methyl mercury. Salihoglu and Yemenicioglu (1986) determined Hg-T and methyl mercury in the macro-algae Caulerpa prolifera. They found a mean (n = 17) of 67 ug Hg-T kg^{-1} DW (FW/DW $\sim$ 10) with a standard deviation of about 17. Methyl mercury made up about 10% of Hg-T.

Vukadin et al. (1986) observed that the percentage of Hg-T as methyl mercury was lower in mussels from a contaminated site than in mussels from an uncontaminated site (see section 3.9). Unusual results were obtained by Najdek and Bazulic (1986). These authors found that the methyl mercury concentration decreased with increasing size of the mussels (see section 3.5.4).

Capone et al. (1986) found that in the crustacean Gammarus 62% of the Hg-T was methyl mercury. In the crustaceans Penaeus kerathurus and Portunus pelagicus Salihoglu and Yemenicioglu (1986) found that 99% of the Hg-T was methyl mercury. Capelli et al. (1986) observed that the organic mercury in shrimps (Nephrops norvegicus) from the Gulf of Genoa was positive correlated with weight and averaged about 60%.

In fishes from the Ligurian Sea, Capelli et al. (1986) found positive correlations with weight in Boops boops, Merluccius merluccius and Scomber scombrus. The mean percentage of organic mercury ranged from 58% to 67%. Capone et al. (1986) determined that in the fishes Aphanius and Anguilla 90% and 54% of the Hg-T respectively was on the average organic mercury. The low percentage in Anguilla is somewhat surprising. Salihoglu and Yemenicioglu (1986) found methyl mercury percentages to be high in the fish Mugil auratus, Mullus barbatus, and Suarida undosquamis (95 to 100%); only in Upeneus moluccensis the percentage was 60%. Capelli et al. (1986) investigated Hg-T and organic mercury in Sarda sarda. In this fish the organic mercury increased with size reaching in the largest specimens ($\sim$ 4 kg FW) about 95% of the Hg-T.

Thibaud (1986) showed that in 100 muscle samples of the bluefin tuna from the Mediterranean methyl mercury (and Hg-T) increased with body weight of the tuna to about 75% of Hg-T while selenium levels remained almost constant.

Halim et al. (1986) present some interesting results. In the flesh of six fish species (M. barbatus, S. vulgaris, B. boops, S. pilchardus, E. alleteratus, R. halavi) the organic mercury concentrations in flesh range from about 70 to 85% of the Hg-T and the concentration of organic mercury in these organisms increased with body weight (Aboul-Dahab et al., 1986); but in the liver of these fishes the percentage of organic mercury is only about 7 to 23%. Eganhouse and Young (1978) found only an average of 9.6% methyl mercury in the liver of the Dover sole (Microstomus pacificus).

These data are in accordance with the observations that the methyl mercury percentage increases with the trophic level of the organism and that methyl mercury increases during life time. The exceptions (mussels) observed need further study. In other oceans, the bulk of mercury in fish occurs as methyl mercury (Westoeoe and Ohlin, 1975). Virtually all the mercury in large

predatory fish such as swordfish is also present as methyl mercury (Freeman et al., 1978), although merlin is an exception with only 10% of the Hg-T as methyl mercury in muscle tissue (Shultz et al., 1976).

3.7 Mercury/selenium relationship

The findings that selenium acts antagonistically to mercury and that in some organs of man and marine organisms high mercury levels are associated with high selenium concentrations has stimulated the simultaneous collection of mercury and selenium concentrations in marine organisms and their environment. Kosta et al. (1975) and Koeman et al. (1975) have shown that for man and for marine mammals in some tissues (liver and kidney) the Hg/Se molar ratio can be about one, examining, however, other marine organisms and other organs the molar ratio is in general far from one (Tables XXVII and XXVIII). Only in some bird tissues (liver and brain), molar ratios near to one have been observed (Fig.24). Loenzio et al. (1982) have recently found that in the fish Mullus barbatus the sum of mercury plus selenium expressed in moles are linear-related to length (age) of the fish (Fig.25 and 26). It seems that even relatively low mercury levels were "compensated" with additional high selenium levels. Recalculating earlier data from Freeman et al. (1978), Leonzio et al. (1982), could show that the sum of molar Hg + Se concentrations in the Atlantic swordfish is also positively correlated with length. It would be interesting to investigate this phenomenon in more species to see if it is general.

Table XXVII
Mercury and selenium concentrations (ug kg^{-1} FW) in marine organisms from the Mediterranean

		Hg		Se		Hg/Se	
	n(*)	mean	range	mean	range	ratio	ref.
Plankton							
Adriatic S.	H22	130	50 - 680	3700	1900 - 6400	0.01	a
N. norvegicus							
Adriatic S.	5	1650	1100 - 2600	1430	390 - 2700	0.47	a
Murex sp.							
Adriatic S.	H2	30	15 - 45	48	390 - 2700	0.25	a
M. galloprov.							
Monaco	H1	330		890		0.15	b
Kastella B.							c
polluted	5H10	10000M	7850 - 2040	980M	820 - 2100	4	
MeHg		28M	14 - 43	same sample			
Ciove, unpoll.	5H10	400M	300 - 750	530M	480 - 1210	0.3	c
MeHg		16M	9 - 30	same sample			
Strunjan,							c
unpolluted	4H10	50M	30 - 90	900M	500 - 1270	0.02	
Elefsis Bay							d
	H10	150	63 - 215	405	310 - 550	0.15	
Ostrea edulis							
Adriatic S.	H1	40		610		0.03	a
Octopus vulgaris							
Adriatic S.	1	70		370		0.07	a

Table XXVII (cont.)

Mustelus vulgar.								
Adriatic	3	1850	890 - 3550	460	410 - 550	1.6	a
Raja clavata								
Adriatic	1	670		450		0.6	a
Torpedo marmorata	adult						
Adriatic S.							
liver	1	1150		1980		0.2	
kidney	1	400		670		0.2	
tail muscle	1	650		260		1	
Torpedo marmorata							a
young liver	2	165	150 - 180	225	220 - 230	0.3	
tail muscle	2	200	180 - 220	350	280 - 420	0.2	
M. barbatus							d
Kissamos Gulf	H2	62		185		0.13	
Gera Gulf	H4	69		350		0.08	
Saronikos G.	H288	290		470		0.24	
M. surmuletus							d
Kissamos G.	H5	80		180		0.17	
P. acarne							d
Kissamos G.	H6	30		450		0.03	
Gera Gulf	H11	137		340		0.16	
Antikyra G.	H2	180		770		0.1	
Boops boops							d
Kissamos Gulf	H10	20		430		0.02	
Antikyra Gulf	1H	110		1030		0.04	
Serranus scriba							d
Gera Gulf	1	230		170		0.5	
S. cabrilla							d
Antikyra Gulf	H10	130		550		0.1	
S. scorfa							d
Antikyra	1	360		750		0.2	
E. guaza							d
Kissamos Gulf	1	270		620		0.2	
D. annularis							d
Gera Gulf	H3	120		530		0.1	
P. erythrinus							
Adriatic coast	2	660	470 - 860	560	480 - 640	0.45	e
Gera Gulf	H2	48		470		3.8	d
Mugil labeo							d
Gera Gulf	H2	490		120		1.6	
Maena smaris							d
Gera Gulf	H3	140		570		0.1	
C. conger							d
Antikyra Gulf	H6	250		880		0.1	
T. mediterraneus							d
Kissamos Gulf	H2	70		370		0.1	

n(*): H followed by a number n stands for composite sample of n specimens
M = median
a = Kosta *et al.*, 1978
b = Fowler *et al.*, 1976; Fowler and Benayoun, 1977
c = Tusek-Znidaric *et al.*, 1983
d = Grimanis *et al.*, 1981, 1977
e = Stegnar *et al.*, 1979

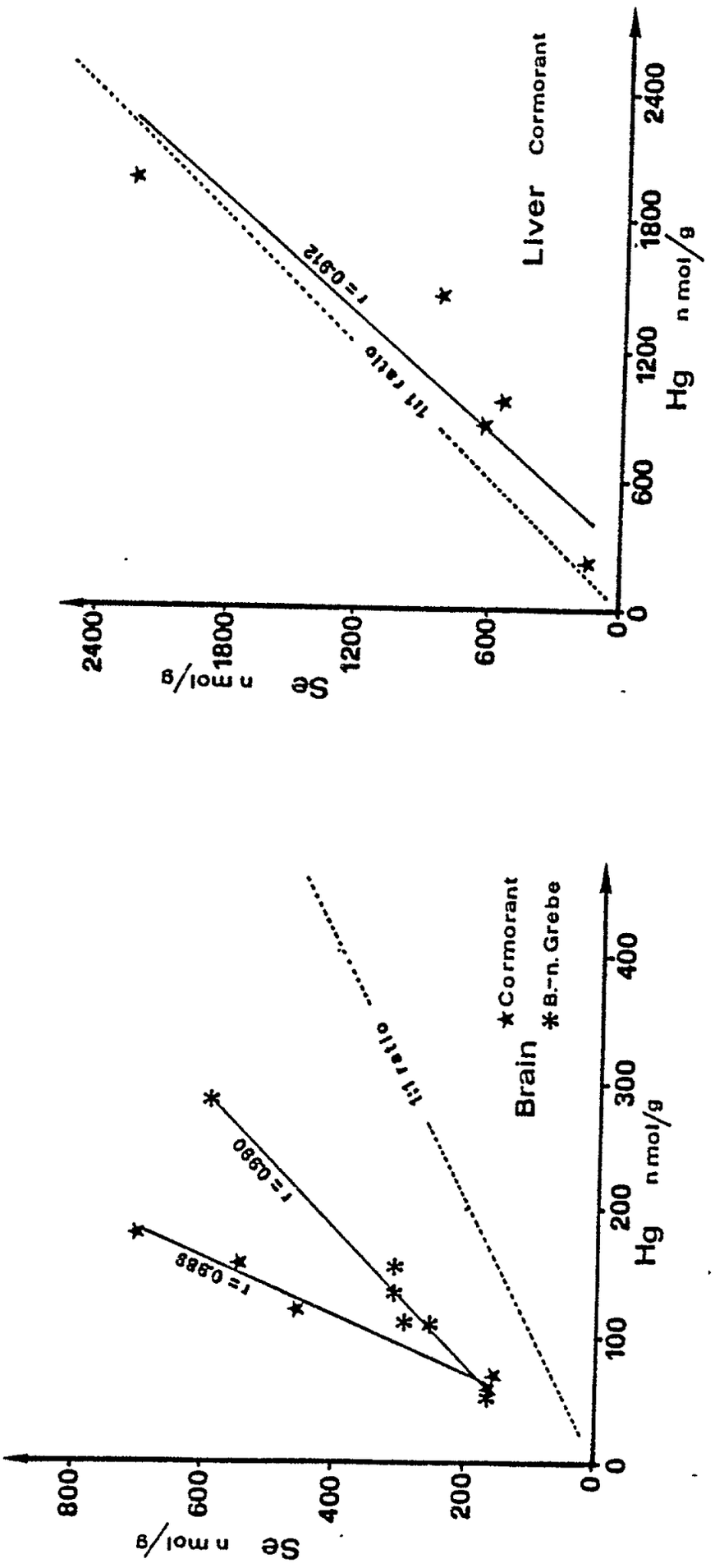


Figure 24. Relationship between selenium and mercury molar concentrations in brain and liver of marine birds (Cottiglia et al., 1983).

Table XXVIII

Mercury and selenium concentrations (ug kg^{-1} FW) and Hg/Se molar ratio in marine birds (Cottiglia et al., 1983) and their eggs (Renzoni et al., 1984)

	n	Hg-T mean	Hg-T SD	Se-T mean	Se-T SD	molar Hg/Se of mean value
Eggs:						
L. argentatus m.	4	(545	+- 185)	(515	+- 215)	0.4
E. garzetta	9	(530	+- 130)	(950	+- 100)	0.2
N. nycticorax	8	(320	+- 50)	(1080	+- 450)	0.1
S. hirunda	22	(2030	+- 710)		-	
R. avosetta	5	(125	+- 35)	(210	+- 60)	0.2
L. ridibunda	17	(350	+- 130)	(480	+- 160)	0.3
G. nilotica	15	(250	+- 110)	(300	+- 95)	0.3
S. hirundo	13	(450	+- 230)	(505	+- 350)	0.4
S. albifrons	16	(1350	+- 960)	(440	+- 125)	1.2
L. genei	33	(445	+- 160)	(560	+- 435)	0.3
G. nilotica	7	(3045	+-1325)	(1410	+- 530)	0.85
S. albifrons	6	(6850	+-4665)	(500	+- 335)	5.4
S. albifrons	6	(1670	+-1040)	(240	+- 90)	2.7
Adults:						
Phalacrocorax carbo S. Gilla						
fat	7	(700	+- 400)	(1000	+- 1000)	0.3
uropy. gland	7	(4400	+- 250)	(1200	+- 880)	1.4
muscle	7	(6750	+- 2000)	(1750	+- 1000)	1.5
brain	7	(5100	+- 2600)	(3700	+- 4350)	0.5
liver	7	(39400	+- 23675)	(10900	+- 11750)	1.4
kidney	7	(27575	+- 17000)	(6600	+- 6550)	1.6
Podiceps nigricollis S. Gilla						
fat	14	(430	+- 235)	(924	+- 925)	0.2
uropy. gland	7	(4845	+- 1950)	(2900	+- 1830)	0.7
muscle	7	(5800	+- 1925)	(2300	+- 1830)	1
brain	7	(5425	+- 2120)	(3545	+- 1490)	0.6
liver	7	(18795	+- 13085)	(4220	+- 2034)	1.8
kidney	7	(14980	+- 7130)	(4955	+- 4095)	1.2
Phalacrocorax carbo Lagoon of Marano						
fat	3	(200	+- 95)	(545	+- 710)	0.1
uropy. gland	3	(1450	+- 1230)	(865	+- 750)	0.7
muscle	3	(2515	+- 2445)	(1175	+- 1000)	0.9
brain	3	(1730	+- 1550)	(1190	+- 395)	0.6
liver	3	(8485	+- 8575)	(7540	+- 9570)	0.4
kidney	3	(8430	+- 3680)	(3300	+- 845)	1
Podiceps nigricollis Lagoon of Marano						
fat	5	(230	+- 60)	(605	+- 725)	0.2
uropy. gland	5	(2050	+- 700)	(1050	+- 850)	0.8

Table XXVIII (cont.)

	n	Hg-T mean	SD	Se-T mean	SD	molar Hg/Se of mean value
muscle	5	(2325	+- 770)	(890	+- 200)	1
brain	5	(2980	+- 740)	(1100	+- 610)	1
liver	5	(11580	+- 2280)	(3115	+- 355)	1.5
kidney	5	(7010	+- 1380)	(2150	+- 710)	1.3
Phalacrocorax carbo						
Lagoon of Corru-e'-s'ittiri						
fat	3	(82	+- 80)	(205	+- 120)	0.2
uropy. gland	3	(380	+- 250)	(335	+- 95)	0.5
muscle	3	(545	+- 40)	(250	+- 250)	0.9
brain	3	(545	+- 410)	(250	+- 75)	0.9
liver	3	(2190	+- 2000)	(515	+- 170)	1.7
kidney	3	(2030	+- 1440)	(565	+- 145)	1.4

Note: concentrations in brackets are FW estimations derived from DW concentrations assuming FW/DW = 5

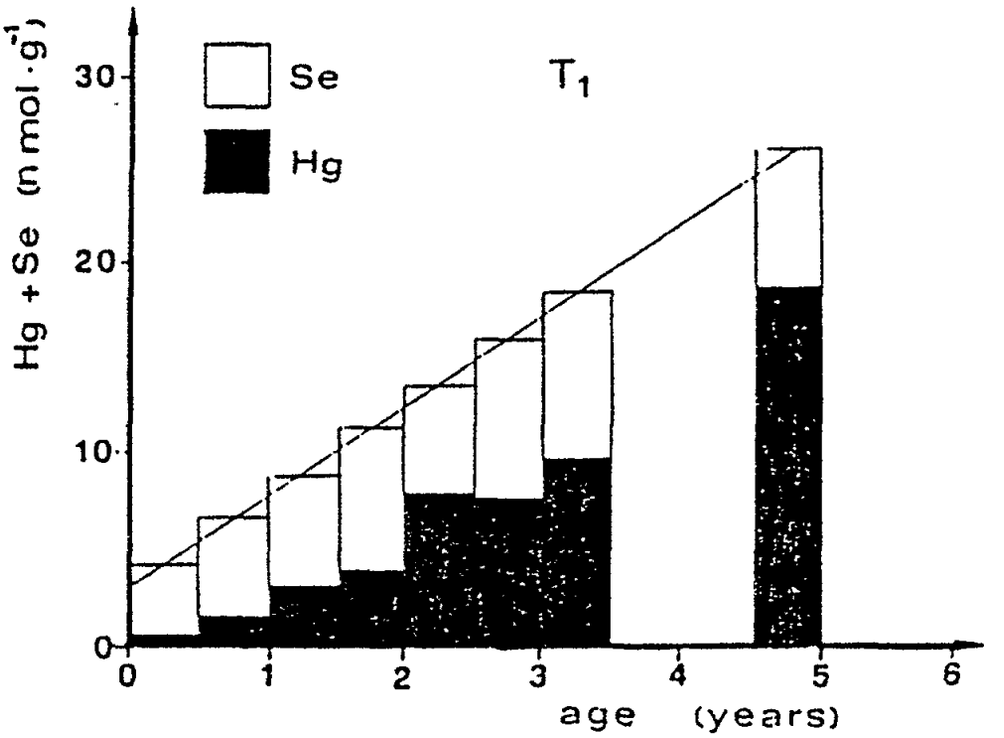


Figure 25. Mercury and selenium in Mullus barbatus from an area high in mercury (Leonzio et al., 1982).

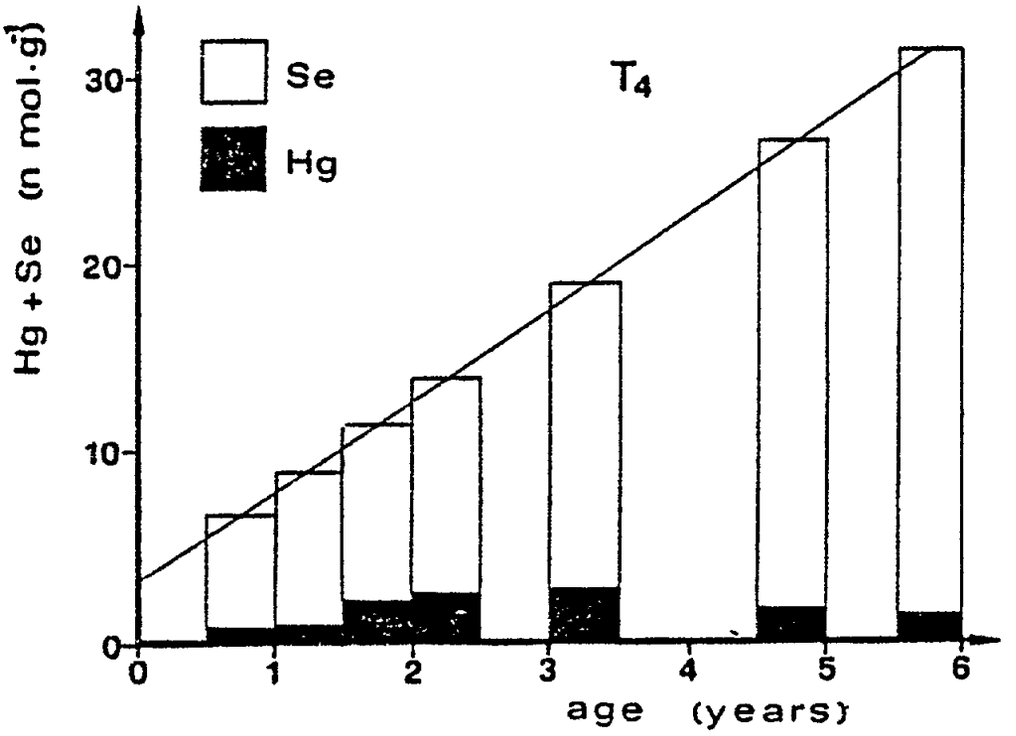


Figure 26. Mercury and selenium in Mullus barbatus from an area low in mercury (Leonzio et al., 1982).

3.8 Levels in ecosystems under the influence of natural mercury sources

Levels higher than background were observed in various components of the marine environment near well-known mercury anomalies of the Monte Amiata area. Dall'Aglio (1974) investigated this anomaly showing clearly that the sediments of rivers draining the anomaly contained sediments with high mercury levels (Fig.27). The water of these rivers had high mercury concentrations only near the mining area e.g. in the water of the upper part of Paglia river which flows into the Tiber. Downstream from the mining area the mercury concentration in the river water diminished rapidly, because the dissolved mercury is readily absorbed by sediment and suspended matter. Near the coastline, the mercury concentrations in the river water fell below 0.05 ug Hg l^{-1}, which was the detection limit of Dall'Aglio's method. Contrary to the river water concentrations, the mercury concentrations in the river sediments remain high right down to the coast; mostly over 5 mg Hg kg^{-1} DW of sediment. All rivers south of Livorno and north of Civitavecchia showed similar high mercury concentrations in their sediments. Much less mercury is contained in the sediments of the rivers Arno and its tributary Serchio. The high mercury levels observed in the upper part of the Serchio river are due to mercury contamination from the felt and leather industry situated there. The mercury concentrations along the Tuscan and Ligurian coasts have been investigated by Baldi and Bargagli (1982, 1984). Fig.28 and 29 show clearly the input of Hg-rich sediments into the coastal zone and their subsequent

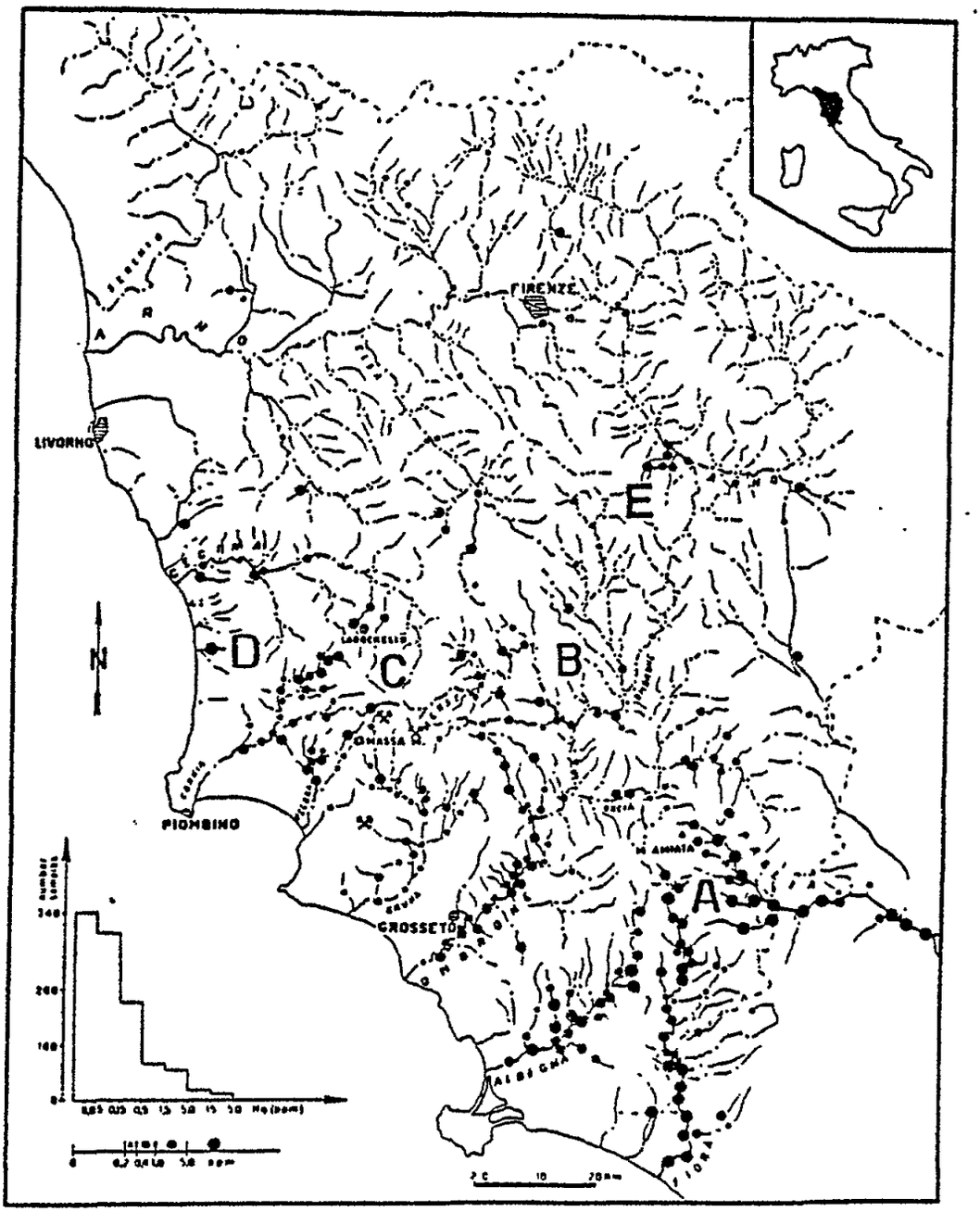


Figure 27. Distribution of mercury in river sediments around the mercury anomaly of Mt. Amiata (Tuscany) (Dall'Aglio, 1974).

mixing with marine sediments low in mercury. The plumes of the rivers draining the cinnabar deposits and the ores containing mercury showed the highest concentrations. Higher than background levels were observed along large portions of the inner continental shelf. High levels were also found in the sediments of the delta of the Tiber. Partly, these high values in the Tiber sediments are probably due to the sediments transported downstream from the Mt. Amiata anomaly through the Paglia river, a tributary of the Tiber, and partly due to industrial activities around Rome (Melchiorri et al., 1983). The mercury concentrations in the sediments of the river mouths along the Ligurian-Tuscan coast have been confirmed by Breder et al. (1981).

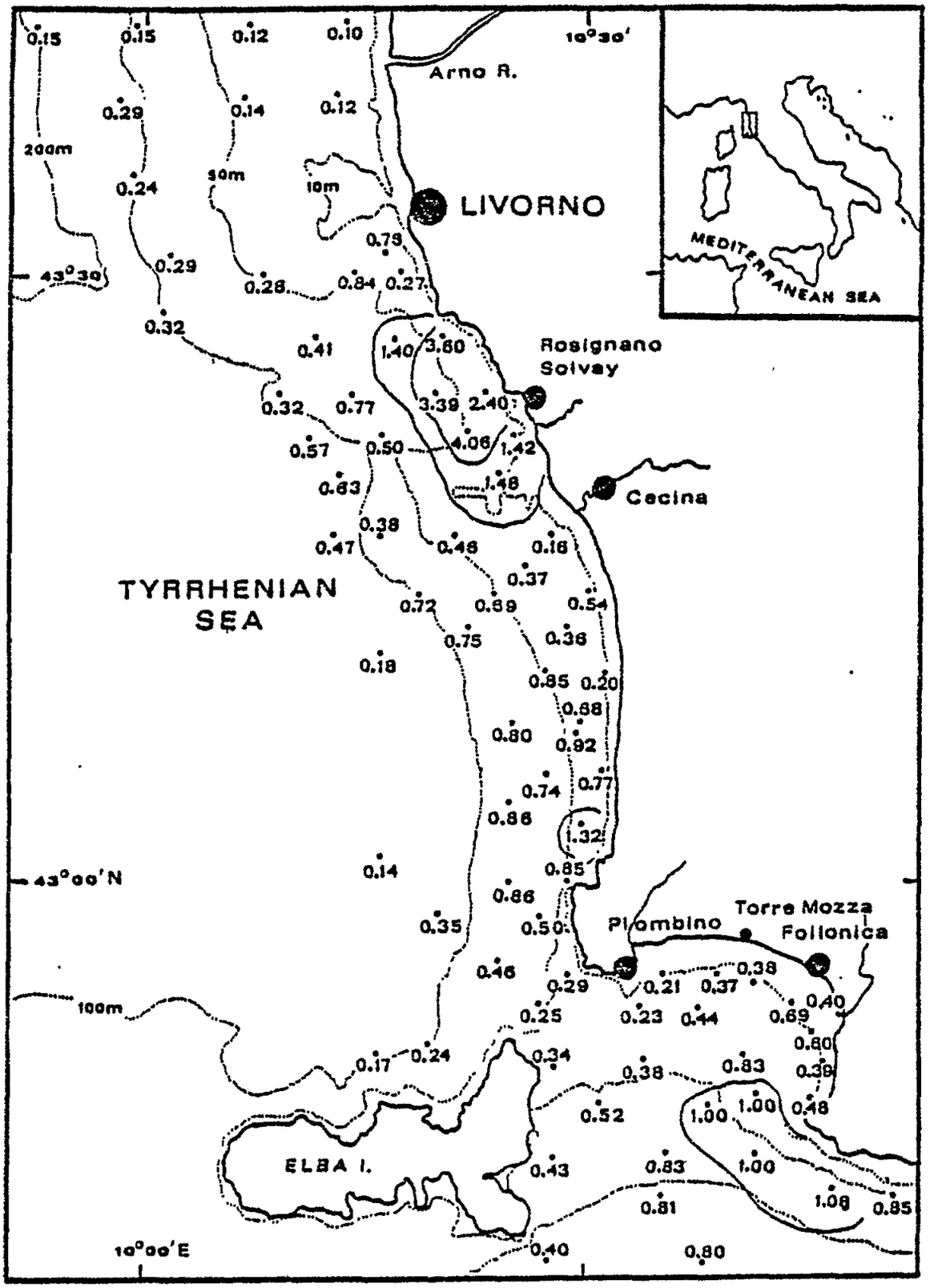


Figure 28. Distribution of mercury (mg Hg-T kg^{-1} DW) in surficial sediments from the western Italian coastline between the Arno and Follonica (Baldi and Bargagli, 1984).

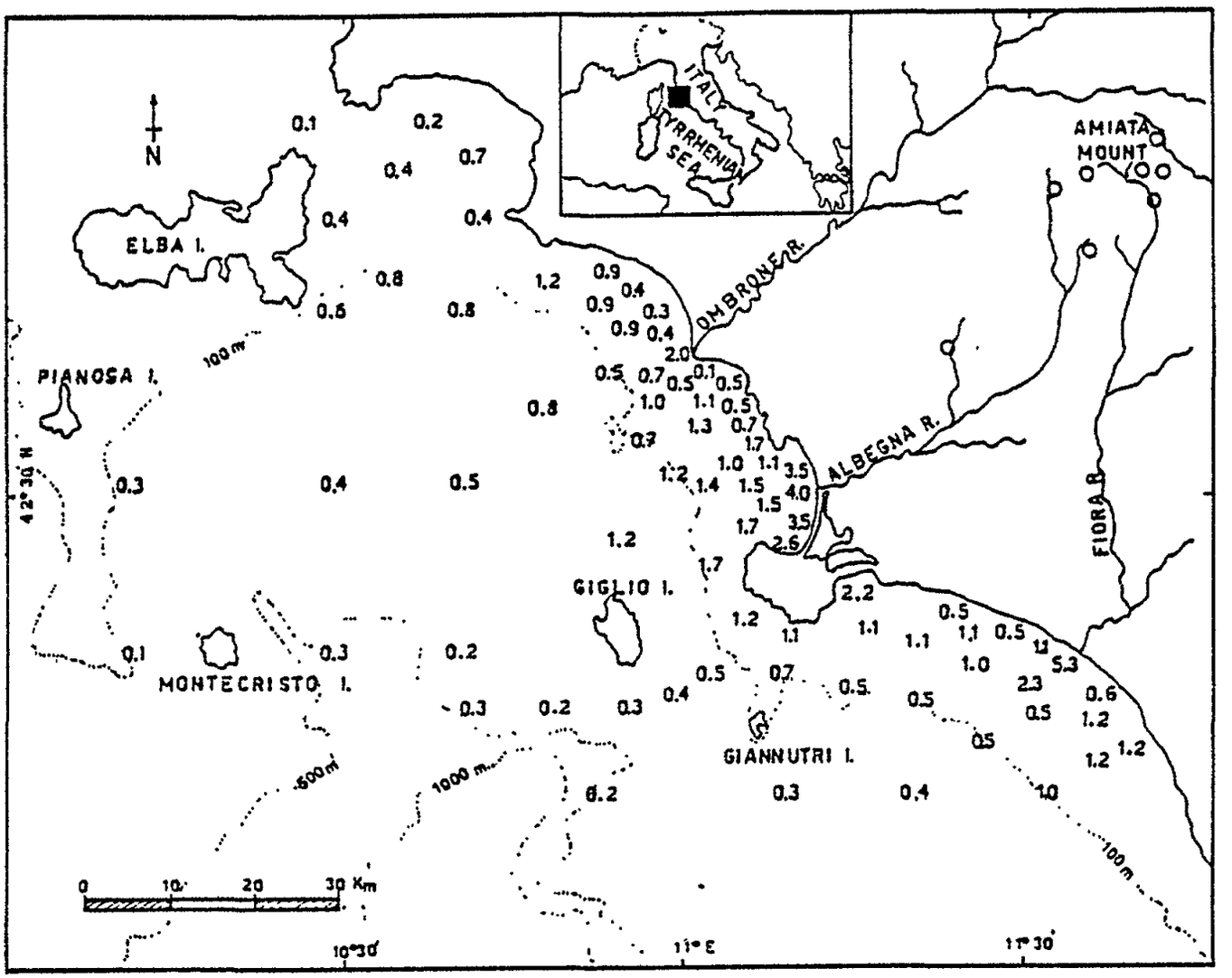


Figure 29. Distribution of mercury (mg Hg-T kg^{-1} DW) in surficial sediments from the western Italian coastline from Elba to the river Fiora (Baldi and Bargagli, 1982). Note the locations of the cinnabar mines (o).

The vertical mercury distribution within the sediments from the Mt. Amiata area and the Gulf of Naples in two cores shows higher mercury concentrations in the upper 10 cm of the cores than below (Fig.29).

Different extracting methods yielded different mercury concentrations, but did not change the horizontal mercury distribution pattern significantly (Baldi and Bargagli, 1982). It was interesting to note that mercury is more leachable (applying acid extraction) in the river mouths, and that areas directly adjacent to the river mouths had higher Hg-T concentrations than further away. The leachability also increased with distance from the

coastline, i.e. with greater depth (Fig.30). In fact, near the shoreline the sediments, which are not influenced by the river plumes, contained only up to about 4% of leachable mercury. At depths greater than 40 metres the leachability increased greatly to reach 30 to 70%.

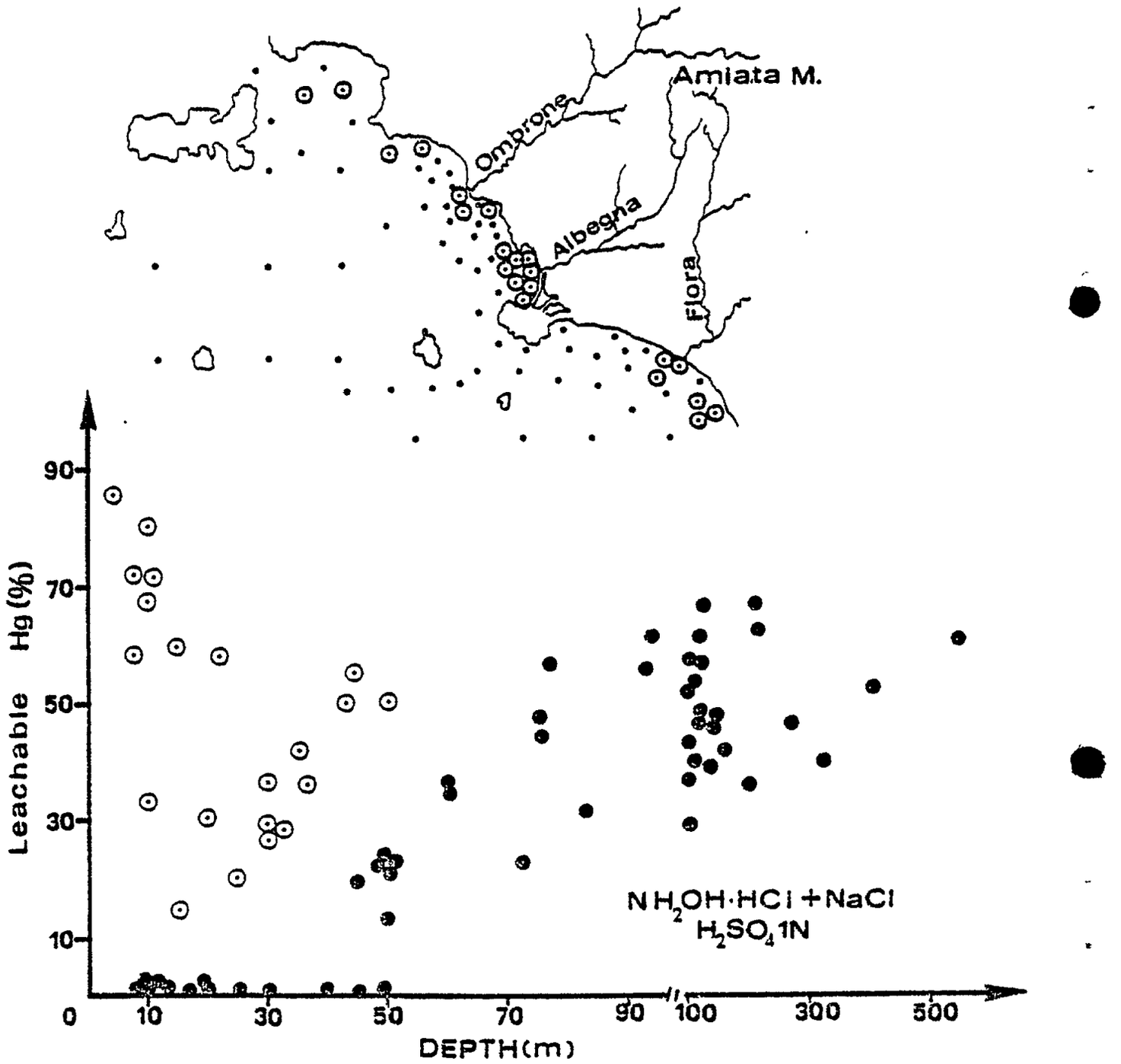


Figure 30. Percentage of acid-leachable (weakly bound) mercury in sediments affected by the Hg anomaly of the Mt. Amiata region (Baldi 1986). Note: circles with a dot mark are sediments which have been collected in Posidonia beds and had an unusually high content of organic matter.

The influence of elevated mercury sediment levels and the bioavailability of mercury present in these sediments have been investigated surveying the concentration of mercury in M. barbatus. M. barbatus feeds mostly on small bottom-living invertebrates (i. e. worms and crabs). While doing so, it burrows through the sediment ingesting part of the sediment on its way. Often its stomach and intestines are found containing mud and sand. Comparing the mercury concentrations versus size distribution in the fillet of M. barbatus caught along the Tuscan coastline, showed that the mercury concentrations increase more with size near the Isles of Elba, of Giglio and Gorgona Island than off the Talamone river and the Gulf of Salerno, the latter being a control area (Fig.31A). At the same time the authors observed that in

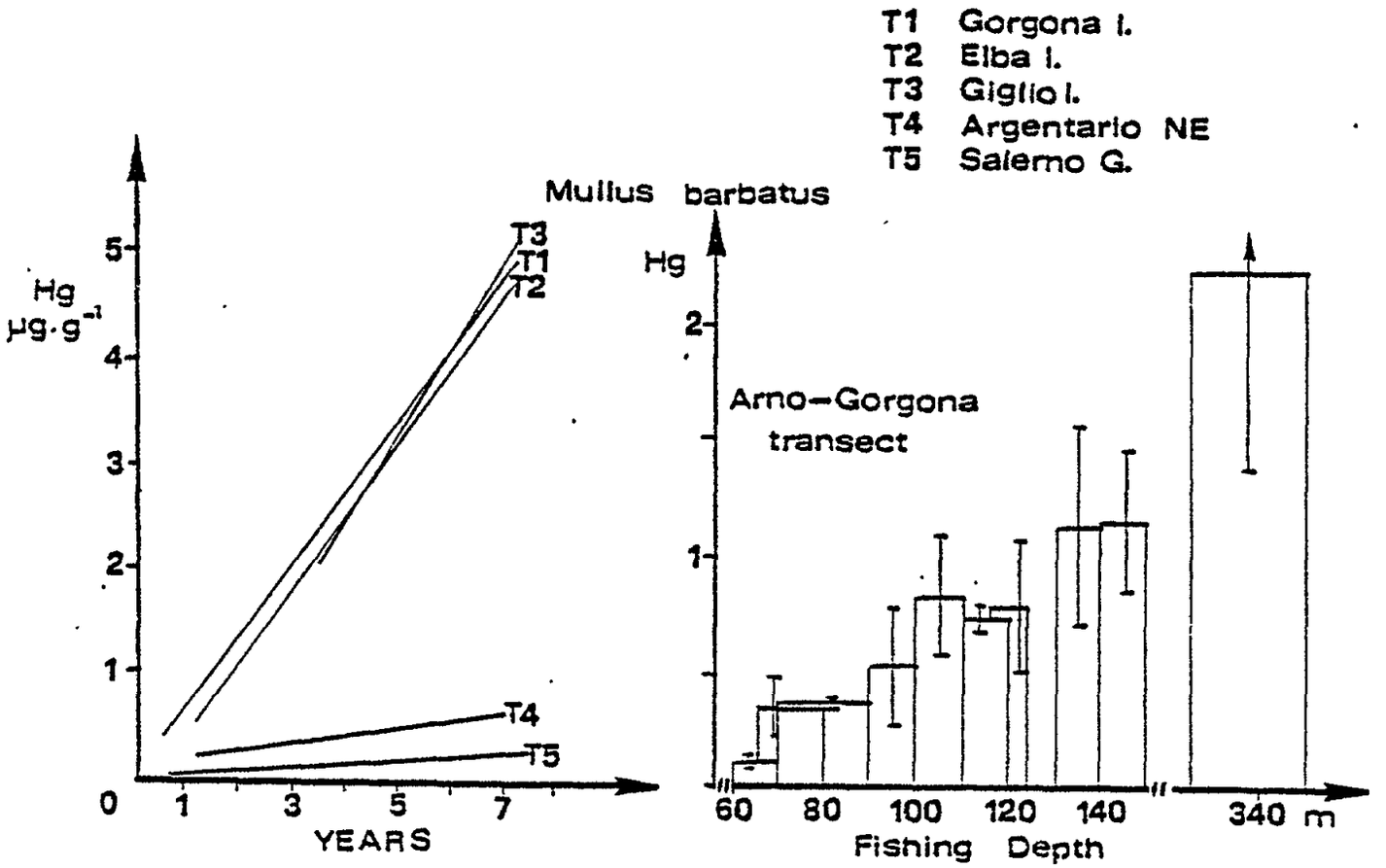


Figure 31. (A) Correlations of mercury concentrations versus age (years) in Mullus barbatus from different locations of the western Italian coast and (B) mercury concentrations in specimens of the same size versus fishing depth along a transect offshore of the river Arno (Baldi, 1986). Locations: T1: offshore Arno river mouth; T2: north of Elba; T3: west of Isle Giglio; T4: offshore Albenga River mouth; T5: Gulf of Salerno.

a transect from the mouth of the Arno river to the Gorgona Island, the mercury concentrations in specimens increased with depth (Fig.31B). Apparently two parameters are causing the mercury enrichment in the fish: one is the distance from the coast and the other the distance from the mercury anomaly. The higher mercury levels in the fish with distance from the coast could result from the greater availability (leachability) of mercury in sediments from greater depths (see above). Also the relatively low mercury concentrations in the fish near the Talamone river may be due to low availability (leachability) of mercury as has been observed in the river mouths of Ombrone, Flora and Albenga. It would be interesting to study the leachability in the Arno-Gorgona transect.

The comparison with another species showed that Scorpaena porcus, which inhabits "littoral waters amongst rocks and seaweeds and feeds mainly on small fishes such as gobies and blennies, but also on crustaceans and other invertebrates" (Fischer, 1973), had a different mercury distribution pattern. The mercury concentration versus size relationship did not show any significant differences between the fish caught near the Talamone river mouth and the Giglio Island, but the relationship increased more rapidly near the Solvay chlor-alkali plant at Rosignano (Fig.32). Probably, the different food-chains of M. barbatus and S. porcus may supply an explanation.

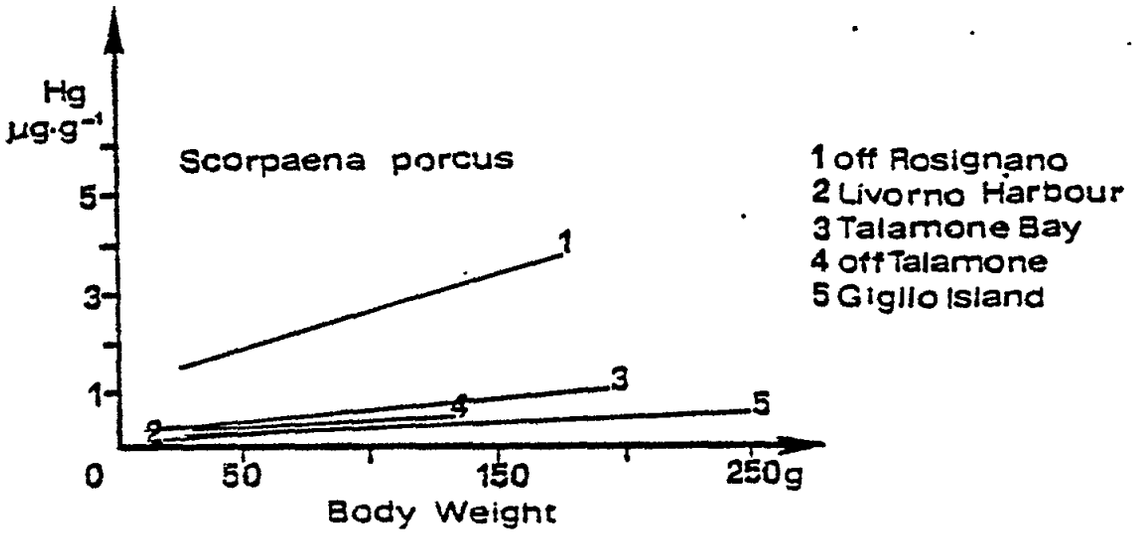


Figure 32. Mercury concentrations (ug Hg-T kg^{-1} FW) in Scorpaena porcus from the western Italian coast (Baldi, 1986). For locations see Fig.31

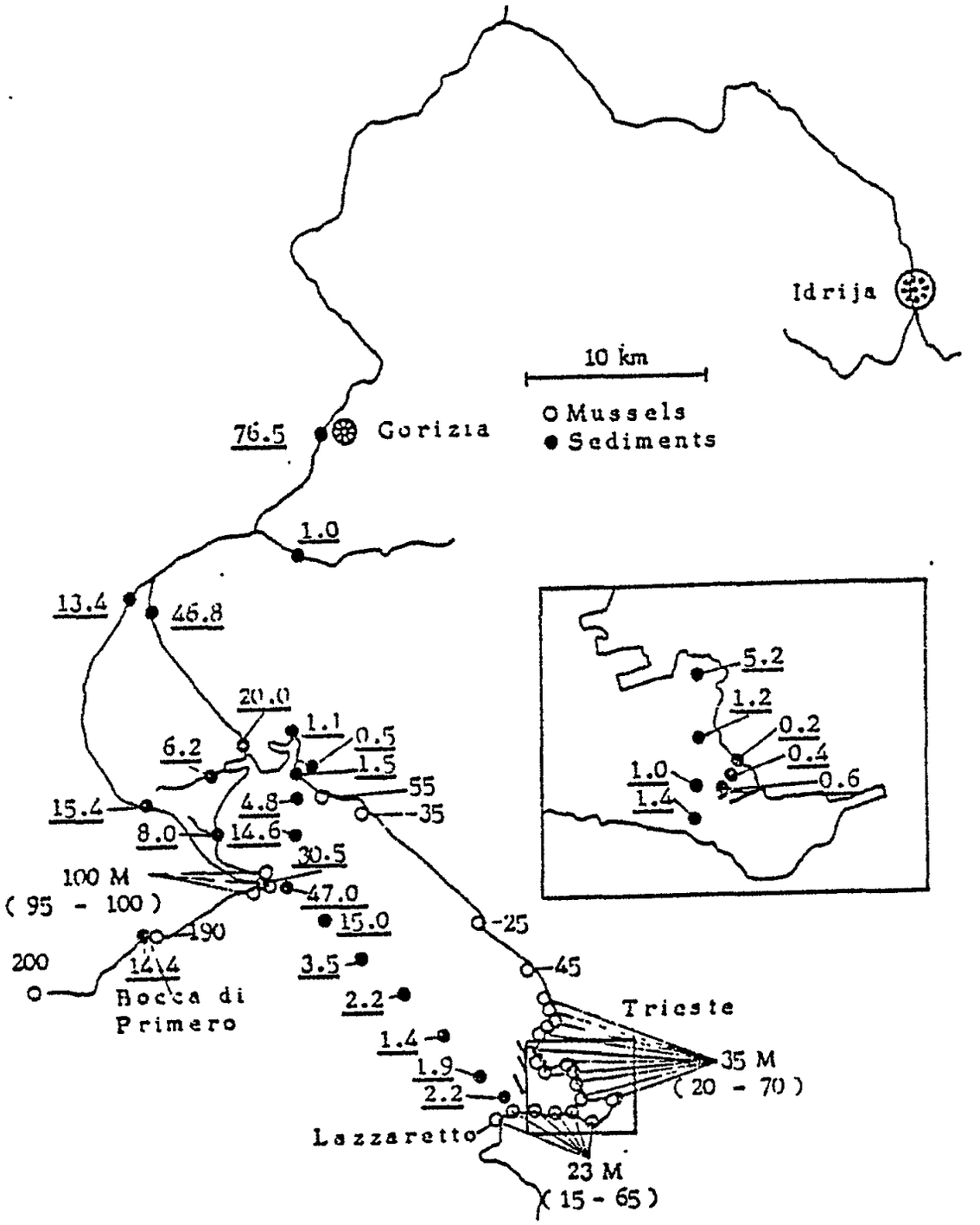


Figure 33. Mercury concentrations (ug Hg-T kg^{-1} DW) in sediments of the river Isonzo (Soca) and in marine sediments (underlined values) as well as in Mytilus (ug Hg-T kg^{-1} FW) from the Gulf of Trieste (Majori et al., 1967, modif.).

Much higher than background levels have been observed near another mercury anomaly. The Idrija anomaly drains through the Isonzo (Soca) river into the Gulf of Trieste (Fig.33 and 34). In river sediments, concentrations as high as 76.5 mg Hg-T kg^{-1} DW were found near Gorizia. Downstream from Gorizia all sediments showed very high levels. From the river mouth where sediment concentrations up to 50 mg Hg-T kg^{-1} DW were observed, the mercury concentrations in the sediments decreased rapidly towards the city of Trieste (2 mg Hg-T kg^{-1} DW) and the open Adriatic Sea. In the inner port of Trieste the mercury levels are slightly above background. Higher seawater concentrations were also observed in the mouth of the river (0.16 to 0.2 ug Hg l^{-1}) than in the open Adriatic (0.01 to 0.21 ug Hg l^{-1}). However, in the light of recent ideas on true seawater concentrations these values must be considered with caution (see section 3.3).

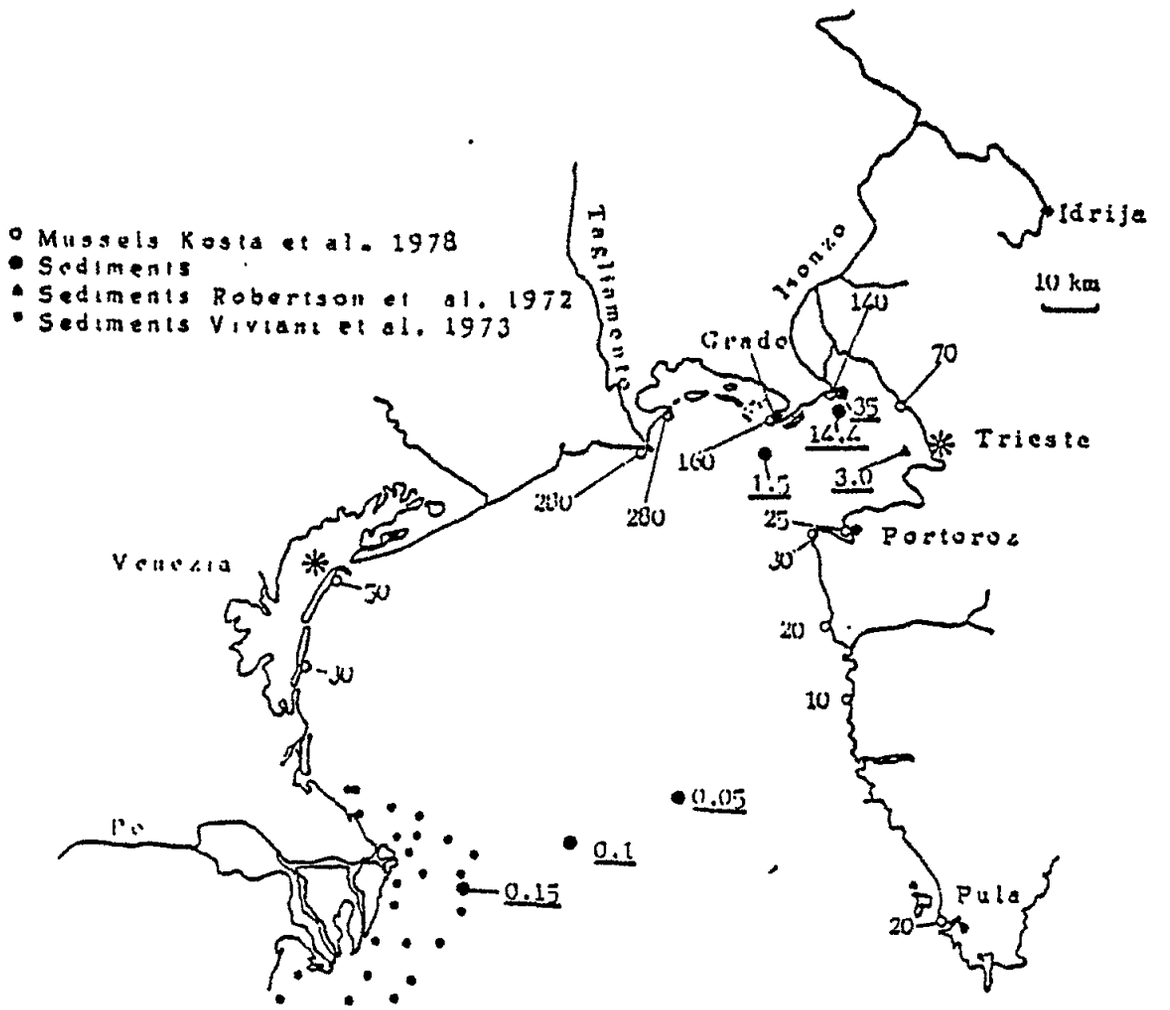


Figure 34. Mercury concentrations (ug Hg-T kg^{-1} DW) in sediments of the river Isonzo (Soca) and in marine sediments (underlined values) as well as in Mytilus (ug Hg-T kg^{-1} FW) from the Gulf of Trieste. Sediment levels in the Po delta: 0.4 (0.07 to 0.97 mg Hg-T kg^{-1} DW. (Review: Bernhard and Renzoni, 1977; data from Kosta et al., 1978; Robertson et al., 1972; Viviani et al., 1973).

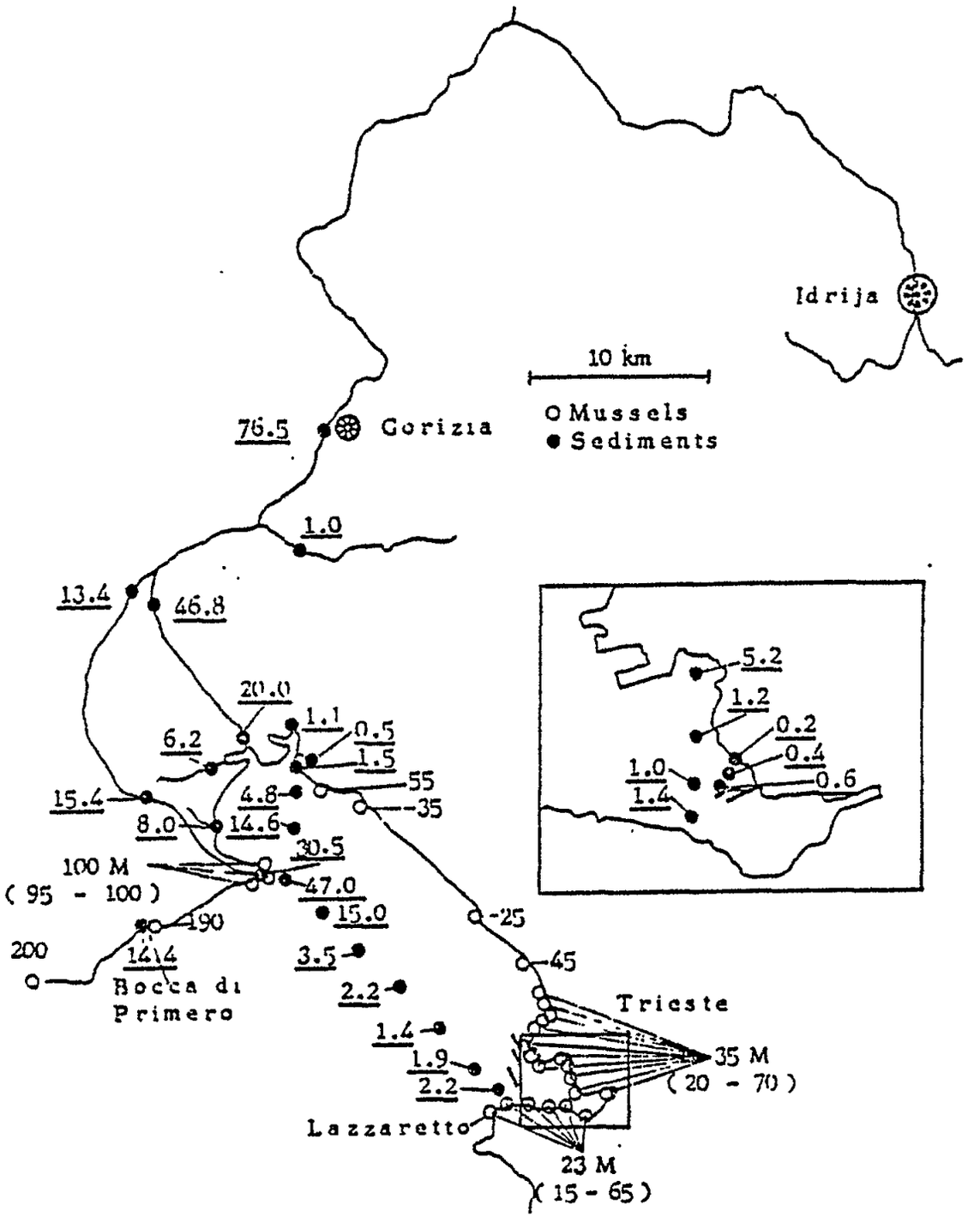


Figure 35. Accumulation and loss of mercury versus time by Mytilus transplanted from a high-Hg-environment (Primero) to a low-Hg-environment (Lassaretto) and vice-versa in the Gulf of Trieste (Majori et al., 1967, modif.).

In the Gulf of Trieste the anticlockwise current carries the mercury discharged from the Isonzo river towards the Italian coast. Mussels on the Yugoslav coast have significantly lower mercury levels than mussels from the Italian coast (Fig.33 and 34). However, the influence is limited to about 100 km west of the river mouth of the Isonzo. Mussels from the lido of Venice already have background levels again. Majori et al. (1967) verified this observation with an in situ experiment (Fig.35). Mytilus grown in the low level area of Lazzaretto were transplanted to the higher level area, Bocca di Primero. After the transplantation, mercury was quite rapidly accumulated. Levels similar to those of the locally cultivated mussels were reached within one to three months. A transplantation in the opposite direction showed a much lower mercury release over a period of five to six months. The difference in the chemical species of mercury discharged from the Isonzo may be the reason for this apparently low uptake by marine biota in the Gulf of Trieste as compared with the uptake near the Mt. Amiata anomaly.

Unfortunately similar investigations have not been carried out near the other mercury anomalies.

3.9 Influences of releases from chlor-alkali and other industrial plants on the mercury concentrations in the marine environment.

Anthropogenic releases have been investigated in several areas of the Mediterranean. Beginning in 1973 Renzoni and collaborators studied the influence of the mercury releases from the outfall of the Solvay chlor-alkali plant situated about 20 km south of Livorno near Rosignano (see Fig.27 for location). They investigated the mercury levels in sea water, sediments, biota and in humans consuming seafood from this area (Renzoni et al., 1973; Renzoni, 1977; Bacci et al., 1976, 1986). The authors have estimated that up to the beginning of 1974 the plant had discharged into the adjacent coastal area about 15 MT/y (metric tons/year) of mercury in wastes together with about 100,000 MT/y of white solids, mainly carbonates. This means that in the first 30 years of the plant's activity several hundreds of tons of mercury were discharged together with other wastes. In fact, the sea floor near the outfall is covered with white solids. At the beginning of 1974 the Solvay plant started treating its effluents and as a result the release was reduced in 1975/76 to 300-400 kg Hg/y and later to the present levels of about 3 kg Hg/y (Bacci et al., 1986).

Fig.36 summarizes the results obtained in 1973, i. e. before the effluent treatment. The highest concentrations for sea water and sediments of all stations examined were observed 2.5 km south of the outfall (station R 4). The mercury concentrations in limpets (Patella) and the crab (Pachygrapsus) were only slightly higher than at the next stations. At about 10 km north and south (stations R 1 and R 6) the sediment (sand) and the crab contained only slightly higher concentrations than the background levels (stations R 7 to R 10). In April/May 1975 and May/June 1976 (i. e. 15 to 16 months and 26 to 29 months, respectively, after the beginning of the effluent treatment) the body levels in the limpet, in the crab and in two fish species were again examined. As can be seen from Table XXIX the mercury concentration in the crab decreased by 80% while in the other marine organisms by 20 to 30%. Also the mercury concentration/size relationship in the fish S. porcus illustrates clearly the reduced level in the environment of the Solvay plant after effluent treatment (Fig.37 and the curves 1a and 1b in Fig.31). Note the different inclination of the regression curve of 1973 (curve 1a) from the 1975 curve (1b) which shows that specimens collected in 1975 had lower mercury concentrations than specimens of the same size collected in 1973. A comparison of this regression with regressions from other sites (Fig.31),

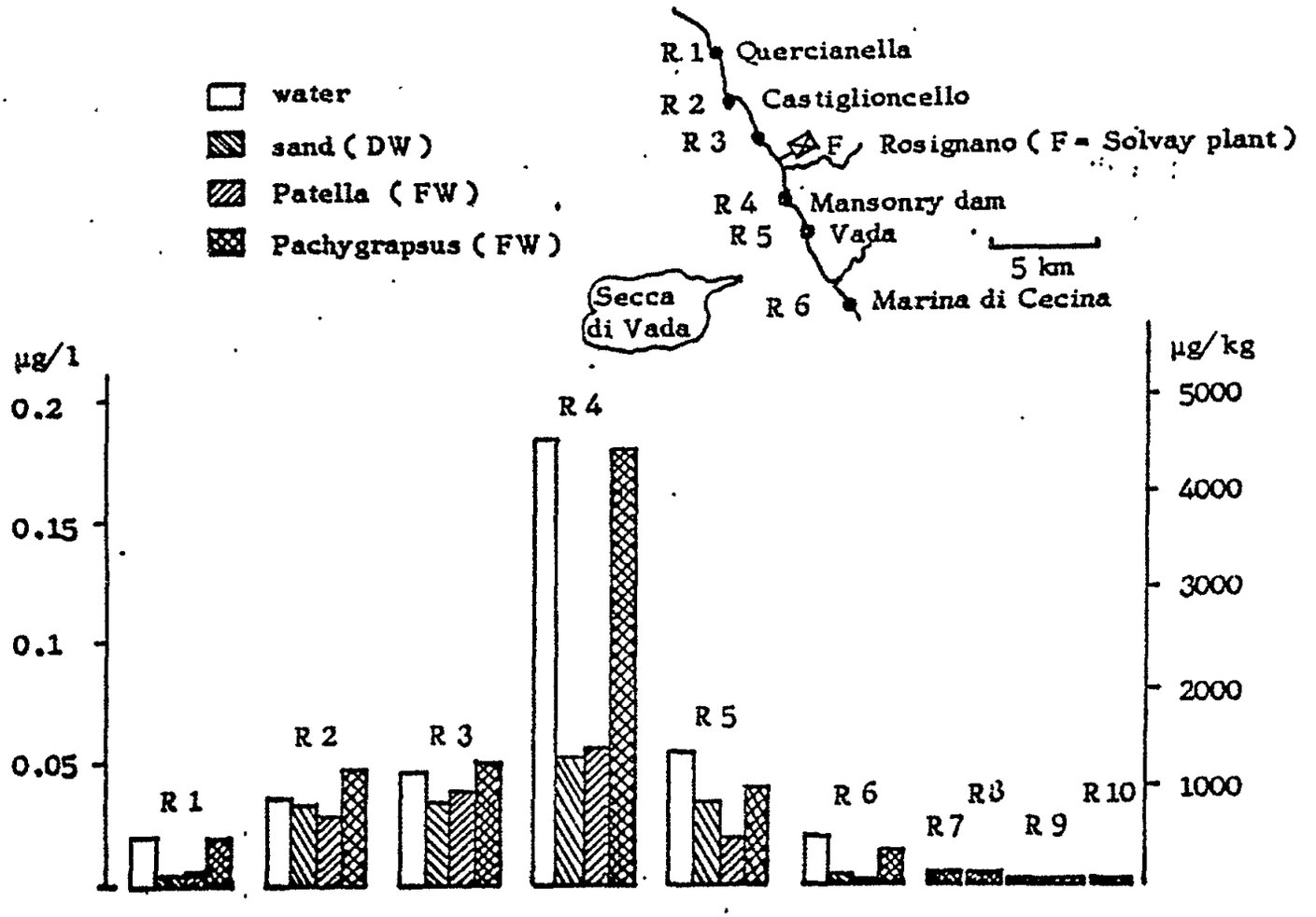


Figure 36. Mercury concentrations in sea water, sediments, Patella sp. and achygrapsus from the outfall area of the Solvay chlor-alkali plant in 1973 before the installation of a mercury waste treatment and in Patella and Pachygrapsus from several other Mediterranean sites as controls (R 7: Fiumicino, R 8: Montecarlo, R 9: S. Stefano, R 10: Talamone) (Bernhard and Renzoni, 1977).

some under the influence of the geochemical anomaly of Mt. Amiata, illustrates that the influence of the chlor-alkali plant on the adjacent site was still high in 1976 (curve 1b).

A recent survey (1981/82) of the area still showed high mercury levels in sediments around the Solvay plant (Fig.27). Bacci et al. (1986) obtained a core at a distance of about 3 km SW of the Solvay effluent outfall at 25 m depth. This core was analysed for calcium carbonate and Hg-T (Fig.38). The depth profile shows an interesting vertical distribution of both parameters. Taking into consideration the operational data of the Solvay plant and assuming a constant sedimentation rate, the authors explain the changes in the vertical distribution of mercury and calcium carbonate in relation to the industrial activity in the Solvay plant. The lower part of the profile shows

Table XXIX

Mercury concentration (ug Hg-T kg^{-1} FW) and percentage decrease in the mercury concentration from 1973 to 1976 in marine organisms before and after the installation of a mercury effluent treatment in the Solvay chlor-alkali plant (Renzoni, 1977)

species	1973 n	1973 mean	1973 SD	1975 n	1975 mean	1975 SD	1976 n	1976 mean	1976 SD	% decrease
Pachygrapsus marmoratus, whole body	50	4470	2770	39	1870	670	66	960	300	78.5
Patella coerulea, visceral mass	45	5920	1740	42	5040	1870	67	4510	200	23.8
foot	45	620	180	42	650	220	68	490	490	23.8
Serranus scriba white muscle	13	4640	1780				16	3460	310	25.3
Scorpaena porcus, white muscle	50	2610	950	49	1470	270	50	1800	600	31

background levels both of calcium carbonate and mercury. A first increase in the calcium carbonate content of the sediment core is associated with the beginning of the ammonia production of the plant in 1914. The first mercury peak at about 35 cm depth is associated with the beginning of the operation of the chlor-alkali plant in 1940 which, however, due to the war, reduced output soon afterwards. After the war, the plant resumed production with the consequent release of wastes which accrued until 1973. There after mercury releases were reduced. Using the mercury concentrations in different organisms and applying a one- compartment model to these data, Bacci et al. (1986) estimated a "recovery time" starting from 1973 that ranged from 13 to 24 years (Table XXX; Fig.39). The high "recovery time" derived from the two fish is explained by the assumption that fish contain higher amounts of methyl mercury than the invertebrates. The biological half-time of inorganic mercury is in the order of 30 days while that of methyl mercury in the order of years (see section 4.2).

Four similar cases are under study in Sardinia, Yugoslavia, Israel and Egypt. Several authors investigated the mercury contamination of the lagoon of S. Gilla (Cagliari). The S. Gilla Lagoon receives industrial wastes from a chlor-alkali and petrochemical plants ("Pet" in Fig.40), from ore processing industries ("Ore") and other industries besides sewage. The lagoon has an area of about 11 km^2 and connects with the sea (Gulf of Cagliari) through a 140 m wide channel. The average depth is only 1 m. For more than 20 years it has received mercury mostly in fine metallic particulates and in flakes of inorganic sulphide from the chlor-alkali plant. Sarritzu et al., (1983) found in all sediment samples from the lagoon mercury levels above 1 mg Hg-T kg^{-1} DW and near the outfall of the petrochemical plant an enormously high 300 mg Hg-T kg^{-1} DW. The mercury concentration was still 5 mg Hg-T kg^{-1} DW at 1 km away from the outfall showing that quite a large area has been highly contaminated with mercury. Cottiglia and collaborators (Cottiglia et al., 1985; Capone et al., 1986; Porcu and Masala, 1983; Cottigia et al., 1983)

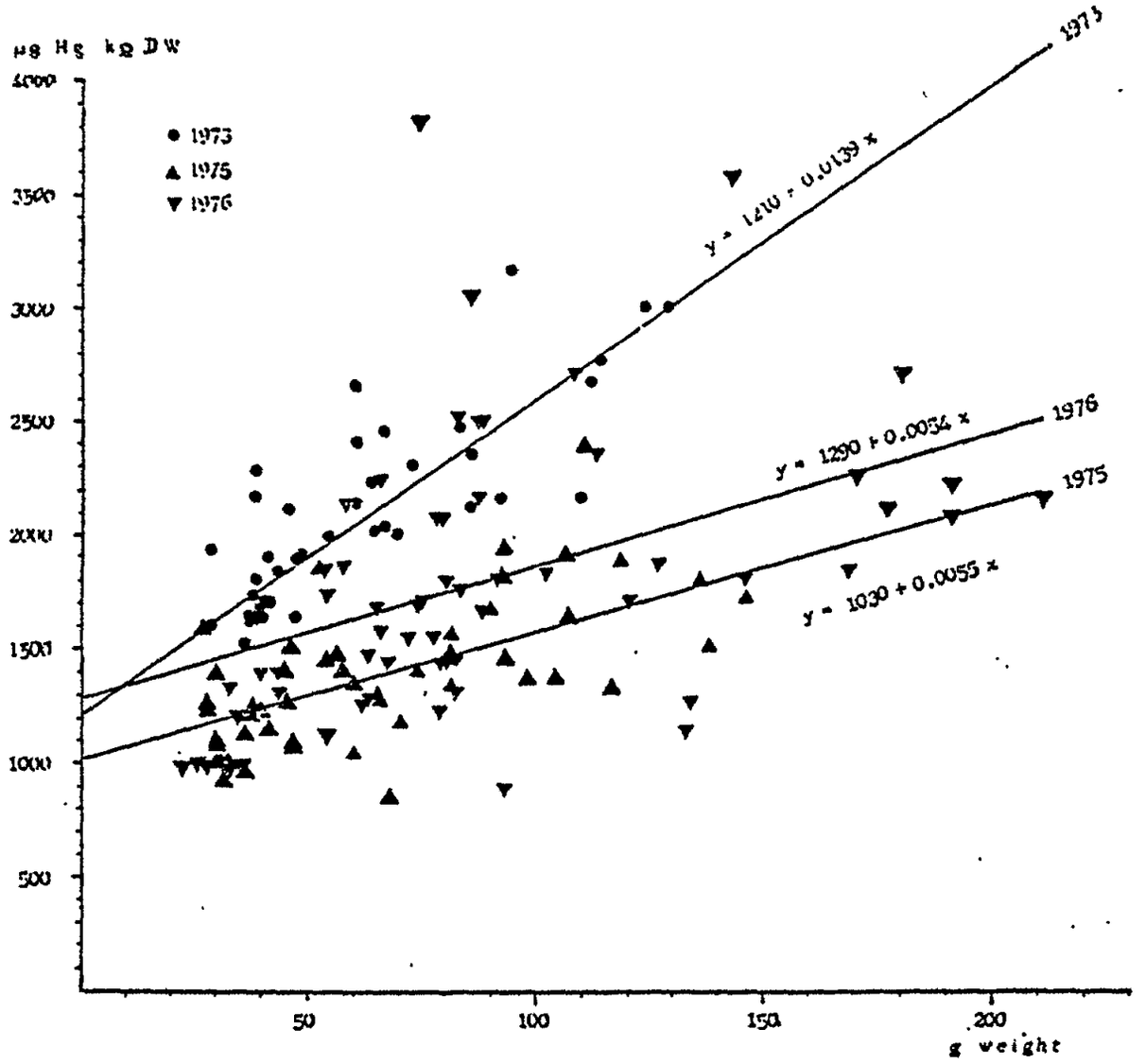


Figure 37. Mercury concentration versus weight in Scorpaena porcus from the banks of Vada before (1973) and after (1975 and 1976) waste treatment began in the Solvay chlor-alkali plant (Renzoni, 1977).

investigated the mercury levels in sediments of the lagoon and in the Gulf of Cagliari and the mercury concentrations in various marine organisms, including birds (see section 3.5.6). Cottiglia and collaborators divided the lagoon into four parts: a highly Hg-polluted area (R), a less Hg-polluted area (S), a low-polluted area (B) and the entrance of the lagoon (A) (Fig.40). Contu et al. (1985) have investigated the remobilization of mercury in these sediments using different extraction procedures. As can be seen from Table XXXI only very strong extraction methods can liberate more than 1 to 5% of the mercury present in the sediments. It is interesting to note the great difference between samples taken in January and April 1981. Despite the fact that only a few percent of mercury can be mobilized, on examining the data of Table XXXII

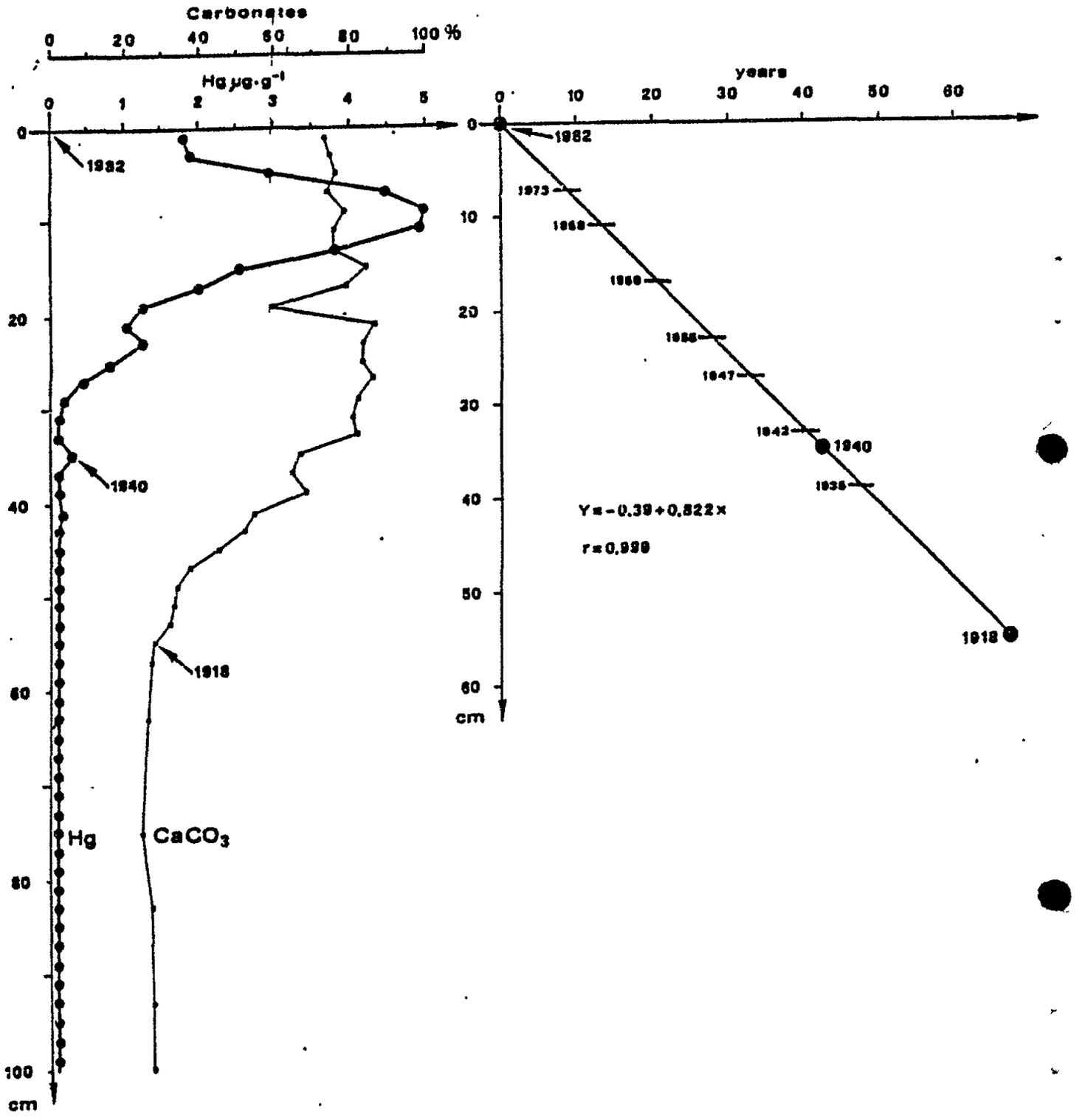


Figure 38. Profiles of mercury and carbonate concentrations in a sediment core taken near the Solvay chlor-alkali and estimation of the sedimentation rate (Bacci et al., (1986).

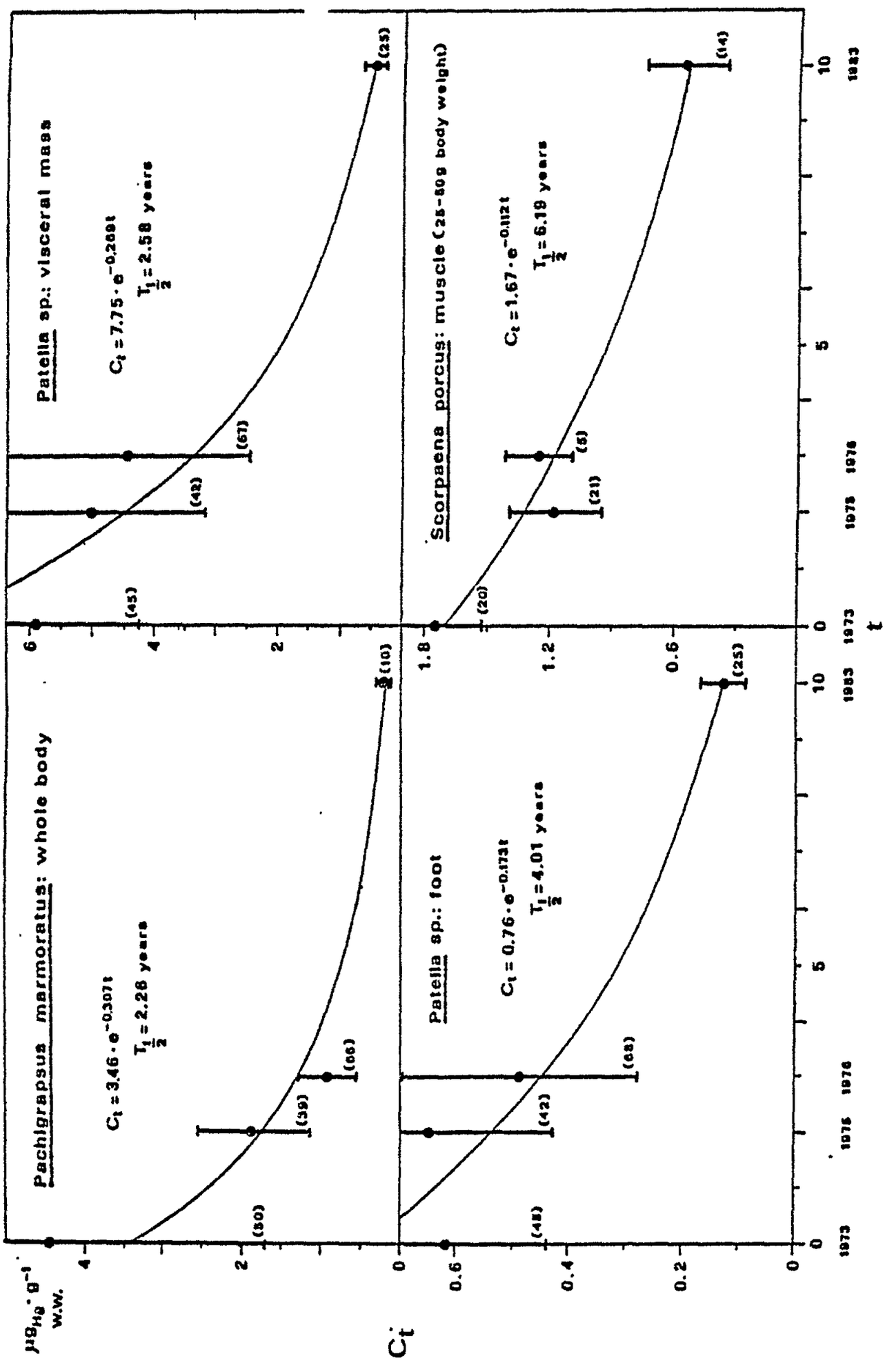


Figure 39. Recovery trends estimated from different "bio-indicators" in the Solvay outfall area (Bacci et al. 1986).

Table XXX

Reference area level and estimation of "recovery time" of the outfall area of the Solvay chlor-alkali plant to reach this reference level (Bacci et al,. 1986)

species	n	mean mg Hg-T kg^{-1} FW	SD	recovery time (years)
Pachygrapsus marmoratus, whole body	11	33	13	15.2
Patella sp. visceral mass	30	208	51	13.4
Scorpaena porcus muscle (25-50 g weight)	17	124	39	23.2
Coris julis muscle (60-90 g weight)	8	340	160	23.8

Table XXXI

Percentage of mercury extracted with different extraction procedures in relation to extraction with $HF/HNO_3/HClO_4$ from the top one-cm layer of sediment samples (<100 mesh) collected in the S. Gilla Lagoon in January and April 1981 (Contu et al. 1985)

station	←-------- percentage of $HF/HNO_3/HClO_4$ extraction --------→							
	4 N HNO_3 + 0.4 N HCl		0.5 N HCl		1 N NH_2OH*HCL + 25% CH_3COOH		0.05 N EDTA	
	Jan	April	Jan	April	Jan	April	Jan	April
1	58	17	4.7	6.5	1.9	2	1	1.3
2	90	84	8.1	4.8	4	0.9	0.1	0.6
3	25	74	1.5	5.8	2.5	3.4	3.1	2.6
4	14	10	0.9	1.1	7.7	3.8	1	1
5	25	49	2.4	6.6	11.5	7.4	1.8	1.6
6	55	14	1.8	2.4	3.8	2.7	1.2	1.4
7	34	27	2.6	3.7	6.2	3.2	1.5	1.1

one is surprised how little the high mercury levels in the sediments of the different zones influence the concentrations in the various biota. The levels suggested for the data observed in the Gulf of Trieste (section 3.8). The greatest effect of mercury pollution is seen on the birds (Table XXIII). The influence of sediment concentrations on levels in marine organisms was also studied in four experimental tanks filled with sediments containing different amounts of mercury: one with sediments and biota from an uncontaminated lagoon (S. Giusta) and three with sediments from the S. Gilla Lagoon containing different mercury concentrations. The results obtained after 18 months clearly showed the influence of the mercury concentrations in the sediments on the biota. The highest influence was observed on Anguilla sp. Certainly the age and food-chain position of the three species examined influenced the relative levels reached (Fig.41).

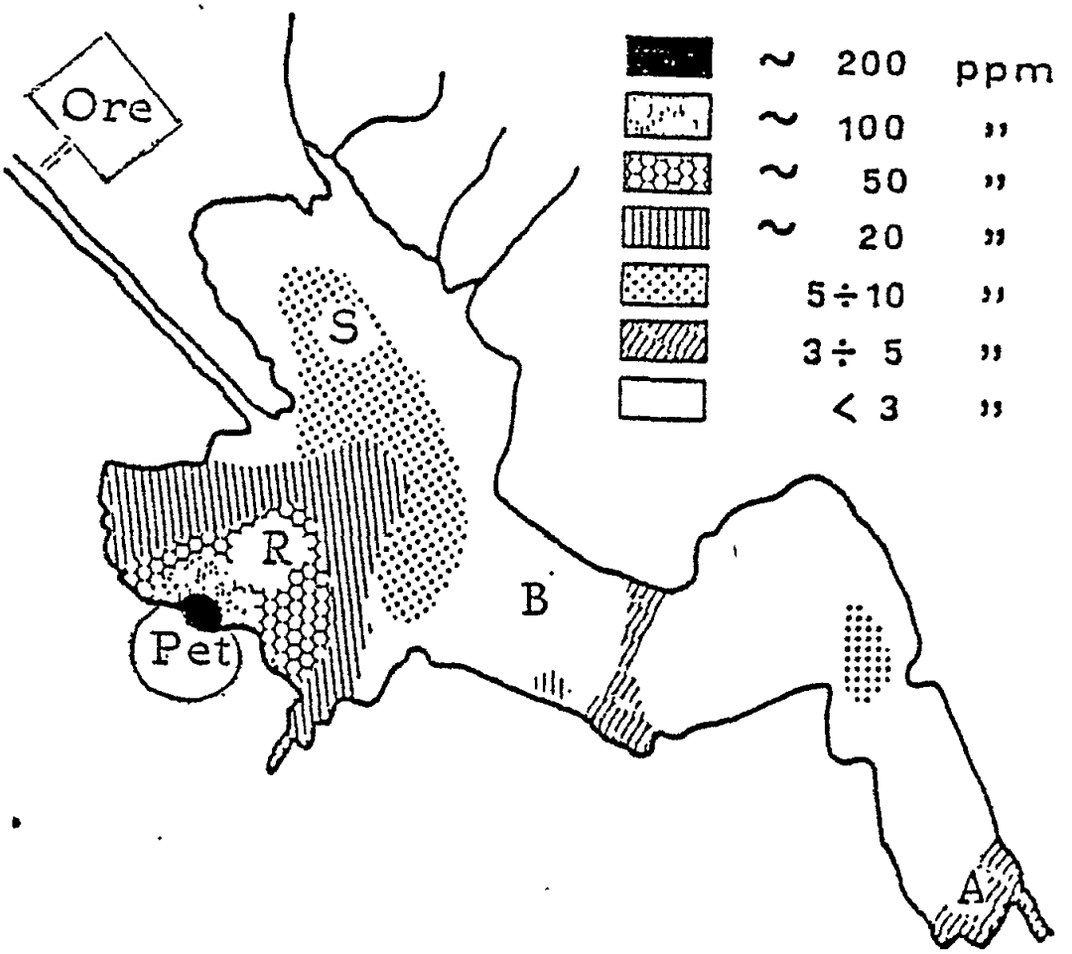


Figure 40. Mercury concentrations in the surficial sediments of the S. Gilla Lagoon (Cagliari). A: entrance from the Gulf of Cagliari; Pet: petrochemical industry; Ore: ore processing industry; B, S, R: different zones in the lagoon (Porcu and Masala, 1983, modif.).

In Yugoslavia, the sediments near the PVC and chlor-alkali plant situated in the Kastela Bay (Split) showed high mercury levels: 8.5 mg Hg kg^{-1} DW maximum concentration at the nearest point determined (Stegnar et al., 1981). The plant has been in operation since 1950. During 1950 to 1985 2 MT Hg/year are estimated to have been released into the Kastela Bay with an effluent concentration of about 0.1 mg l^{-1} and the same amount into air. From 1986 the output to the marine environment has been reduced to about 50 kg Hg $year^{-1}$ with an effluent concentration of 0.01 mg Hg l^{-1}. In the surface layer of the sediments the contamination from the plant is easily detectable (Fig.42). In the subsurface layer of the sediment the mercury levels are about background. Mussels collected near the plant also showed much higher levels than mussels from a remote control location (Table XXXIII). Returning to the same site in 1982 and 1983 Tusek-Znidaric et al. (1983) again

Table XXXII

Average mercury concentration (ug Hg-T kg^{-1} FW) in some benthic macrophytes, crustaceans, molluscs and fishes from various areas of the S. Gilla Lagoon. (Data selected from Porcu and Masala (1983) and Capone *et al.*, 1986)

areas	<-- A -->		<-- B -->		<-- R -->		<-- S -->	
	n	Hg	n	Hg	n	Hg	n	Hg
Ulva	4	22	3	200	3	300	1	40
Enteromorpha	3	85	3	65	3	210	3	50
Cladophora	2	145	1	140	1	80	1	160
Gracilaria	5	154	3	310	7	550	2	185
Ruppia, leaves	1	50	3	40	1	70	2	20
Ruppia, rhizomes	2	75	3	10	2	225	2	20
Gammarus	6	110	5	125	9	385	5	90
C. mediterraneus		560		580		640		460
M. galloprovinc.		220		380		420		-
N. diversicolor		90		70		1350		-
M. surmuletus		45		70		1350		-
D. labrax		1400		1100		2200		-
M. cephalus		180		200		210		200
E. encrasicholus		-		2000		-		-
S. pilchardus		-		670		-		-
Solea vulgaris		200		70		420		-

collected sediment and mussel samples near the chlor-alkali and PVC industry and from remote sites. The Hg-T concentration in mussels taken near the plant was 25 times higher than in mussels collected in a remote site (Ciove) in the same region, but, interesting enough, the methyl mercury concentration in the mussels from the contaminated site was only 1.75 times that of the remote site indicating that little or no MeHg has been transformed from the mercury released.

Table XXXIII

Mercury and selenium concentrations (ug kg^{-1} FW) in mussels (soft parts) from the Kastela Bay (Stegnar *et al.*, 1981)

	mean	range	
Hg-T	9600	4600 - 17400	near PVC & chlor-alkali plant
Se-T	600	200 - 1600	near PVC & chlor-alkali plant
Hg-T		300 - 400	uncontaminated site (Trogir)
Se-T		300 - 400	uncontaminated site (Trogir)

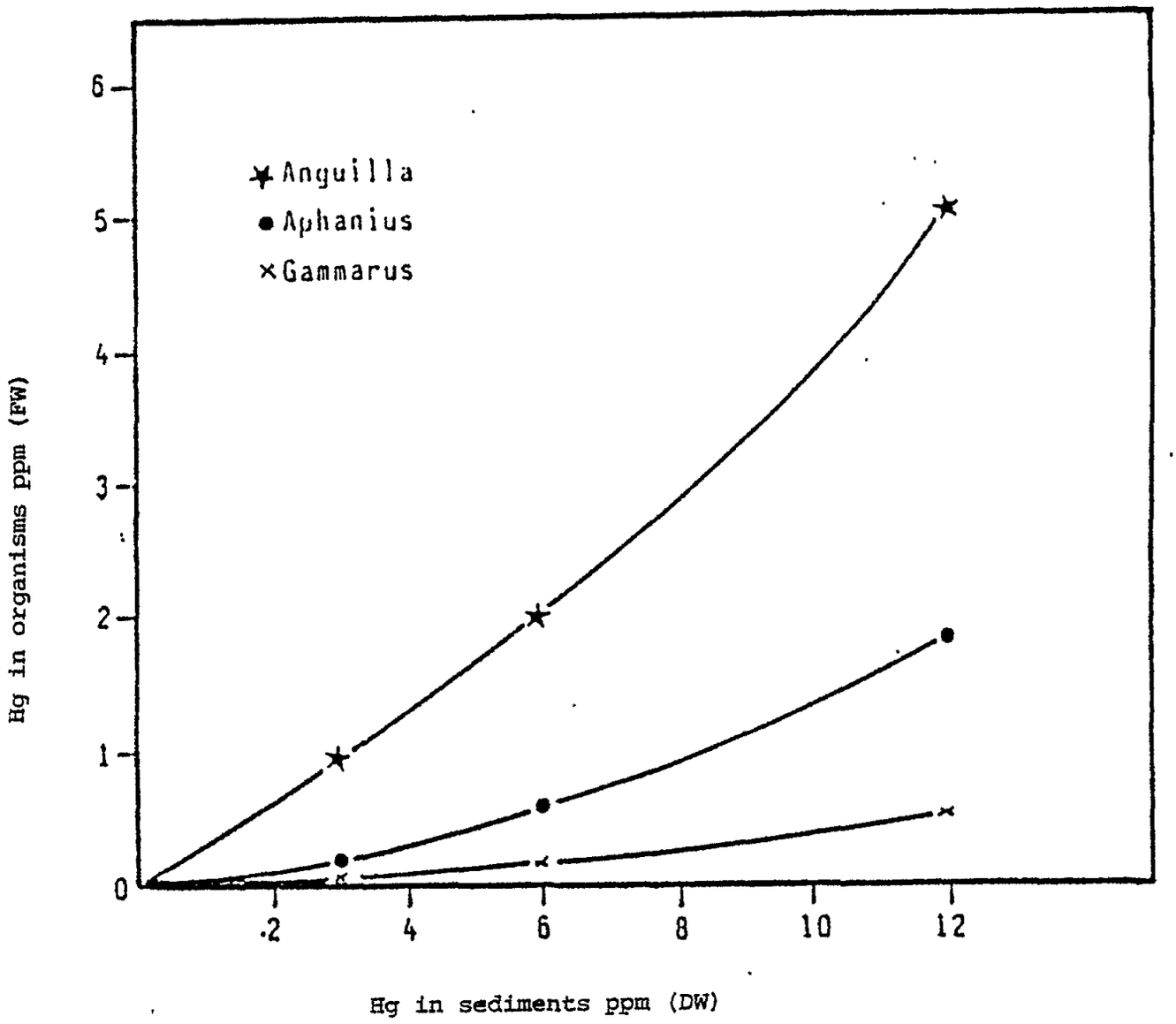


Figure 41. Relationship between mercury concentrations in sediments and biota obtained from tank experiments (Cottiglia et al., 1984).

In Israel, Hornung and collaborators (Hornung et al., 1984, Hornung 1986) investigated the release of mercury from a chlor-alkali plant and its influence on the mercury levels in sediments and biota. Sediment concentrations were high near the plant's outfall and decreased going away from it. At 20 km from the source, background levels were again reached. Likewise, the mercury concentration decreased in benthic organisms. Fig.43 shows the correlation of mercury levels in three invertebrates (a crab, a bivalve and a gastropod) with that of the sediments collected at the same sites as the organisms. The carnivorous gastropod showed higher mercury levels in the same locations than the bivalve. Similar correlations were observed for several other species.

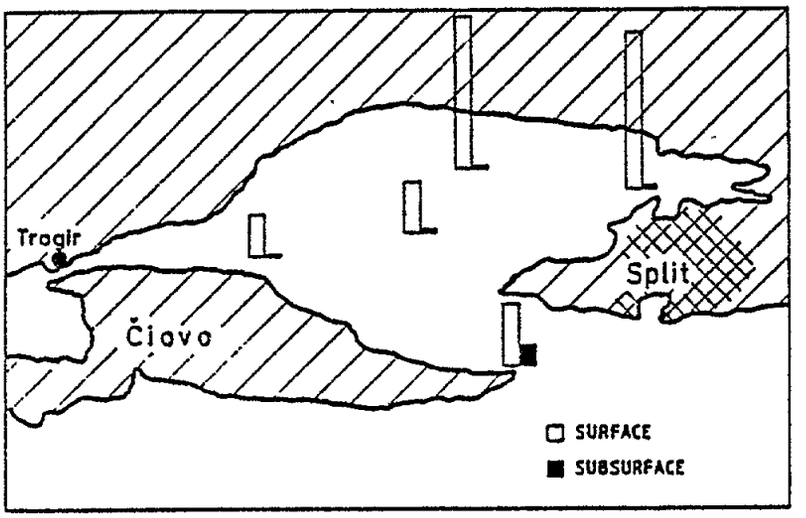


Figure 42. Ratio of mercury concentrations in surface and subsurface layers of sediments from the Kastela Bay (Stegnar et al., 1981).

The impact of yet another chlor-alkali plant and an agricultural drain south-west of Alexandria was studied by El-Rayis et al. (1986) and El-Sayed and Halim (1979). El-Rayis et al. (1986) estimated that more than 3.7 kg Hg day^{-1} were released into the El- Mex Bay from these two land-based sources. In the agricultural drain, the main source, most of the mercury is in particulate form while the chlor-alkali plant discharged mainly dissolved mercury (Table XXXIV). This is different from what has been observed in discharges from the Solvay plant and from the sources in the S. Gilla Lagoon. Dissolved and particulate mercury increased near stations 2a and 3a (Fig.44) to a greater degree in the bottom water with higher salinity and near the chlor-alkali plant which discharged only 1/4 of the amount of dissolved mercury of the Umum agricultural drain. In both stations particulate mercury in the sea-water samples is higher than the dissolved mercury. At the outer stations (e.g. 2b and 3b) both particulate and dissolved mercury are also higher in the bottom waters than in the surface layers. In the sediments from the shoreline near the outfall of the chlor-alkali plant, levels ranged from 11 to 15 mg Hg-T kg^{-1} DW (El-Sayed and Halim, 1979). Stations 2a and 3a in the bay had the highest levels (Table XXXV). Relatively high levels were also found near the Eastern Harbour of Alexandria. High plankton values are found only near the Umum drain (station 3a and 4c), near the chlor-alkali plant (station 2c) and near the Eastern Harbour (station 5c). Also the mercury levels in several fish species were higher in the Mex Bay than in other areas along the Alexandria coast (El-Sokkary, 1981).

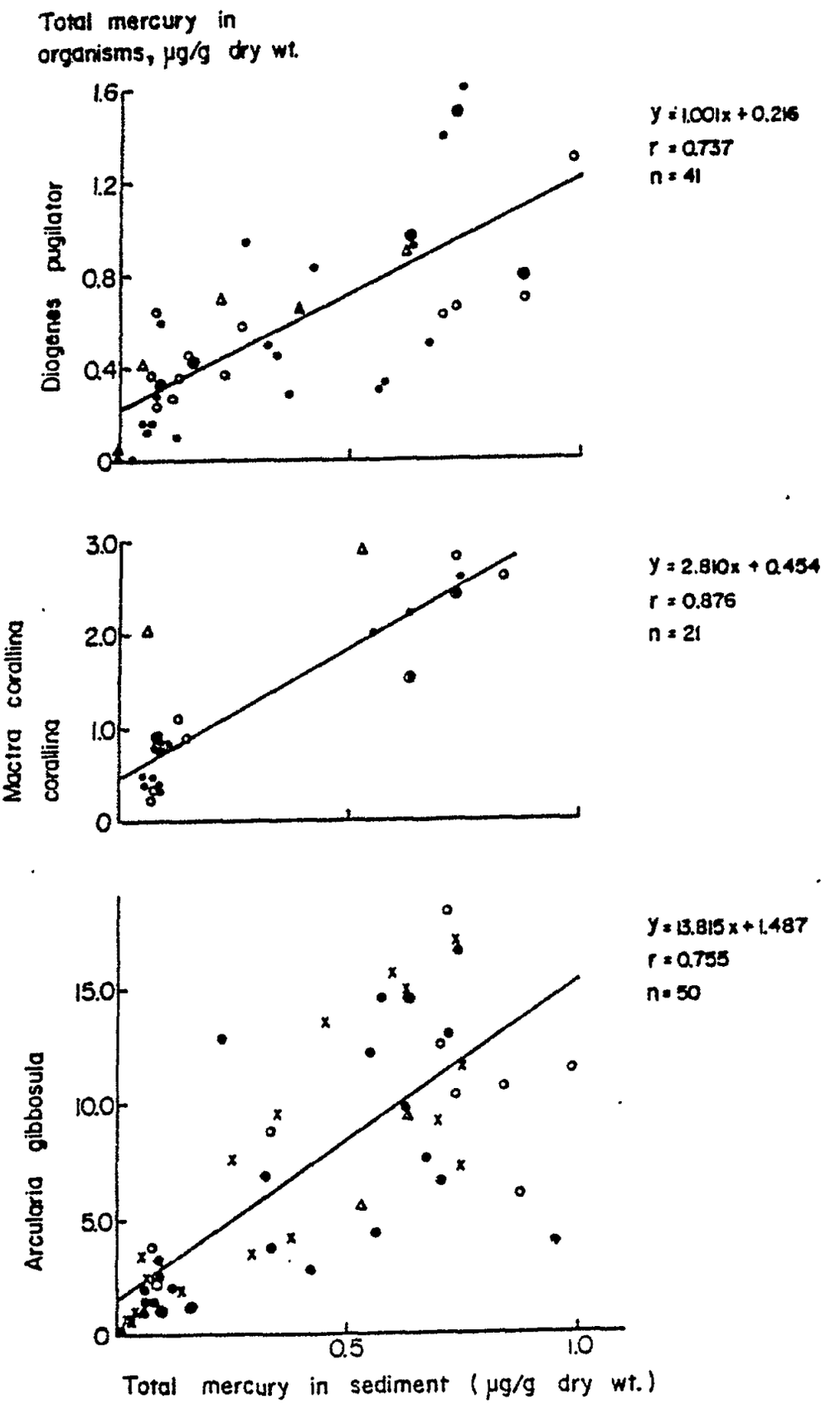


Figure 43. Relationship between mercury concentrations in three benthic organisms and surficial sediments from the coast of Israel (Hornung, 1986). Note: each point represents Hg levels in organisms and sediments sampled on the same date. Symbols: Δ = July 1980 O = July 1981 ● = Sept 1981. • = May 1982 x = Nov/Dec 1982.

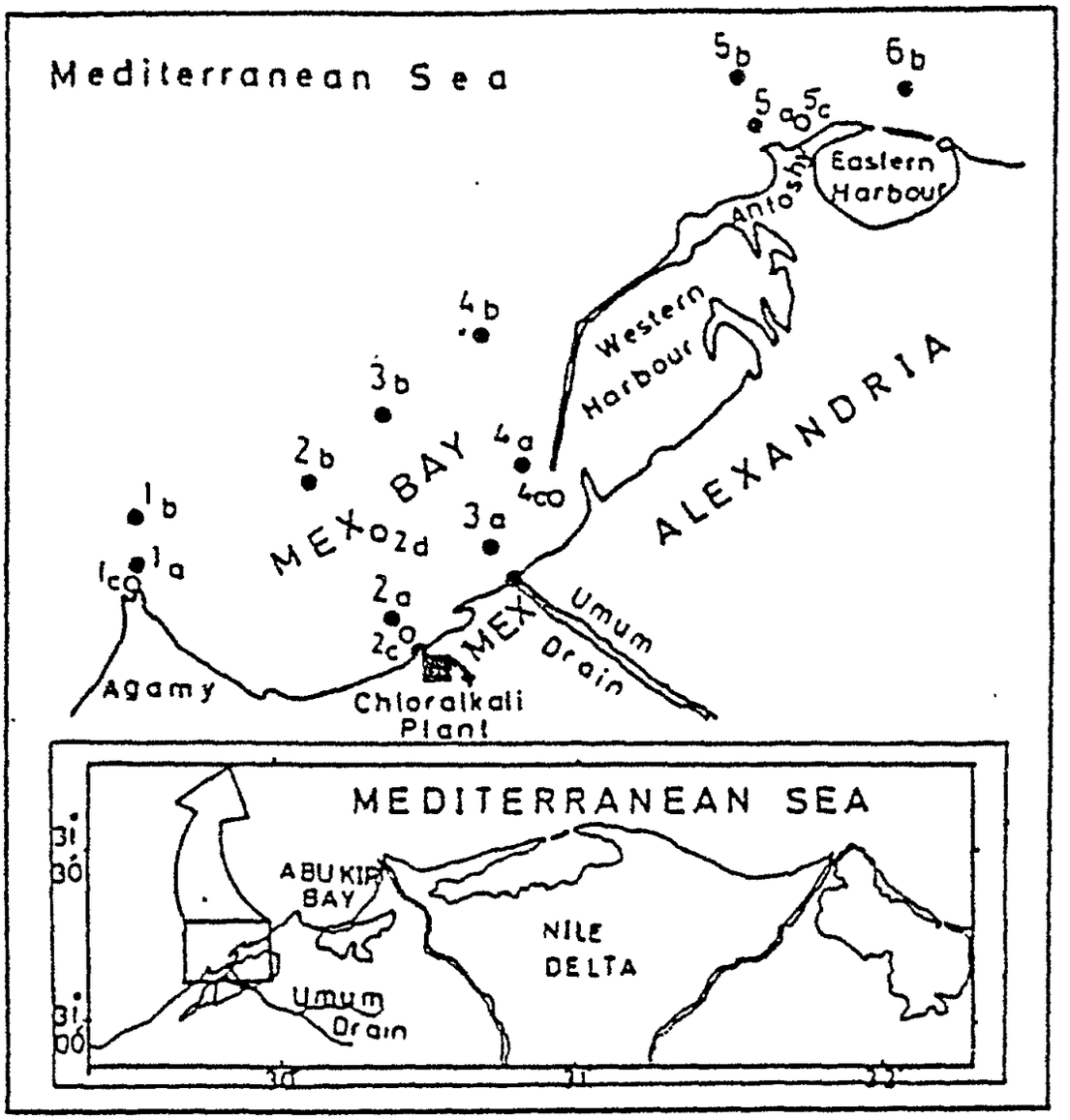


Figure 44. Sampling stations in the coastal area of Alexandria (El-Rayis et al., 1986).

Table XXXIV
Average mercury amounts (g day^{-1}) discharged by two land-based sources into the El-Mex Bay (El-Rayis et al., 1986)

	chlor-alkali plant	agriculture drain Umum
Dissolved Hg	76.9	336
Particulated Hg	27.7	3276
Hg-T	104.6	3612
	Grand total	~ 3720 g Hg-T day^{-1}

Table XXXV
Mercury in sediment and plankton samples from El-Mex Bay (El-Rayis et al., 1986)

stations	sediment mg Hg-T kg^{-1} DW	mixed plankton ug Hg-T kg^{-1} FW *)
1a	0.9	100
2a	8.3	135
3a	10.7	235
4a	5.4	165
5a	-	135
1b	0.3	115
2b	3.2	110
3b	2.4	105
4b	1.5	85
5b	2.5	100
6b	1.3	90
1c	-	70
2c	-	200
2d	-	120
4c	-	185
5c	-	160

*) The authors report ug g^{-1} FW but it must be ug kg^{-1} FW

4. Elements of the biogeochemical cycle of mercury

4.1 Transformation of mercury species

The transformation processes of mercury have received considerable attention because in the abiotic environment (ore, air, soil, sediment etc.) mercury is predominantly present in its inorganic species while in many marine organisms, in particular, most of the mercury occurs as methyl mercury. Also the Minamata incident poses the problem of the origin of methyl mercury which caused the disaster. One hypothesis on its origin suggests that the inorganic mercury released by the chemical factory was transformed to methyl mercury by microorganisms resident in the marine sediments.

The various mercury species have different pathways and routes in the environment. All known pathways have been studied in experimental set-ups, but the ecological and environmental significance of each single route of the biogeochemical cycle of mercury is still very uncertain. In the past, more emphasis has been placed on biological mediated processes than on non-biological with the microbiological ones attracting the greatest attention.

Natural foci of mercury dissemination are usually considered to be ore (HgS) and non-mercury ore deposits such as lead, arsenic and tin, which are of igneous origin and contain traces of mercury. Natural weathering and man's exploitation of these deposits as well as the use of mercury in chloride and caustic soda production, in paper production, in mercury containing fertilizers, etc. have introduced and still introduce many different forms of mercury in the environment. According to Fig.45 the major pathways of the mercury cycle are mediated by microorganisms; however, in a closer examination of the experimental set-ups used to study the transformation of mercury species and the interpretation of field observations show that other abiotic pathways could also play a role. The most important limitation in the transformation experiments is the extremely high inorganic mercury concentrations used. For example, additions of 5 to 100 mg of inorganic mercury salts per kg sediment are usual in these investigations. For comparison, background concentrations of mercury in sediments range from 0.02 to 0.02 mg Hg-T kg^{-1} DW of sediment. The very high mercury concentrations used in the experiments are selective for mercury resistant bacteria and it is not clear if these organisms also carry out the mercury methylation under environmental conditions, since mercury resistance can be induced by high mercury concentrations (Robinson and Tuovinen, 1984).

4.1.1 Mercury tranformation by bacteria and the origin of methyl mercury.

Since it has been shown that Hg^{++} can be methylated in vitro and extracellularly by enzymatically produced methylcobalamin (Ch_3B-12) and non-enzymatic methylation of mercury by the cell-free extract of a methanogenic bacterium can be carried out with methylcobalamin as a donor for methyl groups, the following methylation mechanisms are proposed to occur in bacteria:

$$Hg^{++} \xrightarrow{CH_3B\text{-}12} (CH_3)Hg^{+} \xrightarrow{CH_3B\text{-}12} (CH_3)_2 Hg$$

The first methylation step is 6000 times faster than the second one (Ehrlich 1981; Summers and Silver, 1978).

However, not all microbial cells can synthesize B-12 and, what is more important, the B-12 independent strains cannot methylate Hg^{++}. The cobalamine used in methylating must, therefore, be either excreted from these

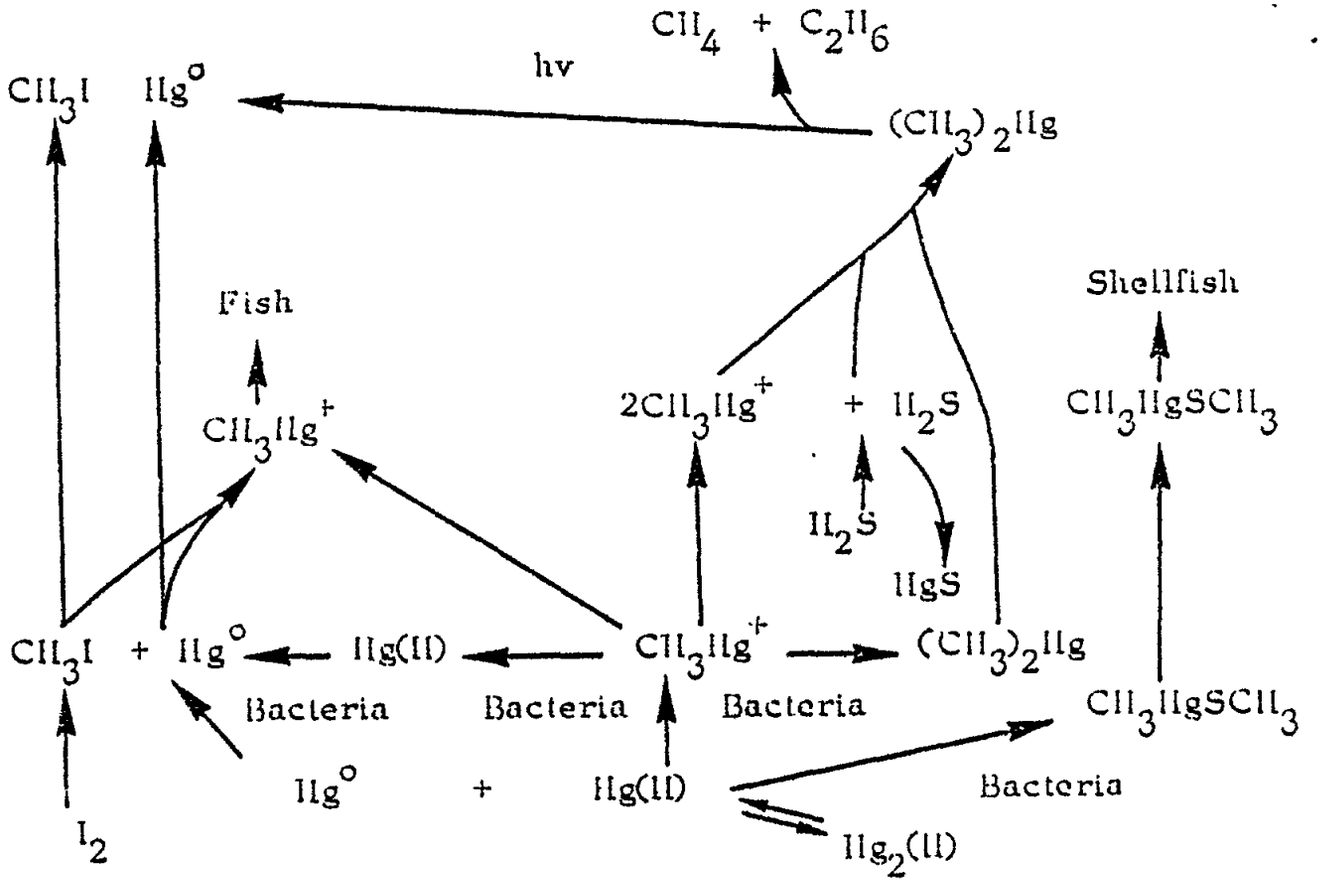


Figure 45. The mercury cycle (Wood and Wang, 1983).

cells or released on cell lysis. Other bacteria, such as E. coli which require B-12 for growth, can accumulate B-12 and methylate it to methyl-cobalamine so that they can use methyl-B-12 for methyl transfer reactions. It is assumed that both bacteria and fungi methylate in this way (Wood and Wang, 1983; Silver, 1984).

The difference between B-12-dependent and independent strains is illustrated by the difference in methylation capacity of Clostrium cochlearium. The B-12-dependent strain of the anaerobic C. cochlearium can methylate Hg(II) salts to CH_3Hg^+ using methyl-vitamin B12 (CH_3B-12).
The B-12-independent strain of C. cochlearium cannot methylate mercury salts. Both strains transport Hg(II) into the cells at the same rate, but the B-12-independent strain is inhibited by at least a 40-times lower concentration of Hg(II) than the B-12-dependent strain. Wood and Wang (1983) suggested that the dependent strain uses biomethylation as a mechanism for detoxication because methyl mercury is volatile. However, one should keep in mind that Hg° is also volatile and much less toxic than methyl mercury.

The uncertainty in the importance of methylation versus transformation and subsequent volatilization of Hg° is also illustrated in the results obtained with single strains of bacteria isolated from freshwater and marine environments. Vonk and Sijpesteijn (1973) showed that pure cultures of Hg-resistant bacteria (P. fluorescens, M. phlei, B. megaterium, E. coli, E. coli W/B12, A. aerigenes, A. aerigenes W/B12) could aerobically methylate

$HgCl_2$. A. aerogens and E. coli also methylated mercury anaerobically but at a lower rate. Hamdy and Noyes (1975) isolated Hg-resistant strains from freshwater sediments. Fourteen were gram-negative short rods belonging to the genera Escherichia and Enterobacter, and six were gram-positive cocci (3 Staphylococcus sp. and 3 Streptococcus sp.). These authors found such large variability in the methyl mercury production of a Hg-resistant E. aerogenes strain, both under aerobic and anaerobic conditions, that no difference in the aerobic or anaerobic production rate could be established. In two Hg-resistant strains isolated from water and sediments of Chesapeake Bay, mercury volatilization was plasmid-mediated (Olson et al., 1979; Barkey et al. 1979). In one strain, mercury volatilization appeared to be chromosomally mediated. All other strains tested could transform Hg^{++} to Hg^{o}. In media containing 10 mg $HgCl_2$ l^{-1} under aerobic conditions, 21.5 to 87.2% of the mercury was volatilized within 24 h to Hg^{o}; under anaerobic conditions 12.7 to 17.8% was volatilized. Mercuric reductase genetically encoded in plasmids mediated the volatilization. Six out of 24 Hg-resistant strains (the majority were Pseudomonas) could methylate $HgCl_2$. Three of these strains contained plasmids. Only two strains could produce methyl mercury under either anaerobic or aerobic conditions. A strain of C. cochlearium which could decompose dimethyl mercury was also isolated (Pan-Hou et al., 1980). This ability was cured with acridine dye and recovered by conjugation of the cured strain with the parent strain. The cured strain then showed the ability to methylate Hg^{++}. Plasmids play an interesting role in methylation and demethylation in that they control the mercury biotransformation in two opposite directions of a single bacteria strain:

- without plasmids --> methylation
- with plasmids --> demethylation

Blair et al. (1974) isolated several Hg-tolerant bacteria from Chesapeake bay. Although most of them produced only Hg^{o}, one obligate anaerobe strain generated both Hg^{o} and CH_3Hg^{+}. One of the facultative anaerobes produced both Hg^{o} and CH_3Hg^{+} under anaerobic conditions but only Hg^{o} under aerobic conditions. Another facultative anaerobe produced anaerobically only Hg^{o} and one of the species transformed mercury species aerobically.

Sprangler et al. (1973) found that 30 bacterial cultures isolated from freshwater could aerobically degrade methyl mercury and 21 cultures could anaerobically degrade methyl mercury. Billen et al. (1974) showed that methyl mercury was decomposed, anaerobically and aerobically, in the presence of bacterial cultures obtained from river sediments. Furukawa et al. (1969) demonstrated that a bacteria strain (Pseudomonas sp.) from soil could decompose CH_3HgCl to methane and Hg^{o}. From these data it seems that more bacteria species are capable of reducing mercury salts to metallic mercury than to methyl mercury and many bacteria are also able to decompose methyl mercury.

At present it is believed that once methyl mercury is released from the microbial system into the surrounding water, it enters the aquatic foodchain either as dissolved methyl mercury associated with organic matter or particles.

As discussed above, a wide range of bacteria can oxidize Hg^{o} to Hg^{++}. However, the enzymes responsible for this oxidation have not yet been identified but it is very likely that the ubiquitous catalase (present in bacteria and animal tissues) may be involved (Silver, 1984).

The reducton of methyl mercury to Hg^{++} and to Hg^{o} are both catalysed by enzymes coded in the DNA of bacterial plasmids and transposons and are not

coded in normal bacterial chromosomes of Hg-resistant strains of micro-organisms isolated from soil, freshwater and marine environments (Silver, 1984; Wood and Wang 1983). The processes and the enzymes responsible are the following:

$$CH_3Hg^+ \underset{?}{\overset{\text{mercuric reductase}}{\rightleftharpoons}} Hg^{++} \underset{\text{catalase?}}{\overset{\text{mercuric reductase}}{\rightleftharpoons}} Hg^o \text{ (volatile)}$$

In the estuarine environment, the reduction of sulfate by Desulfovibrio species to produce hydrogen sulfide is important in reducing CH_3Hg^+ concentrations by S+-catalysed disproportionation to volatile $(CH_3)_2Hg$ and insoluble HgS:

$$2\ CH_3Hg^+ + H_2S \text{ -- } (CH_3)_2Hg + HgS$$

Hydrogen sulfide is extremely effective in volatilizing and precipitating mercury in aqueous environments. This reaction mobilizes metals from the aquatic environment into the atmosphere, but will occur only in organically polluted lakes, rivers, coastal zones, estuaries and salt marshes where Desulfovibrio species have access to sulfate under anaerobic conditions.

The formation of methyl mercury is favoured by, at least, partially aerobic conditions in nature, owing to the fact that H_2S, which is produced in natural anaerobic environments, converts Hg^{++} to HgS. The HgS is not convertible to CH_3Hg^+ without prior conversion to a soluble salt or to Hg^o (Ehrlich, 1981).

4.1.2 Mercury transformation by phytoplankton and seaweeds

The great attention given to the transformation of mercury species by bacteria has diverted interest from other micro-organisms. It seems that unicellular algae can volatize mercury. Ben-Bassat and Mayer (1975) trapped volatile forms of mercury transported by bubbling air into a saturated iodine solution in KI. They observed that during a 9-day experiment the culture solution containing 10 uM $HgCl_2$ without algae lost 22% of the mercury present at the beginning of the experiment while about 75% of the same mercury was lost when the medium was inoculated with Chlorella populations ranging from 300 million to one thousand million cells l^{-1}. Later, Betz (1977) also observed that in a culture of the marine Dunaliella tertialerta an increase of volatile mercury absorbed on charcool coincided with the maximum concentration of chlorophyll a. The experimental design was not optimal and in neither experiment was the nature of the volatile mercury investigated, but, nevertheless, experience shows that micro-organisms other than bacteria and funghi can also transform mercury species.

Sea weeds such as kelp produce iodine and it has shown that methyl iodide can be synthesised by a reaction between molecular iodine and methyl-B-12 (Wood, 1975). Significant concentrations of methyl iodide are present in surface sea waters. This is an excellent methylating agent and is capable of methylating Hg^o. It is possible that this plays an important role in the formation of methyl mercury in open ocean waters isolated from sediments by the thermocline.

4.1.3 Batch and in situ experiments

Many authors have added mercury salts to freshwater and marine sediments and determined the net methyl mercury production (Bisogni, 1979). In these

experiments, sediments have been used to which high amounts of inorganic mercury were added. Usually the experiments lasted 10 to 50 days but some were extended to several months. Because of the high mercury concentrations (selective for Hg-resistant bacteria) and long incubation times used, the results of these experiments cannot easily be extrapolated to natural conditions. Furthermore, under natural conditions other mercury species will be present other than these mercury salts added. There is still another point which has to be taken into consideration. In none of the experiments a distinction between methylation and demethylation processes was possible; therefore, all methyl mercury levels observed are the net result of methylation and demethylation.

Olson and Cooper (1976) experimenting with San Francisco Bay sediments found that under anaerobic conditions the methyl mercury concentration in the sediments was higher than under aerobic conditions (Table XXXVI). Higher methyl mercury concentrations were also observed in sediments with higher organic matter content. After 30 days, under anaerobic conditions, only about 0.1% of the 100 mg $HgCl_2$ kg^{-1} added to the sediment and 0.8% of the 10 mg $HgCl_2$ kg^{-1} sediment were transformed into methyl mercury. In sediments with the lowest organic content, to which 10 mg $HgCl_2$ kg^{-1} was added, no methyl mercury could be detected. Autoclaved and non-autoclaved sediment samples without mercury additions, served as control. It is interesting to note that, with the exception of sediment A, none of the controls produced any methyl mercury neither under aerobic nor under anaerobic conditions and also sediment type A produced methyl mercury only under anaerobic conditions. The non-autoclaved sample of this sediment produced about four times more methyl mercury than the autoclaved sample. This raises the question why no methyl mercury was produced in the controls except under anaerobic conditions. It is also possible that the amount produced was below detection limits.

Similar experiments were carried out on autoclaved and untreated sediments from an anthropogenic-contaminated area in the Haifa bay. Large amounts of mercury (100 ug Hg-T l^{-1}) added with the bacteria medium to the flasks containing the sediments did associate with the sediment and with the surface of the glass flasks. Methyl mercury was observed both under aerobic and anaerobic conditions in the medium above the sediment (Table XXXVII). The methyl mercury in the sediment was not detemined and hence these results are not directly comparable with the experiments discussed above.

Table XXXVI

Estimate of the net amount of methyl mercury produced in three types of sediments from the San Francisco Bay
(data from Olson and Cooper, 1976)

sediment type	$HgCl_2$ added mg kg^{-1} DW	net production in ng g^{-1} dry sediment/day aerobic	anaerobic
A	10	1.5	2.5
	100	1.5	5
B	10	0.2	1.3
	100	0.3	2
C	10	NDc	0.6
	100	0.5	0.8

Ndc = not detected

Table XXXVII
Levels of methyl mercury found in the medium above the sediments in percentage of the original added Hg amounts (data from Berdicevsky et al., 1979)

conditions	Hg in medium ug l^{-1}	MeHg in medium in % of total added after 2nd	5th	12th day
anaerobic	100	77	100	5.2
	3100	-	3.2	0.08
	10100	-	0.07	0.008
aerobic	100	-	-	4.2
	10100	-	-	0.12

Although the data are incomplete, they seem to show that the percentage of methyl mercury formed in the medium decreased with increasing mercury concentration and with the time of exposure. Unfortunately, the methyl mercury in the sediments was not determined. The same authors also observed that under anaerobic conditions the addition of 1 mg $HgCl_2$ l^{-1} already reduced the growth of the natural population present in the sediments, while under aerobic conditions a reduction in growth was only observed at concentrations greater than 5 mg $HgCl_2$ l^{-1}. In order to show that bacteria were necessary for the production of methyl mercury, the authors added Hg-resistant bacteria strains to autoclaved seawater/sediment media. Autoclaved medium without bacteria served as control. Very small amounts of methyl mercury i.e. 0.01% to 0.04 of the mercury added at the beginning of the experiment could be detected. Only in the media with bacteria obviously these results can only serve as a rough indication of what might happen in the environment, since the system also contained, besides sediments, organic substances of the growth medium, and consequently the effective concentration in the solution was certainly lower than the level predicted from the mercury additions. The reduction of methyl mercury production with duration of the experiment also seems to indicate that the bacteria fauna changed considerably. In fact, toxic effects (40 to 60 % inhibition) were observed at 1 ug Hg l^{-1} in natural populations from Chesapeake Bay (Olson and Cooper, 1976).

Recently Compeau and Bartha (1984) investigated the influence of redox, pH and salinity on the transformation of mercury species in estuarine sediments using reactors to control and continuously monitor several parameters. They observed that both salinity and Eh (mV) influenced mercury methylation. After 16 days, sediments spiked with 100 mg $HgCl_2$ kg^{-1} sediment, the concentration of methyl mercury reached a steady state between methylation and demethylation (Table XXXVIII).

These observations clearly show a reduction in methylation both with salinity and with passing from anaerobic to aerobic conditions. After these first 16 days another spiking with 100 mg $HgCl_2$ kg^{-1} sediment slurry produced a doubling of the steady-state methyl mercury concentration. During the experiment, volatilization was minimal. Adding 1 mg of MeHg kg^{-1} of sediment under anaerobic conditions (- 220 mV) showed that demethylation was higher (double) at a salinity of $25^{o}/_{oo}$ than at a salinity of $4^{o}/_{oo}$, but under aerobic conditions (+ 110 mV) the demethylation was practically the same as that under anaerobic conditions and a salinity of $2.5^{o}/_{oo}$.

Again the high additions of $HgCl_2$ have most probably produced artefacts so that these experiments supply only limited amounts of useful information.

Table XXXVIII
Influence of salinity and redox potential on the net formation of methyl mercury (Compeau and Bartha, 1984)

Eh (mV)	salinity °/oo	mg MeHg kg^{-1} sediment	methylation in % of Hg-T in sediment
- 220	4	260	0.25
- 220	25	150	0.16
+ 110	4	70	0.07
+ 110	25	50	0.05

The *in situ* experimens of Bothner *et al.* (1980) are of great interest. These authors placed a bell jar in a contaminated site (station 3A) and another in a relatively uncontaminated site (station 3) on the sediment surface in Bellingham bay (Northern Puget Sound, Washington). Station 3A was situated about 100 m from the outfall of a chlor alkali plant and station 3 at 700 m. The area of station 3A also received wastes from a sewage outfall and from a pulp and cardboard mill. At station 3 the conditions in the sediment were aerobic down to about 20 cm. At station 3A the sediments were anaerobic, but the water circulation above the sediment surface maintained oxidizing conditions. The mercury concentrations in the sediment and the interstitial water at station 3A were much higher than those at the uncontaminated station 3. In the experiments, Hg-free air was passed through the bell jar; volatile mercury in its different (operational defined) forms was determined in the passing air stream as well as dissolved mercury in the water above the sediment. Placing a glass plate under the bell jar in order to isolate the water contained in the bell jar from the mercury coming from the sediment served as a blank. In both stations no volatile mercury from the sediment could be detected since "blank" and "sample" gave statistically equal results. In both conditions, about 1 ng Hg h^{-1} was carried with the air stream into the mercury traps, so it is clear that the mercury was stripped from the water and did not originate in the sediments. On the other hand, the dissolved mercury in the sea water contained in the bell jar of station 3A showed a marked increase over the "blank". The flux from the sediment to the water above the sediment was not measurable at station 3 probably because of the small concentration difference between the mercury in the interstitial water (0.03 ug l^{-1}) and in the overlying water (0.01 ug l^{-1}). It is interesting to note that 50 to 75% of the volatile mercury was Hg^{o} and that the increase in the dissolved mercury in the bell jar at station 3A strangely enough had no measurable effect on the amount of volatile mercury produced, although the concentration of soluble mercury had increased from 30 to 120 ng Hg l^{-1}. From these data the authors estimated a flux of 600 ng cm^{-2} $year^{-1}$ from the sediments to the sea water above. If one assumes a concentration of about 40 ug Hg g^{-1} sediment then the sediment should contain about 70 ug Hg cm^{-3} (FW = 0.7 DW; specific gravity 2.5). That means that during one year, 0.8% of the mercury in the first cm of the sediment was lost to the water as soluble mercury. A second experiment, in which unfortunately the flux of volatile mercury was not determined but one bell jar

was kept under oxygen limitation, showed that the concentration of dissolved mercury in sea water above the sediment increased more in the oxygen-limited conditions than in the previous oxygenated arrangement.

4.1.4 Mercury transformation by higher marine organisms

The data on methylation in higher organisms are still conflicting. The indigenous microflora of isolated intestines of six fresh water fishes could methylate mercury under anaerobic conditions (Rudd et al., 1980). Likewise, pike and walleye intestine contents methylated a larger fraction of ^{203}Hg than those of white fish and suckers. On the other hand, Pentreath (1976a, b) could not detect organic radioactive mercury after plaice or the worm Nereis were kept in sea water containing $^{203}HgCl_2$. Brook trout could not methylate Hg (II) compounds, nor could their tissues or organs. Also pure bacteria cultures isolated from the intestine of tuna did not methylate inorganic mercury (Pan-Hou and Imura, 1981) but some of these pure cultures, which had a higher mercury resistance, could demethylate methyl mercury. The intestinal flora of rats can methylate $HgCl_2$, but no methylation occurs through cow rumen microflora. Most of the mercuric compounds passed through unchanged, only a small amount was reduced to Hg^o. (Thayer and Brinckman, 1982). It seems that only microorganisms (including those in fish intestine) can methylate mercury.

The liver of marine mammals has been indicated as a site for demethylation because methyl mercury is present at low concentrations but experimental evidence is still missing.

CH_3HgSCH_3 has been found in shellfish from the Minamata Bay (Uchida et al., 1961) although it has not yet been identified definitively in shellfish from other areas.

4.1.5 Abiotic mercury transformation

Several abiotic methylation mechanisms of mercury species have been reported. Methyl mercury can be formed from Hg(II)-salts and acetic acid by abiotic means, e.g. transalkylation with methyl tin or tetramethyl-lead or photochemically with UV and visible light (Ehrlich, 1978). DeSimone (1972) observed that water-soluble methylsilicon compounds can react with Hg^{++} to yield methyl mercury.

Photomethylation using methanol, ethanol, acetic and propionic acid produced methyl mercury from mercuric chloride (Akagi et al., 1977). An amount 0.1% of the total $HgCl_2$ present was transformed into methyl mercury in 20 hours. Hayashi et al. (1979) also observed photomethylation of inorganic mercury when aliphatic amino acids were irradiated with UV light for 4 hours. The formation of methyl mercury was not related to the alkyl residues of the amino acids. Photolysis of glycine and phenylglycine did not yield alkyl-mercury compounds indicating that the formation of the methyl mercury was due to an apparent fragmentation of the alkyl residues of the amino acids during photolysis. Creatine and even lead and tin gasoline additives have also been reported to methylate mercury (Tanaka et al., 1978).

Both humic and fulvic acids have the ability to methylate inorganic mercury, albeit under conditions which are far removed from those found in the natural environment. Nagase et al. (1982) investigated several factors which influence mercury methylation by humic acids (HA). Temperature, Hg concentration and HA concentration have considerable influence. If one

attempts an extrapolation to natural environmental conditions, i.e. 20 °C, 1 ng Hg l^{-1} and 1 mg HA, one would obtain the following in 3 days at pH 7. Starting from the influence of temperature (because, as can be easily verified, the standard conditions of the various experiments do not all give the same results) one obtains:

at 20 °C, 6 mg HA yield 2 ug MeHg l^{-1} at a concentration of 750 mg Hg l^{-1}
or
6 mg HA methylate 0.0003% of the inorganic mercury present in 3 days
or
1 mg HA l^{-1} methylate 0.00006% of the inorganic mercury per day
or 1 mg HA l^{-1} methylate 0.006% of the inorganic Hg $year^{-1}$.

This is a very small amount of methyl mercury indeed. Model experiments under conditions which are near those found in the natural environment, especially at much lower mercury concentrations, are needed to confirm this extrapolation.

4.2 Uptake and release of mercury species by biota

Since only a few experiments have been carried out on Mediterranean species, therefore, it was necessary to also consider results on species from other areas in order to gain an understanding of the dynamics of uptake and release of mercury species.

Fisher et al. (1984) compared heat-treated cells (45 °C) of unicellular algae with live cells using radioactive inorganic mercury diluted in different concentrations of stable inorganic mercury and comparing the concentration factors. Easily bound radioactivity was removed from the filtered cells by washing the cells with 0.0001 M EDTA. For all four algae studied, the degree of mercury association with the cells was directly proportional to the external mercury concentration; this was expected since the internal mercury concentrations were not regulated. As the cells divided to produce new cells the total particulate mercury content increased but the mercury concentration per cell remained constant. Heat-killed cells accumulated larger amounts of mercury than living cells. The authors interpreted this to mean that the mercury is adsorbed non-metabolically. However, it is not clear if the cell surface has not been altered by the heat treatment. In fact Glooschenko (1969) had already observed that formaline killed diatoms accumulated more mercury than live cells, most probably because the surface of the cells had been changed by the formaline treatment. Also Davies (1976) concluded that mercury is taken up by passive diffusion.

Results with freshwater planktonic organisms indicate a very rapid elimination of methyl mercury, with a biological half-time T_b of about three days (Huckabee et al., 1979). This is most probably due to biological elimination.

The uptake of mercury by molluscs has been studied by Cunningham and Tripp (1975), Fowler et al. (1978), Miettinen et al. (1970), Unlu et al. (1970) and Wrench (1978). Working on Mediterranean species Fowler et al. (1978) investigated the uptake from food and water and release (loss) of radioactive-labelled $HgCl_2$ and methyl mercury by mussels (M. galloprovincialis) and shrimp (Lysmata seticaudata). In mussels, the uptake of methyl mercury from sea water was greater than that of $HgCl_2$, but the great variability of the data did not result in a statistically significant

difference. The data also showed that the uptake of methyl mercury from water is not an important route into the mussels. When both labelled water and labelled food (phytoplankton for the mussels and mussels for the shrimps) were offered, after 35 days the mussels had accumulated about twice as much radioactive methyl mercury as $HgCl_2$ and the shrimps had 10 times more methyl mercury than $HgCl_2$. This shows that methyl mercury is accumulated easier than inorganic mercury, the relative amounts accumulated depending, of course, on the amount of labelled food offered. The loss of radioactivity from mussels and shrimps (labelled both from water and food) in clean sea water in the laboratory and in cages situated in the natural environment showed that the mussels lost the inorganic mercury and methyl mercury faster under in situ conditions than in the laboratory. Probably more food was available under in situ conditions. But strangely enough, the methyl mercury was lost by mussels under in situ conditions faster than the $HgCl_2$. Unfortunately the authors did not report whether the in situ mussels had grown more than the "laboratory" mussels. In shrimps no difference was noted.

		biological half-times in days	
		MeHg	$HgCl_2$
mussels	in situ	63	82
	in lab	380	140
shrimps	in situ/lab	530	110

The validity of the results on mussels and shrimps depends on the assumption that the mercury species were not transformed during the experiments. This was not checked, only the radioactivity was determined and no attempt was made to distinguish between organic and inorganic radioactive mercury. Summarizing also the results from other authors in molluscs the biological half-times for inorganic mercury range from 20 to 40 days and for methyl mercury from 150 to 1000 days. Without information on the metabolic activity during loss experiments it is difficult to compare the results.

Experimental studies of uptake, accumulation and loss of methyl mercury and inorganic mercury in two species of flatfish (plaice and thornback ray) both from water and from food have been carried out by Pentreath (1976a, 1976b, 1976c, 1976d). Uptake of inorganic mercury by plaice from water only was directly proportional to the water concentration up to 3 ug Hg l^{-1}. The loss occurred with a T_b of 190 days. A similar T_b was observed in the thornback ray. However, when exposed to methyl mercury in sea water no measureable loss in the ray could be detected. When mercury was fed to plaice in the form of radioactive labelled worms (Nereis) the uptake efficiency for inorganic mercury was low (3 to 14%), while the efficiency for methyl mercury was very high (80 to 100%). The loss of inorganic mercury was quite rapid (Tbs from 30 to 60 days) and the loss of methyl mercury was very slow (Tbs from 275 to 325 days). Also the tissue distribution of the two mercury forms was very different. When the fish were exposed to methyl mercury, the methyl mercury was partitioned strongly into the muscle, as has been observed in fish sampled from the field. On the other hand when the fish were exposed to inorganic mercury the inorganic mercury was largely found in the body organs. These results are consistent with the diet being the major source of methyl mercury, almost complete uptake of methyl mercury from the food, and little or no demethylation and subsequent little or no elimination from the organism. For inorganic mercury, the uptake efficiency is poor, and may be due to low absorption and fairly rapid metabolism in the liver as well as to rapid excretion.

The uptake of mercuric sulphide from sediments by freshwater fish has been studied (Gillespie and Scott, 1971). Although uptake from control sediments (0.024 ug Hg kg^{-1} DW) was appreciable, fish exposed to sediments containing 50 mg Hg kg^{-1} DW as mercuric sulphide accumulated still higher amounts of mercury.

No data exist on the uptake and loss of mercury by marine birds and mammals.

Another approach has been adopted by Buffoni et al. (1982) and Bernhard (1985). These authors have used a relatively simple model of a pelagic food-chain (sea water, plankton, sardine, tuna), based on general data available on mercury metabolism (section 4.2) and specific mercury concentration in pelagic marine organisms from the Mediterranean and the Strait of Gibraltar. Since data on mercury concentration in natural phytoplankton and zooplankton versus size are lacking, the authors used a concentration factor for the first trophic levels (plankton). It should be noted that this way the first part of the model is static and only the part of the model which deals with the uptake by sardines and by tuna is dynamic.

As discussed in section 3.5.5 the bluefin tunas caught in the Western Mediterranean can be divided into two distinct populations according to their mercury concentrations: one "low-mercury population" and a "high-mercury population". Likewise, sardines (and other pelagic fishes) from Gibraltar and the North Sea have lower mercury levels than specimens of the same species caught in the western Mediterranean.

On the basis of their modelling simulations the authors could explain the differences in the mercury concentrations observed in the two bluefin populations and how the Hg-T can increase with the size of the organisms, how at the same time the percentage of methyl mercury can grow both in the individual species and with the level of the food-chain. In addition, the model showed that it is not necessary to assume that higher organisms can methylate mercury because the difference in the uptake and loss kinetics between methyl mercury and inorganic mercury are sufficient to explain the high methyl mercury enrichment observed in older specimens and in species located in the higher trophic levels. Simulating different growth rates in the "high-mercury-tuna" showed that only an eight to ten times reduction in the growth rate could produce mercury levels which were similar to those obtained in the low mercury-tunas. Although different growth rates of 10 to 20% have been reported for anchovies from different parts of the Mediterranean such a reduction cannot occur in nature (Demir, 1965). The data on growth of tuna from the Atlantic and the Mediterranean reported by Sella (1924), Rodriguez-Roda (1957), Tiews (1960), Scaccini (1965), Sara (1973) and Mather (1974) differ insignificantly from each other. The model also predicted that the mercury concentrations in the sardines depended on the mercury concentrations in the sea water and hence the mercury concentrations in the sea water should be higher (about five times) in the (western) Mediterranean than in the Atlantic or that the amount of organic mercury is higher in the (western) Mediterranean than in the Atlantic, but that this difference would not show up due to the uncertainty of the data. This prediction has recently been criticized by Aston and Fowler (1985) on the grounds that sardine is not a typical tuna food. The authors observed during a fishing contest near Monaco that all small tunas caught had exclusively euphausids in their stomachs. In addition, they maintain that seawater concentrations of mercury in the Mediterraean and the Atlantic are the same. Scaccini (1965) summarizing the biology of Thunnus thynnus explains that very small tuna feed on micro- and macro-plankton, larger tunas feed on many different pelagic

species such as sardines, anchovy, scomber spp, but also molluscs such as sepia, squid and crustaceans. In the model, the sardine was taken as a typical food item and because extensive mercury data existed for this species. Like all models it needs verification which in part has already taken place by the findings of Capelli et al. (1986), (Fig.19) who found that the distribution of inorganic and organic mercury in Sarda sarda occurs as predicted for the tuna. Similar distribution has recently been observed for the sardine (Cerrati et al., 1986). In addition, the static part of the model. i. e. the model's first trophic levels need dynamic modelling since at present it is based only on concentration factors.

4.3 Biogeochemical cycles

The uncertainties in many mercury concentrations and the lack of data on fluxes allow only a qualitative general description of possible pathways and sinks (Zafiropoulos, 1986). The heterogenic distribution of mercury in the geological formations of the land surrounding the Mediterranean does not seem opportune to attempt a general description of the entire Mediterranean. It seems more appropriate to attempt to describe the biogeochemical cycle in general terms and illustrate the possible pathways on an example of an area of the Mediterranean.

The most important sources of mercury for the marine environment are the rivers and atmosphere. The mercury in the atmosphere originates from degassing of the land and of the sea, and emissions of volcanoes (section 3.2). The degassing over mineral deposits (Hg geochemical anomalies) should be considerably higher than over land with a background concentration and the degassing over land has shown to be higher than over the ocean. The large majority of mercury in the atmosphere is Hg^{o}. Soluble and particulare mercury constitutes about 1% of the Hg-T, but these fractions are the most important fluxes from atmosphere to the sea and land through wet and dry deposition. Anthropogenic mercury species will also contribute to these natural sources and according to their origin may contain small amounts of organic mercury. Organic mercury is also thought to be released from natural sources.

The mercury naturally present in soil and minerals will be solubilized during weathering by abiotic and biotic processes and transported by rivers and land run-offs into the sea. The concentration of dissolved free Hg-ions in river water should be low since most of the inorganic and organic mercury will be bound to organic dissolved matter or associated with particles (either as suspended matter or in the bedload sediments). The high sediment concentrations in the rivers draining natural geochemical anomalies and the higher than background mercury concentrations in sediments of the adjacent coastal areas illustrate this transport route. In estuaries, mercury is partially mobilized from the particulate matter. The larger mercury containing particles are deposited near the river mouth while the lighter particles are transported further into the sea. At the same time inorganic mercury and the organic mercury produced biotically and abiotically in the river system and which is bound to organic dissolved matter will be released into the sea water and taken up by marine organisms, mainly autotrophs. These autotrophs will then pass on both inorganic and organic mercury along the foodchain. During the path through the foodchain the different uptake efficiencies and release half-times of inorganic and organic mercury enrich the organic mercury (methyl mercury) with respect to inorganic mercury (section 3.5.5 and 4.2) resulting both in higher total and organic Hg concentrations in older specimens and in species occupying higher trophic levels (sections 3.5.5, 3.5.6 and 3.5.7). The inorganic mercury will increase during the growth of an organism to a certain relative amount until the uptake

and release will attain a dynamic equilibrium at which the concentration of the inorganic mercury will remain about constant and the increase in Hg-T will be entirely due to the increase in methyl mercury. Faecal materials and dead organisms will sink in the water column and after partially cycling through various detritus feeders and bacteria will reach the bottom sediments. There, mercury associated with inorganic and organic particles and contained in organisms will cycle through the benthic fauna and finally be deposited and adsorbed in the sediment.

In the sediment, a complicated process mediated by microorganisms will transform inorganic mercury into monomethyl and dimethyl mercury (section 4.1). The monomethyl and dimethyl mercury produced in the sediments is believed to be released into the sea water and taken up by biota. At present it is not known whether an abiotic process in the sediments or in the water column can also produce organic mercury species. The volatile dimethyl mercury passes through the sea water column into the atmosphere where it is decomposed by sun light.

Baldi (1986) has proposed a scheme of such a biogeochemical cycle for the Tyrrhenian Sea with indications on the concentrations of mercury in the various compartments (Fig.46).

The available data to date do not allow us to be more specific about biogeochemical cycles in the Mediterranean.

5. Effects of inorganic and organic mercury species on marine organisms and ecosystems

From the point of view of fishery management the effects of pollutants on marine organisms and their habitat must allow an acceptable level of productivity. From the point of view of environmental protection, major alterations of the marine environment can not be accepted. Not mere survival of important organisms but the maintenance of truly viable populations is required which can only be guaranteed if successful reproduction can be achieved (Perkins, 1979). This means that in order to assess the effects of pollutants, information on their effects not only on adults but also on reproduction, development and growth rates are needed. Many biological effects of pollution may not show up in the short-term bioassay test for acute toxicity since the effects are slow to develop or slow to produce a general debility that interferes with some of the normal life functions of the organism instead of killing it directly during the short-term exposure. The fact that organisms which survived the short-term exposure die later after being transferred into clean non-toxic water is also indicative for the short-comings of short-term exposures for estimating water quality. Long-term exposure to sublethal concentrations are necessary to estimate the reproductive success, growth rate, alterations in the life span, adaptations to environmental stresses, feeding habits, migration pattern, changes in physiological and biochemical functions, predisposition to diseases etc. (Water Quality Criteria, 1972; Perkins 1979). The practice of using short term acute exposure (LD-50 bioassay) to estimate long-term effects by applying an application factor is also questionable. Moreover, in LD-50 bioassays the organism is exposed only to one route of entry, namely the direct pathway from water and the effects of pollutants through the organism's food is completely neglected. However, even if appropriate data are available for a single species' reactions to pollutants during a life cycle their effects on ecosystems cannot be easily predicted. Natural changes of ecosystems are not well enough understood to distinguish between the effects of specific pollutants and changes occurring naturally. Only under certain circumstances, changes on natural ecosystems due to specific pollutant effects can be identified. The effects in large enclosed ecosystems can help to understand the possible effects of pollutants but their application has so far been restricted to pelagic environments. At present, there seem to be no adequate data available to assess the general risk of mercury on marine biota and ecosystems.

Evidence presented in section 4.2 shows that the uptake of mercury in marine organisms depends both on the chemical species of mercury and on the route of entry into the organism. Organisms which belong to the first trophic level such as algae and aquatic plants take up inorganic and organic mercury directly from the surrounding sea water. Since the first trophic level enriches mercury by a concentration factor of about 5000 over the concentration in sea water, the uptake of higher trophic levels should occur primarly through the foodchain. Methyl mercury is an accumulative pollutant with a near 100% uptake efficiency and very long retention times (Tb of years) while the uptake efficiency of inorganic mercury is less than 10% and its Tb in the order of tens of days. This means that older organisms, contain more mercury as methyl mercury. Since organisms belonging to high trophic levels generally feed on larger fish than organisms in lower trophic levels, the distribution between inorganic mercury and methyl mercury in the prey's tissues will shift from inorganic mercury towards methyl mercury making the intake of methyl mercury through the foodchain of increasing importance in higher levels of the foodchain.

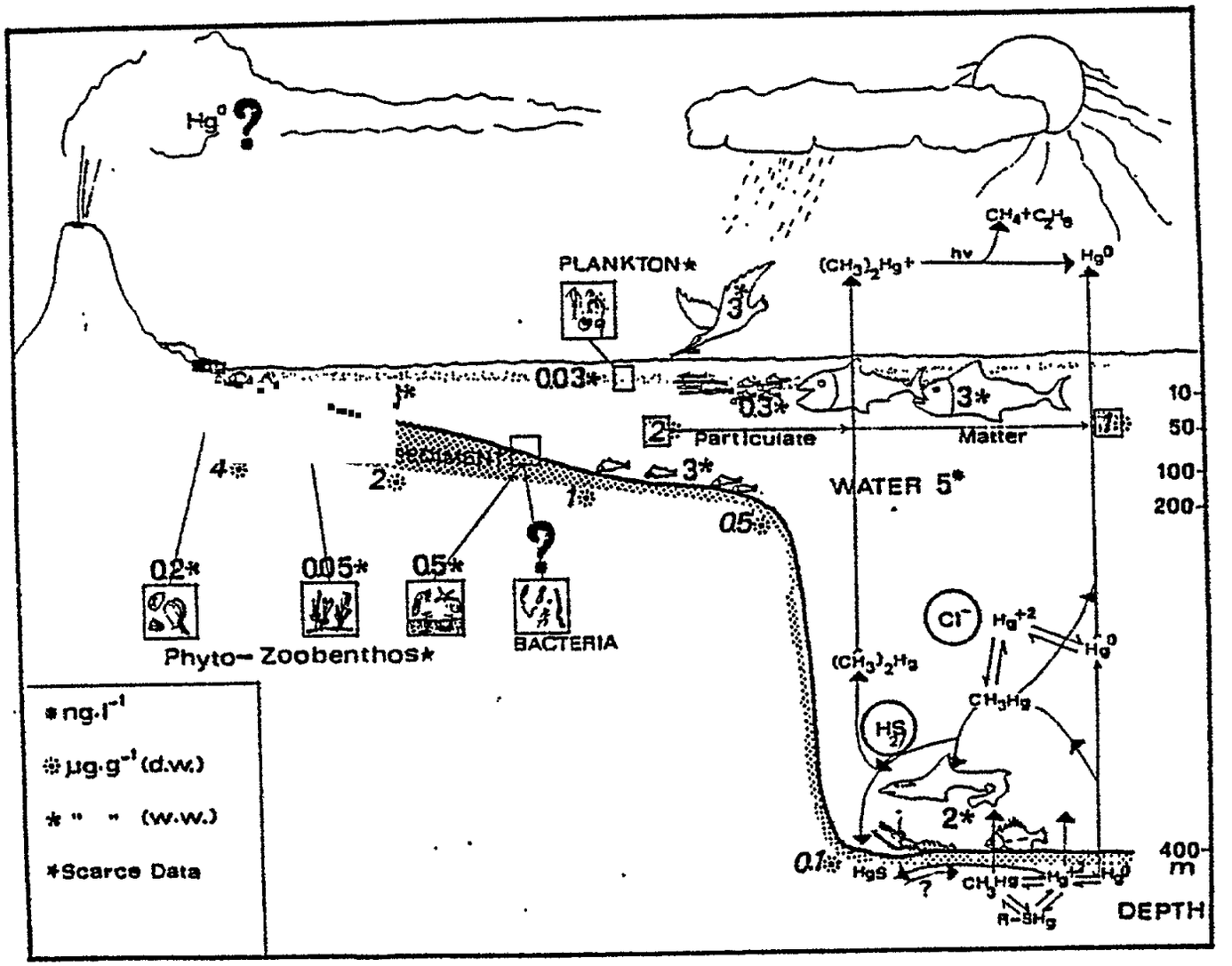


Figure 46. The biogeochemical cycle of mercury (Baldi, 1986).

Data on chronic and sublethal effects of mercury are limited for the Mediterranean species and therefore, data from other regions are also considered.

5.1 Phyto- and zooplankton

Davies (1978) reviewed the effects of 'heavy metals' on phyto- and zooplankton organisms. Unfortunately, in the majority of cases the effective concentrations are unknown since neither the resulting concentration was measured nor the effect of chelating substances and in culture media were taken into consideration. If the phytoplankton organisms are tested in batch culture the nominal concentration of mercury in the sea water is reduced markedly during the first days and most of the mercury is associated with the algae (Smith, 1983). Later, during growth the cell number of the algal

population increases and consequently the mercury concentration/cell decreases rapidly reducing the internal and external exposure concentration. Without chelators the lowest nominal effective concentrations observed ranged from 0.02 and 0.35 ug Hg l^{-1}. However, even without chelators some algae can withstand much higher mercury concentrations ranging from 1 to 10 ug Hg l^{-1}. The greater tolerance is due to a reduced uptake of mercury (Davies, 1976). But apparently also different strains of the same species have different tolerances. Dunaliella tertiolecta tested by Davies (1976) was 1000 times less sensitive than the same species examined by Sick and Windom (1975). A comparison of the effects of $HgCl_2$ and methyl mercury showed that an inhibition of C-14 uptake in natural phytoplankton populations began at less than 0.1 ug Hg l^{-1} for MeHg and at 1 ug Hg l^{-1} for $HgCl_2$ (Knauer and Martin 1972). For comparison, Holderness et al. (1975) observed that the growth of freshwater green alga Coelastrum microporum was not inhibited at concentrations of 0.8 ug MeHg l^{-1}. Inhibition started only at 3 ug MeHg l^{-1}. In zooplankton organisms 2 ug Hg l^{-1} decreased the faecal pellet production during the first 2 days, but not in successive days (Reeve et al., 1977) probably because the effective mercury concentration had decreased in the meantime.

5.2 Macrophytes

Fucales (seaweeds) exposed in a continuous flow system to concentrations of mercury ranging from 0.9 to 1250 ug Hg(as $HgCl_2$) l^{-1} showed that at the lowest concentrations tested no effects could be detected on the growth of vegetative apices. A small reduction of growth as compared with controls occurred at concentrations greater than about 10 ug Hg l^{-1} (Stroemgren, 1980).

5.3 Bacteria

Very few data exist on the toxicity of mercury compounds on marine bacteria. Jonas et al. (1984) observed that natural populations from Chesapeake Bay showed 40 to 60% growth inhibition at 1 ug inorganic Hg l^{-1}. A similar inhibition was also observed for 1 ug MeHg l^{-1}. Toxic effects of methyl mercury were observed even at 0.1 ug Hg l^{-1}. Unfortunately the authors did not test low concentrations of inorganic mercury so that the onset of the inhibition of inorganic mercury was not determined. Their data seem to indicate that inorganic and organic mercury have the same toxicity to marine bacteria. Pan-Hou and Imura (1981) found differences in the minimal inhibitory concentrations of $HgCl_2$ and CH_3HgCl on pure bacteria strains isolated from the intestines of yellowfin tunas. Of the 14 strains tested 9 showed effects at lower concentrations: 800 to 1600 ug CH_3HgCl and 4000 to 8000 ug $HgCl_2$ l^{-1}. Five strains were more resistant and showed effects only at 6400 to 12800 ug CH_3HgCl l^{-1} and 16000 to 32000 ug $HgCl_2$ l^{-1}. It is not clear why the strains examined by Pan-Hou and Imura (1981) are about 1000 times more resistant than the natural populations studied by Jonas et al. (1984). Probably the strains of Pan-Hou and Imura which were obtained from another author were isolated on a medium which was selective for Hg-resistant strains.

5.4 Crustaceans

The LC-50 48h for newly hatched zoeae of Palaemonetes vulgaris (shrimp) were 10 ug $HgCl_2$ l^{-1} for unfed and 15 ug $HgCl_2$ for larvae fed with Artemia salina. No effects to 48 h exposure were estimated to occur at 5 ug $HgCl_2$ for fed and 3 ug $HgCl_2$ for unfed larvae. Transferring larvae into clean sea water after a 48 h exposure to study delayed effects showed that

none of the larvae exposed to 32 ug $HgCl_2$ survived for more than one day demonstrating the severe limitation of short-term bioassays. 48 h exposure to 10 and 18 ug $HgCl_2$ l^{-1} showed a marked delay in the first molting and caused deformations. The growth of young Penaeus indicus was significantly reduced up to 6 ug Hg l^{-1} (McClurg, 1984).

Vernberg and Vernberg (1972) and De Coursey and Vernberg (1972) showed that U. pugilator adults (fiddler crab) could survive for months in seawater containing 180 ug Hg l^{-1} while all stage I zoeae died after only 48 h when exposed to the same concentration. In three species of fiddler crabs 100 ug MeHg l^{-1} had no effects on regeneration of limbs and molding (Weis, 1977). However, this concentration caused a complete inhibition of melanogenesis in U. thayeri, partial inhibition in U. pugilator but no inhibition in U. rapax. A 500 ug MeHg l^{-1} concentration inhibited U. rapax the most and U. rapas the least. Inorganic mercury inhibited limb generation at 1000 ug Hg l^{-1} but had no effect at 100 ug Hg l^{-1}. U. pugilator pre-exposed to 60 and 100 ug MeHg l^{-1} did not reduce the inhibitory effects of 500 ug MeHg l^{-1}, although differences in the inhibitory effects could be observed when three populations from an unpolluted site, a slighly polluted site and a chronic polluted site were compared. The inhibitory effect was smaller in the population from the chronic polluted site (Callaghan and Weis, 1983). This may indicate that mercury does not induce methionin but that methionin is induced by other pollutants. Similar results were obtained by Green et al. (1976) who found that pre-exposing postlarval shrimps (Penaeus setiferus) to 0.1 and 0.5 ug Hg l^{-1} for 59 days did not increase the 96h-LC-50 value obtained for non pre-exposed shrimps. Chronic exposure of the shrimp to 0.5 and 1 ug Hg l^{-1} did not effect respiration rate, growth, or molting frequency. Higher concentrations were not tested.

Although not a marine organism, the brine shrimp exposed during an entire life cycle to inorganic and methyl mercury in water may give some indications on truly marine organisms. Significant reduction in adult lifespan was observed at 10 ug $HgCl_2$ and 5 ug MeHg (Cunningham and Grosch, 1978). The survival of nauplii from treated parents was not reduced at 10 ug $HgCl_2$ l^{-1} but was reduced at 1 ug MeHg l^{-1}. Pairs exposed to 10 ug $HgCl_2$ l^{-1} exhibited only a slight reduction in brood production while pairs exposed to 5 ug MeHg l^{-1} and higher concentrations did not produce any nauplii.

5.5 Molluscs

Very few data exist on molluscs. The 7d-LC-50 for mussels (M. edulis) is 150 ug Hg l^{-1} (Martin et al., 1975). Growth of the shell is reduced to 50% after exposure to only 0.3 ug Hg l^{-1} (Stromgren, 1982). At concentrations above 1.6 ug Hg l^{-1} growth stopped within 3 days.

5.6 Fish

The killifish Fundulus heteroclitus, because it is easy to culture, was used for several studies on toxicity of inorganic mercury and methyl mercury. Sharp and Neff (1985) exposed embryos of F. heteroclitus at different times after hatching to various concentrations (0 to 100 ug Hg l^{-1}) of $HgCl_2$ and methyl mercury. Comparing 4 days mortality and abnormal development showed that embryos exposed immediately after fertilization were more sensitive to both $HgCl_2$ and MeHg than older (up to 5 days) embryos. In general methyl mercury was more toxic but the relative toxicity to $HgCl_2$ varied widely from about half as toxic to several times more toxic than inorganic mercury.

Embryos of the killifish Fundulus heteroclitus from a polluted and an unpolluted site exposed for one week to 30 ug MeHg l^{-1} exhibit different degree of malformations. The embryos from the polluted site had virtually no anomalies while those from the other site showed a range of malformations from unaffected to rather severely affected (Weis et al., 1981). Also when exposed to 50 ug MeHg l^{-1}, 55% of the embryos from the polluted site exhibit no malformations while the embryos from the unpolluted sites showed marked malformations. For comparison, the 96 h-LC-50 of inorganic mercury for adult F. heteroclitus ranges from 230 and 2010 ug Hg l^{-1} which is about 8 to 70 times greater than the teratogenic dose for this species (Jackim et al., 1970; Klaunig et al., 1975) and for MeHg the 96h-LT-50 of F. heteroclitus larvae is 5320 ug MeHg l^{-1} (Weis et al., 1985). But when Fundulus heteroclitus adults were maintained in only 5 ug MeHg l^{-1} they failed to produce additional clutches of eggs (Weis et al., 1985).

Weis et al., (1982) investigated whether the pretreatment of embryos and adults of F. heteroclitus with methyl mercury could increase their tolerance to later exposure. They observed that embryos of F. heteroclitus from an unpolluted site showed more malformations after exposure to methyl mercury than $HgCl_2$. In a polluted site, however, the tolerance to $HgCl_2$ was smaller than to methyl mercury. Metallothionein was found in some batches of unfertilized eggs but at very low concentrations; probably too low to have any influence on toxicity. After exposing adult fishes to pretreatment with 10 ug methyl mercury, caudal fins were regenerated more slowly than the controls when exposed to 10 to 50 ug MeHg l^{-1}. This failure to develop a protective mechanism is supported by the observation that when embryos were exposed to methyl mercury the level of metallothionein did not increase more than in the controls (Weis, 1984). Therefore, it seems that the acquired greater tolerance of embryos from a polluted site must have been induced by trace metals other than methyl mercury. Weis (1984) observed that eggs had very little metallothionein (MT) but untreated embryos of tolerable clutches had twice as much MT as non-tolerable clutches at the time of hatching suggesting that MT is produced during embryo development. Treatment of embryos with either Hg^{++} or MeHg will not produce any MT.

An interesting experiment on fresh water fish may be mentioned here because it lasted over several generations. Exposure of three generations of brook trout to methyl mercury in freshwater only (food was not contaminated) showed that methyl mercury concentrations of 0.3 ug Hg l^{-1} or lower had no effect on all three generations. Maximal acceptable toxicant concentrations were between 0.93 and 0.3 ug Hg(as MeHg) l^{-1} (hardness 45 mg l^{-1}; pH 7.5). On the other hand the mean 96h-LC-50 for 20-wk-old (12 g) and yearlings was 75 ug Hg (as MeHg) l^{-1}. This would result in an application factor between 0.004 and 0.013. A follow-up on the toxicity studies showed that concentration factors (CF) between water and tissue ranged from 1000 to 10000; maximum CF: 7000 to 63000. Blood, spleen and kidney had the highest mercury levels, followed by liver, gill, brain, gonad and muscle. 90 to 95% of the total methyl mercury body burden was located in muscle. The mean muscle concentration in first generation trouts dying after exposure to 2930 ng Hg (MeHg) l^{-1} was 23.5 mg Hg kg^{-1} FW, while in the second generation dying after exposure to 930 ng Hg l^{-1} the mean muscle level was 9.5 mg Hg kg^{-1} FW. Relating toxicity to mercury concentrations in the body tissues showed that body levels of 2.7 mg Hg kg^{-1} FW had no effect but at body levels of 5-7 mg Hg kg^{-1} FW effects could be detected. No appreciable elimination of mercury was observed after 12-16 weeks.

5.7 Marine mammals

Two seals exposed to daily oral dosage of 250 ug MeHg kg^{-1} body weight did not show any abnormal blood values but showed reduction in activity and body weight. Another two seals dosed with 25 mg MeHg kg^{-1} body weight died after 20 and 26 days of exposure after showing previously severe symptoms of poisoning (Ronald et al., 1977)

5.8 Enclosed pelagic ecosystems

Pulse addition of 5 ug Hg l^{-1} to large plastic containers (1.5 m^3 and 15 m^3) showed that mercury concentration decreases rapidly in the bulk of seawater and inhibited the relative carbon assimilation rate in the bag without nutrient addition during the whole experiment (15 days) (Kniper et al., 1983). In nutrient-enriched enclosures the phytoplankton growth was inhibited by concentrations above 2 to 2.5 ug Hg l^{-1} in the bulk. Similar observations were made by other authors (e.g. Grice and Menzel, 1978). Pulse additions of 5 ug Hg l^{-1} decreased phytoplankton productivity for 12 days, influenced the distribution of phytoplankton and mesozooplankton species, and reduced the number of copepod nauplii for 34 days. Copepods (Pseudocalanus) taken from the enclosure failed to molt until the concentration of mercury in the enclosure had droped below 2 ug Hg l^{-1}. On the other hand, pulse additions of 1 ug Hg l^{-1} had no observable effects. Studying the biochemistry and toxicity of mercury in a controlled experimental ecosystem Wallace et al. (1983) found that the high affinity of mercury to the organic matter present in the system was the most important parameter governing the distribution of the chemical species of mercury. Ninety percent of the mercury was present in particulate, colloidal and high molecular weight dissolved forms and thus not bioavailable. In fact, when these fractions of organic matter were removed by ultrafiltration from sea water, the bioassays showed that 1 ug Hg l^{-1} was toxic to natural phytoplankton populations.

6. Human exposure

6.1 Toxicokinetic properties and doses causing health effects

Ingested or bound to protein methyl mercury is absorbed almost completely (95-100%) in the intestines. It is rapidly distributed throughout body tissues, the distribution phase being complete in approximately 3 to 4 days (Clarkson et al., 1984). Animal experiments indicate that the distribution of mercury among the different tissues after the administration of methyl mercury is more uniform than after the administration of inorganic mercury salts. Methyl mercury passes the blood-brain "barrier" into the central nervous system and the placental "barrier" into the foetus (Berlin, 1963). About 10% of ingested methyl mercury ends up in the brain and 7% in the blood. A rough rule of thumb is that in a 70 kg person approximately 1.0% of the body burden of methyl mercury is found in one litre of blood. The brain to blood concentration ratio in humans is about 5 to 1 (Clarkson et al., 1984) There is also a relatively constant ratio between concentrations in blood and hair, making hair a convenient indicator of body levels. The concentration of mercury in hair near the scalp is 200 to 300 times higher than in blood. Segmental analysis of mercury in hair can be used to evaluate blood levels (and body burden) at the different times when the hair segments were formed (Bakir et al., 1973).

After experimental ingestion of methyl mercury in humans, two phases of clearance from blood have been identified with half-times of about 8 hours, representing distribution to the tissues, and about 50 days, representing excretion from the body (Miettinen, 1973; Kershaw et al., 1980). Other studies have confirmed the slow component half-time in blood and the whole body half-time has been estimated at 70 days (WHO, 1976). Data derived from human experimental studies indicate that the blood level is proportional to the long-term intake when it is in the non-toxic range.

About 80% of the total excretion of methyl mercury in human beings takes place via the faeces. There is a considerable secretion of mercury to the intestines via the bile and much of this is re-absorbed to create an "entero-hepatic" system (Bakir et al., 1973). The total daily excretion via urine and faeces is about 1% of the body burden (Clarkson et al., 1984). Virtually all mercury excreted is in the form of inorganic mercury even after methyl mercury exposure. It is known that the intestinal microflora can demethylate methyl mercury. There is also evidence of a demethylation in body tissues, because inorganic mercury is secreted via the bile after methyl mercury exposure, but the site of demethylation is not known.

The toxic effects of methyl mercury are primarily manifested in the damage of the sensory part of the nervous system. According to WHO (1976) it is expected that 5% of an adult population will have overt symptoms when the blood concentration of total mercury is between 0.2 and 0.5 mg l^{-1}. This corresponds to 50 - 125 mg Hg kg^{-1} hair or to a long-term daily intake of 3-7 ug Hg kg^{-1} body weight in the form of methyl mercury. The foetus and infants are more sensitive than adults to the toxic effects of methyl mercury. Later reviews of methyl mercury toxicity have confirmed these conclusions (e.g. WHO, 1980).

The earliest clinical sign and symptom of methyl mercury poisoning is abnormal sensation or numbness (paraesthesia) in hands, feet and around the mouth. Increased exposure may result in lack of coordination of movements (ataxia), constriction of the visual field, slurred speech, and hearing difficulties. In the most severe cases of poisoning, the patient may develop

blindness, deafness, involuntary muscle spasms, paralysis and general physical and mental debilitation (WHO, 1976). Many patients died in Iraq in 1971/72 after eating contaminated bread prepared from wheat and other cereals treated with organic mercury fungicides (WHO, 1976). The nervous system is irreversibly damaged by methyl mercury, but some clinical improvement may occur because the function of some dead neurons are taken over by others and slightly damaged neurons regenerate (Clarkson et al., 1984). On the other hand, when the exposure is short there may be a latent period between the end of exposure and the onset of the intoxication, because both methyl mercury accumulation and neurological damage take time (Magos et al., 1978).

Methylmercury exposure in early childhood and before birth (via the placenta of an exposed pregnant woman) also causes central nervous system damage. In severe cases in Minamata (Tsubaki and Irukayama, 1977) the children had cerebral palsy and some of them died. Other authors have reported faulty brain structure (Choi et al., 1978), lower than normal brain size, blindness and severe motoric disorders (Gerstner and Huff, 1977) after intra-uterine exposure. In Minamata, a higher mercury concentration was found in umbilical cords of children with mental retardation than in control children (Harada et al., 1977).

In the poisoning incident in Iraq, less severe symptoms of brain damage were studied. Marsh et al. (1980) found a significant increase in the occurrence of developmental retardation, neurological signs and seizures in children exposed prenatally.

Apart from the nervous system effects, methyl mercury has no known other effects of relevance to the marine food chain.

In animal experiments and in cell culture, selenium and vitamin E can delay the onset of methyl mercury intoxication, but whether selenium or vitamin E at realistic doses can interfere with the toxic effects of methyl mercury in human beings is unclear (for further details see: GESAMP, 1987).

6.2 Sea food consumption patterns

Food preference, prices and availability greatly influence seafood consumption patterns. In general, in the coastal areas seafood is more available than in the hinterland, especially in the less developed countries. Certain population-sectors such as fisher men, fish vendors and their families have greater access to seafood than other persons. Also, persons on diet may preferentially consume fish and shellfish. No general seafood consumption studies have been carried out in Mediterranean countries. Based on seafood supply data (considering landings, export and import) national averages and percentages of seafood of Mediterranean origin can be estimated (Table XXXIX), but these data are not suitable for an estimation of the risk of mercury intake from seafood as these averages are based on supply (with consumption estimated as 50% of such supply) and the estimated averages provide no indication of consumption differences between population groups. How misleading these figures may be, is illustrated by the food consumption survey carried out for three different age groups in nine regions of the United States (Rupp et al., 1980). For example, in New England, the average saltwater finfish consumption for adults was 4.55 kg $year^{-1}$, while the 50% percentile was only 3.46 kg finfish $year^{-1}$. This means that 50% of the population consumed only 3.46 kg while the average was higher by about one kg $year^{-1}$. The 90% percentile was 9.85 kg $year^{-1}$ and the 99% percentile 20.27 kg $year^{-1}$. Or in other words, 10% of the New Englander consumed more than 2.2 times the average and 1% consumed more than 4.5 times the average.

Table XXXIX
Estimated average national consumption of fish and fishery products for the years 1979-1981 in Mediterranean and other selected countries

Country	weekly consumption in grams live weight per caput total (FAO, 1983)	% of Mediterranean origin (UNEP/FAO/WHO, 1983)
Algeria	20	100
Cyprus	80	30
Egypt	45	10
France	230	4
Greece	155	60
Israel	160	8
Italy	120	55
Lebanon	55	25
Libya	75	30
Malta	200	20
Morocco	55	10
Spain	300	10
Syria	15	10
Tunisia	75	100
Turkey	60	10
Yugoslavia	30	45
World	115	-
Faeroe Island	950	-
Iceland	855	-
Japan	800	-
USA	155	-
USSR	245	-

Consumption is estimated to be 50 % of the supply taking into consideration exports and imports

The maximum consumption was 29.76 kg salt finfish year^{-1} or 6.5 times the average. For the consumption of freshwater fish the consumption pattern is even more skewed. The average consumption was 0.11 kg year^{-1}, the 50% and the 90% percentile were both zero, but the 99% percentile was 2.44 kg year^{-1}. Or in other words more than 90% of the New Englander consumed no freshwater finfish at all. One percent of the population comsumed at least 22 times the average and the highest consumption (8.2 kg year^{-1}) was 74.5 times higher than the average.

Unfortunately similar data are not available for the Mediterranean and the estimates for national averages are of limited use for estimating the intake of seafood. Probably some general observations may also be considered. In Mediterranean countries with predominantly Christian background many persons eat seafood on Friday i.e. once a week. In summer, a large number of holiday makers choose the seaside and hence are more likely to consume fresh seafood than in their habitual residence in the hinterland. This seafood is more likely to be of Mediterranean origin, and therefore contains more mercury than the frozen fish available in the hinterland which,

in many countries is imported from non-Mediterranean fishing grounds (see Table XXXIX) and thus contains less mercury than the local seaside food. These qualitative scenarios seem to indicate that a large section of the general population consumes at least one meal a week with a higher frequency during summer but, with the exception of extreme consumers, will not exceed two meals a week on a long-term basis.

This means that attention must be directed towards the identification of critical groups with high seafood consumption. But also here problems arise. The individual with the highest consumption of seafood is not necessarily the person most exposed since the mercury intake depends also on the mercury concentration in fish and shellfish species consumed. This has been illustrated by the Australian Working Group (1980). As can be seen from Table XL, the persons who ate only about half the amount of the highest consumer had a calculated mercury intake which was about three times that of the highest consumer. In fact, if the highest consumer had consumed the same seafood species as the lower consumer his intake would have been 7.5 times higher or his weekly intake about 80 ug Hg kg^{-1} body weight. For comparison the Provisional Tolerable Weekly Intake is 5 ug Hg kg^{-1} body weight (see section 9.2). Similar results were obtained in estimating the mercury intake in Italy where the highest consumer of seafood had only about 40% of the mercury intake per kg body weight than a lower consumer (Table XLI). At this point it appears obvious that the attention has to be directed to the seafood consumption of critical groups (heavy seafood consumers) and to mercury concentrations in the species eaten by these persons.

Table XL
Influence of seafood species consumed on the calculated mercury intake (Australian Working Group, 1980)

Fish consumption g/week	weight of consumer	calculated Hg intake ug/kg body weight/week
3580	73.1	3.3
2840	74.7	8.5
2000	95.4	5.0
1440	54.5	10.4

Very sparse seafood consumption data of critical groups exist for the Mediterranean. Some have estimated the food consumption directly and others have, instead analysed mercury in hair and blood without supplying data on the amounts of the seafood species eaten (section 6.3).

Paccagnella et al. (1973) selected the population of Carloforte (Sardinia) for an epidemiological study, because its average consumption of seafood was about 4 times the national Italian average and because, during the summer months, fresh tuna meat from the local tuna trap was consumed. From 6200 residents 195 persons chosen at random agreed to give information about their food habits, take a medical examination and allow a blood and hair analysis. About 65% of these persons ate seafood more than 3 times a week. Eleven point seven percent consumed 7 or more meals of seafood and 1.5% as many as 13 to 14 meals equal to about 1400 g seafoods a week. Nauen et al. (1980) reported that fishermen from three Italian locations had consumed 5 to

11 kg FW of 71 different species in 3 weeks (1.6 to 3.6 kg/week/person). They gave 5 examples of fishermen consuming 27 fish species, 4 crustacean species and 5 different mollusc species with total consumption ranging from 1840 to 3820 g FW/week/person (Table XLI).

Other estimates and data from the Mediterranean and other European regions range from 2100 to 5600 g/week/person (Bernhard et al., 1972; Riolfatti, 1977; Cigna-Rossi et al., 1967; Bacci et al., 1976; Preston et al., 1974; Haxton et al., 1979). Especially aboard fishing vessels the crew eats only from the fish and shellfish caught and this may happen 3 times a day.

High consumption rates are also found in heavy fish eaters from other seas. Especially in Japan, high fish consumers have been found (Doi and Ui, 1975). Of 34 tuna fish retailers 22 ate 100 to 200 g tuna meat daily besides 70 to 300 g of shellfish and other fish meat. One person consumed daily 200 g FW of tuna meat in addition to 1000 g of other seafood. The daily tuna consumption of tuna fishermen aboard the ship ranged from 50 to 400 g during seasonal periods of between 130 and 180 days.

In order to be on the safe side it is reasonable to assume that there may exist extreme consumers of seafood which are able to consume 1 kg of seafood per day.

Table XLI

Examples of seafood consumption and estimated mercury intake in fishermen recorded during a period of 20 days (Nauen et al., 1980)

	Classif.	Marina	Ravenna	Fumicino	Bagnara	Calabra
Age (years)		52	55	54	36	28
Weight (kg)		65	86	82	68	60
Species		seafood consumed (g in 20 days)				
Anguilla anguilla	F			685		
Arnoglossus laterna	F		300			
Atherina hepsetus	F				250	
Auxis auxis	F				670	1030
Boops boops	F				200	
Callinectus sapidus	F		500			
Dicentrarchus labrax	F			170		
Diplodus sargus	F			685		
Engraulis encrasicholus	F	500		200	250	120
Euthunnus alletteratus	F				145	
Gobius sp.	F		600			
Lepidopus	F				250	
Loligo vulgaris	M	400	900		640	330
Maena sp.	F				570	150
Merlangus merlangus	F				970	860
Merluccius merluccius	F			1675		
Mola *)					200	370
Mugil cephalus	F	500	700			
Mytilus galloprovincialis	M		600		450	400
Octopus vulgaris	M			1250		
Parapenaeus longirostris	C			350	350	270

Table XLI (cont.)

	Classif.	Marina	Ravenna	Fumicino	Bagnara	Calabra
Age (years)		52	55	54	36	28
Weight (kg)		65	86	82	68	60
Species		seafood consumed (g in 20 days)				
Penaeus kerathurus	C			150		
Salmo salar	F			150		
Sardina pilchardus	F	4835	500	100	400	
Scomber sp.	F			485		
Scorpaena sp.	F				160	
Scyllarus arctus	C			350		
Sepia officinalis	M	500		1090	200	
Sprattus sprattus	F		1700			
Sphaeronassa mutabilis	F		1600	580		
Squilla mantis	C	1500	1500			
Tapes decussatus	M	2670				
Thunnus alalunga	F				335	
Thunnus thynnus	F		110		935	340
Torpedo	F			100		
Xiphias gladius	F				1590	1390
Total consumption in 20 days		10900	9010	7945	8560	5260
Total Hg intake ug/20 days		2000	1670	1755	4720	3260
Weekly consumption		3815	3155	2780	2995	1840
Weekly Hg intake		700	585	615	1650	1140
ug Hg/kg body weight/week		10.5	7.0	7.7	24.5	19.0

*) unidentified species
C = crustacean, M = mollusc, F = fish

6.3 Direct and indirect intake of mercury through seafood

Only a few studies in the Mediterranean area have directly investigated the mercury intake and others determined the mercury in blood and hair. At Carloforte (Sardinia) Paccagnella et al. (1973) analysed typical diets containing the edible parts of tuna and other seafood:

Tuna	1230 (50-2800) ug Hg-T kg^{-1} FW
other fish and shellfish	330 (10- 490) ug Hg-T kg^{-1} FW

Since tuna is available only during summer (July/August) from the local tuna trap the authors estimated that the average intake of mercury during summer was 150 ug/week/person and during winter 100 ug/week/person. The group with the highest consumption (14 seafood meals per week) had an estimated mercury intake of 700 ug Hg/week/person in summer when tuna was available and 460 ug Hg/week/person in winter without the supply of fresh tuna.

Nauen et al. (1983) estimated the amount of mercury intake from a food consumption study on the basis of a survey in three Italian locations. Information on individual seafood consumption over a period of 20 days was matched with analytical data on mercury levels in the fish and shellfish consumed. Special attention was given to fishermen and their families (Table XLI). Applying a consumer risk simulation model the authors found that a high

percentage of the persons interviewed exceeded their daily allowance, among them many children. In fact the maximum average intake recorded was in a 3-year old child, which reached 30 ug Hg kg^{-1} body weight/week, i.e. six times the FAO/WHO Provisional Tolerable Weekly Intake.

For Japanese tuna, Doi and Ui (1975) assuming an average concentration of 0.5 mg Hg kg^{-1} FW and correlating this with the average daily consumption rate of fishermen, they estimated that the weekly intake from tuna was about 500 ug Hg. The retailers ingested an additional mercury intake of about 140 ug Hg per week from other seafood which contained on an average 0.1 mg Hg kg^{-1}. This high mercury intake, in particular from tuna, was reflected in hair and blood mercury concentrations. The hair of these tuna fishermen contained from 25 to 46 mg Hg kg^{-1}. The mean mercury concentration in the hair of the retailers was 26 mg kg^{-1} (range 6.4 - 44 mg Hg kg^{-1}) while blood levels averaged 100 ug Hg l^{-1} (range 45 - 175 ug Hg l^{-1}). One individual had at one time 65 mg Hg kg^{-1} hair.

Indirect evidence for high mercury intake from seafood is supplied from hair and blood analyses. Astier-Dumas and Cumont (1975) studied the seafood consumption in four French regions. They found that persons eating more than three meals a week had higher mercury levels in their hair (mean = 7.60 $\pm$ 3.4 ppm with n=5) than persons consuming less seafood (mean = 1.1 $\pm$ 0.6 ppm with n=6). The average hair mercury level in the high consumers (estimated summer intake 700 ug Hg/person and winter intake 460 ug Hg/person) from Sardinia was 11 mg Hg kg^{-1} (range: "not detected" to 60 mg kg^{-1}), which fits well with the estimate that of an average intake of 300 ug Hg/week the hair level would be about 6 mg Hg kg^{-1} (Paccagnella et al., 1973). Riolfatti (1977) compared hair mercury levels in an inland town with a coastal town, where 13% of the 52 persons examined had consumed more than four fish meals per week. One man in the coastal town had hair levels which fell within the range of possible earliest effects of mercury poisoning i.e. his hair concentration was about 45 mg Hg kg^{-1}. Six others reached hair concentrations between 16 and 20 mg kg^{-1}. In the inland town relatively high hair concentrations were observed. One woman had about 30 mg kg^{-1} and three had levels between 16 and 25 mg kg^{-1} despite the fact that none of the persons examined in the inland town had consumed more than two fish meals per week.

Bacci et al. (1976) studied the total and methyl mercury concentrations in the blood, urine, hair and nails of 16 persons from the town of Vada who consumed from 0 to more than 6 meals of seafood per week. The fish came from the banks of the Vada river about 10 km west of the Solvay chloralkali plant. As expected, the mercury concentrations increased with the amount of seafood meals consumed. The concentration in the hair ranged from 4 to 110 mg Hg kg^{-1}. Although this high hair concentration is within the range of possible effects, no symptons were observed.

Preliminary results have recently been reported (WHO/FAO/UNEP, 1986) from the pilot studies being carried out within the framework of the WHO/FAO/UNEP project on methyl mercury in Mediterranean populations and related health hazards. A dietary survey conducted in Greece among 1500 individuals identified 250 with a consumption of two or more fish meals per week. Of these, 140 had their hair analysed for total and methyl mercury. Only one individual had a methyl mercury content exceeding 10 mg kg^{-1}. A preliminary survey in Italy among 200 persons revealed that within this group, 51 out of the 58 fishermen interviewed consumed two or more fish meals per week. Analysis of 26 hair samples showed that while the concentration of methyl mercury was below 2.1 mg kg^{-1} for 19 non-consumers of fish, the hair of the 7 fishermen analysed showed methyl mercury concentrations ranging from 3.58 to 30 mg kg^{-1} with only one being below 4 mg kg^{-1}.

As part of the same project, studies carried out in Yugoslavia showed that the mercury content of seafood consumed by a coastal population with a relatively large industrialized concentration was higher than that of a non-industrial area. A dietary study among 314 individuals from the former area and 255 in the latter, when correlated with analysis of the seafood species consumed for both total and methyl mercury, gave a calculated average weekly intake of 64.5 to 177 mg total mercury, with 34.5 to 90.8 mg methyl mercury in the industrialized are, and 44.5 to 125.7 mg total mercury, with 27.5 to 102 mg mentylmercury in the non-industrialized area. The higher intake of methyl mercury in the less polluted area is ascribed to a higher fish consumption. Twenty individuals in the industrialized area, and 43 in the non-industrialized area were estimated as having a methyl mercury intake above the Provisional Tolerable Weekly Intake established by the Joint FAO/WHO Expert Committee on Food additives. The hair of 42 individuals form each area was analysed for total and mehtylmercury, only one individual showing a consumption of above 4 mg kg^{-1} of methyl mercury.

In general, results obtained within the project so far did not reveal any single case of high exposure, apart from fishermen, thus confirming that a highly selective approach should be adopted in order to identify potential groups at risk in the Mediterranean area.

Another (indirect) route of mercury to human populations results from the use of fishmeal and other feeds in raising poultry, pigs, etc. The Hg-T and the methyl mercury concentrations in fishmeal were higher than in meat and bone-meal (Szprengler, 1975). For example chicken-fed herring meals containing 0.014 to 0.018 mg Hg-T kg^{-1} DW raised their body levels (March *et al.*, 1974).

The species used for the production of fishmeal vary with regions. In northern Europe, fish-meal is produced mainly from capelin and herring, in the Mediterranean mainly from large catches of sardines and anchovies (Table XLII). Wastes from tuna, herring, mackerel, lobster, crab, shrimp and various other species are also used. In some countries meal is still produced from whales. Of course, not all fishmeal produced is used in the country of origin. For example, Peru exports 96%, Chile 91% and Norway 81% of their pproduction, while large amounts are imported by many European countries.

The mercury content of these fishmeals can be estimated from the mercury concentration in fresh species and a FW/DW ratio of 5. For example direct determination of herring meals from British Colombia, Canada, Newfoundland, Denmark and Norway range from 0.09 to 0.29 mg Hg-T kg^{-1} DW (Anonymous, 1971). White fish meals from Britain, Canada, Denmark, Iceland and S. Africa also had similar ranges (0.04 to 0.29). Beasley (1971) found a mean concentration of 0.44 mg Hg-T kg^{-1} DW in *Engraulis mordax* from the Californian coast, 0.6 mg Hg-T kg^{-1} DW in *Clupea harengus* from the Massachusetts coast, 0.5 mg Hg-T kg^{-1} DW in menhaden (*Brevoortia patrona*) from the coast of the state of Mississippi, and 0.34 mg Hg-T kg^{-1} DW in the menhaden (*B. tyrannus*) from Chesapeake Bay. Taking into consideration that these are dry weight levels and applying a DW/FW ratio of 0.2 will reduce these levels by a one-fifth on a fresh weight basis. Since the Hg-T concentrations in Mediterranean white fishes are higher than those mentioned above also fish-meal produced from Mediterranean species should be proportionally higher.

Table XLII

Nominal catches and net imports of fish (in metric tons) in the Mediterranean for 1980 (UNEP/FAO/WHO, 1983)

Country	Total production	Net imports	Mediterranean catch	Clupeidae (sardines)	*Engraulis encrasicolus* (anchovy)	Carangidae (*Trachurus*)	Bonito and tuna	Gadiformes	Sparidae	Mullidae	Cephalopods
Algeria	38 678	69	38 678	22 773	3 290	1 597	515	1 739	3 676	1 090	
Cyprus	1 336	2 771	1 304			11	17	4	324	126	112
Egypt	140 397	47 502	19 939	6 501		100			2 162	1 576	743
France and Monaco	793 458	299 557	46 800	15 393	2 448	812	1 701	3 706	1 684	276	1 735
Greece	103 042	25 732	75 745	12 541	9 860	8 300	794	2 385	8 284	2 397	2 320
Israel	25 718	20 644	3 702	816		187		52	627	277	
Italy	447 696	209 701	352 631	47 712	79 282	8 126	4 299	14 895	12 950	8 134	31 937
Lebanon	2 500	7 713	2 400	800							
Libya	4 803	10 167	4 803	634			634	130	634		
Malta	1 023	4 223	1 023	3		192	43	40	118	7	26
Morocco	323 907	-59 857	27 316	9 403	7 127	3 205	56	50	3 871	185	174
Spain	1 264 680	121 731	149 606	37 083	31 239	7 244	3 415	16 919	8 248	2 575	3 436
Syria	3 911	9 692	976	121		50	80	70	90	80	
Tunisia	60 154	-6 398	60 154	13 969	536	1 534	2 646	620	5 608	2 336	5 489
Turkey	426 855	-9 085	41 405	8 384	1 509	1 421	15 301	220	2 780	1 435	354
Yugoslavia	58 396	19 576	34 968	24 004	2 214	1 283	639	799	922	228	743
TOTAL	3 696 554	703 738	861 450	200 137	137 505	34 062	30 140	41 629	51 978	20 722	52 069

Sources: (a) FAO, 1981. Yearbook of Fishery Statistics: (i) Catches and landings Vol. 52
(ii) Fishery commodities, Vol. 53

(b) FAO/GFCM, Statistical Bulletin No. 4

6.4 Mercury intake through food of non-marine origin

Most of the data on mercury in foodstuffs report only the total mercury content and do not distinguish between methyl mercury and other mercury compounds (WHO, 1976). Recent data are not published in the open literature but it can be assumed that the mercury levels have decreased during the last 10 to 15 years since in most countries pesticides containing mercury are banned. Most mercury in fish and other seafood is in the form of methyl mercury. The older data on total mercury intake via food in some countries has been reported to be 20 ug day^{-1} or lower (WHO, 1976). Cigna-Rossi et al. (1967) estimated an intake of 7 to 12 ug Hg-T day^{-1} for the average Italian, Schelenz and Diehl (1973) reported 70 ug day^{-1} for the Federal Republic of Germany and Cohen (1974) reported 5 to 10 ug Hg day^{-1} for England. For Sweden, it was estimated (Swedish Expert Group, 1971) that about 5 ug Hg day^{-1} came from sources other than freshwater fish and seafood (i.e. drinking water and "terrestrial" food). Bread and cereals contribute more than 50% to the mercury intake from terrestrial food. Since mercury pesticides are no longer used for treating seeds, the mercury intake from terrestrial sources may have decreased since the 1960s. Most studies on mercury content in food suggest that the contribution of methyl mercury from terrestrial food is negligible (Swedish Expert Group, 1971).

7. Risk assessment of mercury

7.1 Risk to marine biota

Three types of data can supply information on the risk of mercury to organisms: bioassays, body concentrations and observations in ecosystems near mercury sources.

Valid experimental data from bioassays for the toxicity of inorganic and, especially, of methyl mercury on marine biota are very scarce. Since only in the first trophic levels (autotrophs and herbivor invertebrates) the uptake from water is more important than the uptake through the foodchain, exposing marine organisms to mercury in seawater only, and not also through the foodchain, has a very limited validity for organisms situated in higher trophic levels. The use of safety factors in the extrapolation of short-term toxicity data in seawater data for the estimation of long-term chronic effects is highly questionable and should be abandoned. The limited data available on autotrophs show that in bioassays, inorganic mercury is toxic to the most sensitive species at about 20 ng l^{-1}. For less sensitive species methyl mercury was effective at 100 ng l^{-1} and $HgCl_2$ at 1000 ng l^{-1}. These concentrations are nominal ones tested in batch cultures. Since during the experiment the mercury exposure concentration decreased, the really effective mercury concentration must have been lower. In order to arrive at some estimation of mercury toxicity one could assume that no effects should occur at concentrations 5 times lower than the nominal effective concentration to the most sensitive autotrophs so far tested. This would result in a "minimal risk" concentration for inorganic mercury salts of about 4 ng Hg l^{-1}. The effective concentrations of methyl mercury may be estimated at a concentration 100 times lower i.e. 0.04 ng Hg l^{-1}. It appears that some strains of phytoplankton species are much less sensitive than others. This means that bioassays must be carried out on freshly-isolated strains, which have not yet become resistant and the effective mercury concentrations in the culture solution must be monitored. Extrapolation of such experiments to natural conditions will still be difficult because mercury in waste releases will certainly be in a non-ionic form and thus its bioavailability will differ from that of ionic forms. In many discharge situations, the ionic effective concentration of the inorganic mercury released will be only a few percent of the Hg-T determined in the discharge. The bioavailability of organic mercury discharged into the marine environment is difficult to predict, but should be much greater than that of inorganic mercury.

High body levels have been observed in many species in polluted and unpolluted areas. Past discharges of large amounts of mercury from chloralkali and petrochemical plants (~10 MT/year) have locally increased the mercury concentration in the biota. Organisms living within a range of 10 to 20 km from the discharges have mercury levels 1000 to 10000 times above background levels, but any adverse effects on marine biota observed could not be attributed to the higher mercury concentrations but rather appear to be due to the release of other wastes discharged simultaneously. Discharges of such magnitude should not occur anymore in the Mediterranean because increasingly stringent controls and changes in process technology have led to a marked reduction in industrial mercury discharges, but the release of mercury from past discharges will keep levels in marine ecosystems high for many years.

In marine areas near mercury anomalies elevated mercury concentrations have been found in marine biota. However, no adverse effects on the marine organisms and on ecosystems have been observed.

7.2 Risk to humans

The high mercury concentrations observed in edible marine organisms and the high intakes reached by some population groups raise the question of possible health risks caused by these intakes. WHO (1976) estimated that the earliest poisoning symptoms in the most sensitive group of an adult population may appear following a long-term daily ingestion of 180 to 420 ug Hg (as MeHg) for a 60 kg person. This long-term intake is associated with a blood level in the approximate range of 200 to 500 ug l^{-1} and a hair concentration of between 50 to 125 mg Hg kg^{-1}. Applying a safety factor of 10 would result in a "safe intake" of 18 to 42 ug Hg day^{-1} for a 60 kg person or on a weekly basis 126 to 294 ug Hg/week. FAO/WHO (1972) suggested a Provisional Tolerable Weekly Intake (PTWI) for a 60 kg person of 300 ug Hg of which not more than 200 ug should be methyl mercury. For persons having different weights (e.g. children) the weekly intake can be estimated on a ug Hg kg^{-1} body weight basis to be 5 ug total mercury of which not more than 3.3 ug should be methyl mercury. These PTWIs for mercury have been reconfirmed (WHO, 1980), but with the additional restriction for pregnant and lactating women as the re-evaluation of the WHO Environmental Health Criteria for Mercury emphasized the sensitivity of the growing foetus to methyl mercury.

Table XLIII shows the weekly intakes of methyl mercury that could be reached by different combinations of fish consumption and methyl mercury concentration in different seafood species. From this table one can see that a heavy consumer, for example a fisherman aboard, who consumes 2 fish meals per day or 14 meals a week exceeds the PTWI if he consumes seafood which contains more than 100 ug MeHg kg^{-1} FW. On the other hand, a person who eats seafood only once a week can safely consume seafood containing about 1500 ug MeHg kg^{-1} FW provided he is not taking in mercury from other sources. These estimates are valid for long-term consumption, and in addition contain a safety factor of 10. Therefore, effects are only to be expected if an intake of ten times the PTWI is exceeded for periods of ingestions lasting over months and years. High hair and blood levels are indicative for persons eating large amounts of seafood.

Table XLIII

Intake of methyl mercury (ug kg^{-1} FW) from seafood based on number of meals per week (one meal = 150g) and MeHg concentration in fish

Concentration in seafood ug MeHg kg^{-1} FW	1	2	3	4	5	6	7	14	no of meals of seafood/week g/week of seafood
	150	300	450	600	750	900	1050	2100	
100	15	30	45	60	75	90	105	210	
250	38	75	113	150	188	225	262	525	
500	75	150	225	300	375	450	525	1050	
750	112	225	338	450	562	675	788	1575	
1000	150	300	450	600	750	900	1050	2100	
1250	188	375	562	750	938	1125	1312	2625	
1500	225	450	675	900	1125	1050	1575	3150	

It should be pointed out that the PTWI incorporates an assumed "safety factor" of 10 from an intake that has caused a 5% prevalence of symptomatic methyl mercury poisoning. It is compatible with the fact that relatively small scale studies fail to demonstrate an increased prevalence of health effects at intakes higher than the PTWI. Even with an intake of 10 times higher than the PTWI one should expect only one person among 20 studied to be affected.

In summary, there are critical groups consuming methyl mercury via sea food (particularly fish) to the extent that they exceed the established PTWI. Where the average methyl mercury concentration in fish consumed is high, rather modest fish consumptions (one meal/week or less) will not lead to the PTWIs being exceeded. A quantitative estimate of the number of people who exceed the PTWI is difficult to make because of lack of data, but in the Mediterranean with high mercury concentrations in many of its regions critical groups should be identified on a comprehensive scale in the various countries.

8. Conclusions on mercury assessment

The analytical uncertainty of the measurements, especially in air and sea water, but also in sediments, make the evaluation of, and comparison between, the data of different authors extremely difficult, if not impossible. Reference materials and reference standards at the levels at which mercury occurs in the marine environment are only available for biota and sediments. However, these standards are valid only for the standardization of total mercury concentrations. No standards exist for the comparision of key mercury species (e.g. methyl mercury).

It is fair to say that data which have not been obtained under good quality control (comparison with reference standards and/or intercalibration, frequent periodical checks against the laboratory's own substandards) cannot be considered without reserve. The responsible scientist, of course, realizes that management decisions based on wrong analytical data can have great economic consequences.

The different areas of the Mediterranean have been surveyed very unevenly. For instance, very few data are available from the southern coast of the Mediterranean, Egypt being an exception.

Air: the data available up to now are limited to the western Mediterranean and even these are still scarce and sporadic. Nevertheless, the data indicate that the mercury levels in air over open sea areas are lower than over land. As expected, urban air has higher mercury levels than rural air. Mercury levels in air over rural areas in the Mt. Amiata mercury anomaly are considerably higher than over rural areas not influenced by natural mercury sources. The chemical species of mercury in air are at present only operationally defined and a true identification is necessary to understand the role different mercury species play in the atmosphere and which role these species play in the transport from air to ocean and vice-versa.

Sea water: The lack of proper quality control for seawater data makes it very difficult to state which levels may be typical of the open Mediterranean. Taking into consideration only recent data for the "open ocean" seawater samples, the means of "total dissolved Hg" concentrations range between 7 and 25 ng Hg-T l^{-1}. For comparison, the range of means of recent equivalent data from non-Mediterranean areas extends from 2 to 14 ng Hg-T l^{-1}. Table XLIV shows some "typical" values for Mediterranean and non-Mediterranean areas. Data on coastal zones seem "very high" in certain locations and urgently need confirmation by other workers. Most important of all, workers engaged in sea water analyses should try to intercalibrate at least on a local level i.e. between laboratories which can analyse the same samples simultaneously. All these data do not supply any information on the chemical species present in sea water. This information is urgently needed in order to make progress in the understanding of the biogeochemical cycle of mercury.

Sediments: High mercury levels have been detected near some towns and in the adjacent areas to river mouths. Investigating other near-town sediments, especially near their sewage outfalls, will likely turn up other "hot spots" in the 1 to 10 mg Hg-T kg^{-1} DW range.

Biota: The large number of mercury levels in edible marine organisms investigated during MED POL Phase I has greatly contributed to a better understanding of the distribution of mercury concentrations in seafood.

However, more relationships between mercury concentration and size are needed for an accurate comparison of the mercury levels in individual species from different locations and for a prediction of the possible mercury levels to be expected in various seafood. For some areas (e.g. the southern coast of the Mediterranean) the data base available is still very limited. However, despite these limitations there is no doubt that marine organisms from many areas in the Mediterranean, not polluted by anthropogenic sources, generally have higher levels than marine organisms from unpolluted areas of other regions (e.g. the North Atlantic) (Table XLIV). Mercury concentrations in mixed unrepresentative plankton samples of unknown species composition have often been determined mainly outside the main fishing areas and hence the usefulness of these data is limited to the establishment of a seawater/plankton concentration factor of 1000 to 5000. Molluscs, crustaceans and fishes have generally much higher mercury levels than the corresponding taxonomic groups in the Atlantic. Mean mercury concentrations of 1000 ug kg^{-1} FW and maximum concentrations above 2000 ug Hg-T kg^{-1} FW are not rare. The highest concentrations in seafood were observed in large predatory fishes situated at the highest trophic levels such as tuna (maximum 6300 ug Hg-T kg^{-1} FW). High mercury levels in seafood have been observed in areas II, IV, V and VIII. Typical mercury concentrations are difficult to identify. However, it is indicative that mean concentrations are rarely below 100 ug Hg-T kg^{-1} FW. Nearly all results have been obtained under quality control measures, so that in general these data are to be considered reliable. Birds pose high mercury concentrations and even these organisms appear to have higher Hg-T levels in the Mediterranean than in the Atlantic. The highest mercury levels of all biota were found in marine mammals. Again higher Hg-T concentrations seem to occur in the Mediterranean.

Table XLIV

Some levels in the Mediterranean and in other seas which may be considered "typical" at the present state of knowledge taking into consideration the many reservations expressed in the text

Mediterranean:		
Air:	coastal	2 - 3 ng "gaseous" Hg m^{-3} 1 % particulate Hg
	urban	10 - 20 ng "gaseous" Hg m^{-3}
	chlor-alkali plant	up to 73 ng "gaseous" Hg m^{-3}
Sea water:	open sea	7 - 25 ng Hg-T l^{-1}
	coastal	up to 100 ng Hg-T l^{-1}
Sediments:	open sea	0.01 - 0.03 mg Hg kg^{-1} DW
	coastal	up to 45 mg Hg kg^{-1} DW
Plankton:	open sea	15 - 560 ug Hg-T kg^{-1} DW (3 - 120 ug Hg-T kg^{-1} FW)
Crustaceans:		20 - 300 ug Hg-T kg^{-1} FW
	area II+IV	1000 - 1100 ug Hg-T kg^{-1} FW

Table XLIV (cont.)

Molluscs:		70 - 200 ug Hg-T kg^{-1} FW
	area IV+V	250 - 870 ug Hg-T kg^{-1} FW
Fish	pelagic	100 - 300 ug Hg-T kg^{-1} FW
	area IV	300 - 400 ug Hg-T kg^{-1} FW
	tuna	850 - 1700 ug Hg-T kg^{-1} FW
	M. barbatus	55 - 215 ug Hg-T kg^{-1} FW
	area II+IV	590 - 1450 ug Hg-T kg^{-1} FW
	var. spp.	10 - 815 ug Hg-T kg^{-1} FW
non-Mediterranean:		
Air:	open-sea, Atlantic	
	Northern Hemisph.	1 - 3 ng "gaseous Hg" m^{-3}
	Southern Hemisph.	0.5-2.5 ng "gaseous Hg" m^{-3}
	over remote land	2 - 9 ng "gaseous Hg" m^{-3}
Sea water:	open-sea	2 - 14 ng Hg-T l^{-1}
	coastal	8 - 12 ng Hg-T l^{-1}
Plankton:	open-sea	100 - 1100 ug Hg-T kg^{-1} DW
		(50 - 500 ug Hg-T kg^{-1} FW)
Crustacean:	brown shrimp (N. Atlantic)	20 - 390 ug Hg-T kg^{-1} FW
Molluscs:	M. edulis (N. Atlantic)	20 - 130 ug Hg-T kg^{-1} FW
Fish:	Herring	20 - 240 ug Hg-T kg^{-1} FW
	cod	30 - 480 ug Hg-T kg^{-1} FW
	hake/haddock	20 - 130 ug Hg-T kg^{-1} FW
	plaice (N. Atlantic)	20 - 500 ug Hg-T kg^{-1} FW

Natural sources: The data discussed above show clearly that environmental levels of natural origin influence the mercury levels observed in biota. The mussel transplant experiment, in particular, is very illustrative in this respect. However, determination of the total amount of mercury in water and sediment is not sufficient for a prediction of the levels in biota. The very high concentrations in the sediments in the Gulf of Trieste (up to about 50 mg Hg-T kg^{-1} DW), confirmed by two authors, result in only a relatively small increase in the mercury levels in mussels. Much lower concentrations in sediments (up to 5 mg Hg-T kg^{-1} DW) off the coast of the Mt. Amiata anomaly increased the mercury concentration in M. barbatus to much higher levels. Unfortunately the mercury concentrations in this fish have not been investigated in detail in the Gulf of Trieste, but the few data (without size indications) showed only slightly higher levels than those from other parts of the Mediterranean not under the influence of natural mercury

anomalies. The leaching experiments carried out on the sediments from the Mt. Amiata anomaly showed that investigating the chemical species of the mercury present is very important for understanding the distribution pattern of mercury in the environment. Similar experiments, taking into consideration the processes involved in the mercury uptake by marine organisms in different positions in the food-chain may supply an explanation for the differences observed in the Gulf of Trieste and the Tuscan coast.

Anthropogenic sources: The release of mercury from industrial complexes, mainly chloralkali plants, showed that mercury is highly enriched in sediments and in suspended matter near the plant's outfall, but, somewhat unexpectedly, only slightly in the biota inhabitating the immediate surroundings. At a distance of 10 to 20 km, mercury levels, even in areas with massive mercury inputs, again reach background levels. The chemical species (physico-chemical form) of the mercury released seem to play a very important role in its bioavailability. As already discussed in section 4.3, the determination of total mercury concentrations is not sufficient to understand and predict the distribution pattern of the mercury release in the various components of the marine ecosystem.

Organic mercury: The few data so far available show that the relative amounts of organic mercury increase with the age of the organism and its increasing position in the foodchain. Plants and plankton have relatively much lower amounts than crustaceans and fish. Bivalve molluscs seem to be an exception as their content of organic (and total) mercury decreases with size. In the liver of some fishes a low percentage of organic mercury has been found.

Mercury/selenium relationships: Considerable attention has been given to the simultaneous increase of mercury and selenium in marine organisms because selenium is an antidote to mercury poisoning. In most cases the selenium levels seem to be independent of the mercury levels. But in some special tissues, such as the liver and brain, molar ratios near to one have been observed. Recently it has been proposed that the sum of molar concentrations of mercury plus selenium are correlated with length (age).

Pollution indicators: Since mercury is an accumulative element, i.e. mercury concentration increases with the size of the marine organism (bivalves seem the only exception) various marine organisms may serve as pollution indicators of areas of different extent e.g. sessile organisms may serve as indicators of very small areas, organisms migrating over medium to large areas can serve as indicators of more or less wide areas.

Effect on biota: A review of the data on the toxicity of mercury on marine organisms shows that many important parameters influencing toxicity have been identified. The organisms which show effects at the lowest concentrations are phytoplankton because uptake from water is the predominant exposure route. The lowest apparent concentration which caused an effect is given as 20 ng of inorganic Hg l^{-1}. However, since the actual concentration in sea water was not determined by chemical analysis but deduced from the amount of mercury added to the medium, the actual effective concentrations may well be lower. Organisms higher in the foodchain can apparently withstand considerable concentrations of both inorganic and organic mercury. This is most probably due to the fact that the dominant exposure route of mercury is through the foodchain, a pathway which has not been investigated. However, the data are not sufficient to assess the risk of mercury pollution.

Furthermore, future studies on the effective toxic concentrations should be accompanied by data on the actual levels determined by chemical analysis of the water, the food and the body tissues of the organisms and the target organs or tissues identified because this information may be used to compare data obtained in the laboratory with field data.

Risk to humans: Persons eating one or less than one meal of seafood per week are very unlikely to exceed the Provisional Tolerable Weekly Intake (PTWI), even consuming seafood containing high amounts of methyl mercury. There exist, however, many critical groups (fishermen, fishvendors and their families) which eat large amounts of fish. Estimations from seafood consumption studies carried out on persons belonging to these critical groups have shown that at present nearly all persons belonging to these groups exceed the PTWIs. The limited number of analyses on mercury levels in blood and hair of members of these critical groups give sufficient evidence that the PTWIs are exceeded. Some of the hair levels found are within the range where mercury poisoning can be expected.

II. CONTROL MEASURES

9. Existing international and national controls and measures to prevent mercury pollution

The Information on existing national provisions in the Mediterranean has been received from the national focal points. The only international provisions covering also Mediterranean countries are those of the EEC and appear in section 9.2.

9.1 Existing national provisions

Table XLV summarizes the information provided by the MED POL national coordinators on national legal limits for maximum mercury concentrations in seafood in force in 1986 in Mediterranean countries. Table XLVI lists the information on water quality criteria for mercury and effluent standards.

Table XLV
Maximum permissible mercury levels in seafood in Mediterranean countries

Country	Year of implementation	Maximum permissible mercury concentrations	Remarks
Albania	*	*	
Algeria	*	*	
Cyprus	1983	0.5 mg kg^{-1}	All fish (dry, frozen, fresh, canned) All shellfish (fresh, frozen
Egypt	*	*	
France	1976	0.5 mg kg^{-1}	All fish, crustacea and mollusca, except tuna and swordfish
		0.7 mg kg^{-1}	Tuna and swordfish. No legislation in force, but random tests made on important fish. Those which exceed limits are banned from the market
			Both of the above levels apply to domestic and imported products
Greece	1974	0.7 mg kg^{-1} (methyl-mercury)	Limit for all seafood caught locally or imported, and intended for local consumption. Enforcement through veterinary practice
			New legislation under preparation
Israel	1979	1.0 mg kg^{-1}	All edible fish

Table XLV (cont.)

Country	Year of implementation	Maximum permissible mercury concentrations	Remarks
Italy	1971	0.7 mg kg^{-1}	In force for fish and fishery products imported from outside the EEC region
	1976	0.7 mg kg^{-1}	In force for frozen tuna (Thunnus thynnus) and other tunas and bonitos of domestic and EEC origin
	1978	0.7 mg kg^{-1}	In force for bivalve molluscs of domestic production
	1980	0.7 mg kg^{-1}	In force for fresh sharks and dogfish
Lebanon	*	*	
Libya	*	*	
Malta	1983	0.7 mg kg^{-1}	For tuna and "similar fish"
		0.5 mg kg^{-1}	Other seafood
Monaco	*	*	
Morocco	*	*	
Spain	1973	0.5 mg kg^{-1}	In force for fresh, chilled and frozen fish and seafood if at least 5 kg weight, and for any canned or processed fish and fishery product
Syria	*	*	
Tunisia	*	*	
Turkey	-	-	Legislation not considered necessary following low mercury concentrations found on analysis of canned sardines, anchovy and tuna

Table XLV (cont.)

Yugoslavia	1983	0.5 mg Hg-T kg^{-1}	Fresh fish
		1.0 mg Hg-T kg^{-1}	Fresh tuna, shells and crabs
		0.8 mg Hg-T kg^{-1}	Canned fish
		1.5 mg Hg-T kg^{-1}	Canned tuna, shells and crabs
		0.4 mg Hg-O kg^{-1}	Fresh fish
		0.8 mg Hg-O kg^{-1}	Fresh tuna, shells and crabs
		0.6 mg Hg-O kg^{-1}	Canned fish
		1.0 mg Hg-O kg^{-1}	Canned tuna, shells and crabs

\- no standards in force
* no information available
Hg-T = total mercury
Hg-O = organic mercury

Table XLVI
Water quality criteria and effluent standards in force in Mediterranean countries

Country	Year of implementation	Maximal Hg conc. in seawater	Effluent Standard	Remarks
Albania	*	*	*	
Algeria	*	*	*	
Cyprus		-	-	
Egypt	*	*	*	
France				The limits of the European Community apply
Greece				The limits of the European Community apply
Israel		-	-	Control exercised on a case by case basis
Italy	*	*	*	The limits of the European Community apply
Lebanon	*	*	*	
Libya	*	*	*	

Table XLVI (cont.)

Country	Year of implementation	Maximal Hg conc. in seawater	Effluent Standard	Remarks
Malta		-		Administrative controls are set at 1 ug Hg l^{-1} for effluents
Monaco	*	*	*	
Morocco	*	*	*	
Spain				The limits of the European Community apply
Syria	*	*	*	
Tunisia	*	*	*	
Turkey		4 ug l^{-1}	200 ug l^{-1}	For discharges into sewage systems with complete treatment or discharge into deep waters
			50-160 ug l^{-1}	For different types of industries
Yugoslavia (Croatia)	1984	0.2 ug Hg-T l^{-1} 0.02-0.1 ug Hg-O l^{-1}	-	Depending on category of seawater

* = no information available
- = no standard in force

9.2 Existing international provisions

The European Economic Community elaborated detailed directives for the control of mercury discharges by the chlor-alkali electrolysis industry and by sectors other than the chlor-alkali electrolysis industry. The annexes of these directives appear in Tables XLVII and XLVIII respectively.

Table XLVII
Annex I to IV of Council Directive of 22 March 1982
Official J. European Communities No. L 81/29-34, 27.3.82

Limit values, time limits by which they must be complied with, and monitoring procedure for discharges by the chlor-alkali electrolysis industry.

Table XLVII (cont.)

1. The limit values expressed in terms of concentration which, in principle, should not be exceeded are set out in the following table.

Unit of measurement	Monthly average limit values not to be exceeded from 1 July		Remarks
	1983	1986	
Recycled brine and lost brine Micrograms of mercury per litre	75	50	Applicable to the total quantity of mercury present in all mercury-containing water discharged from the site of the industrial plant

In all cases, limit values expressed as maximum concentrations may not be greater than those expressed as maximum quantities divided by water requirements per tonne of installed chlorine production capacity.

2. However, because the concentration of mercury in effluents depends upon the volume of water involved, which is different for different processes and plants, the limit values expressed in terms of quantity of mercury discharged in relation to installed chlorine production capacity given in the following table must be observed in all cases.

Unit of measurement	Monthly average limit values not to be exceeded from 1 July		Remarks
	1983	1986	
Recycled brine Grams of mercury per tonne of installed chlorine production capacity	0.5	0.5	Applicable to the mercury present in effluent discharged from the chlorine production unit
	1.5	1.0	Applicable to the total quantity of mercury present in all mercury-containing water discharged from the site of the industrial plant

Table XLVII (cont.)

Lost brine Grams of mercury per tonne of installed chlorine production capacity	8.0	5.0	Applicable to the total quantity of mercury present in all mercury-containing water discharged from the site of the industrial plant

3. The daily average limit values are four times the corresponding monthly average limit values given in points 1 and 2.

4. In order to check whether the discharges comply with the emission standards which have been fixed in accordance with the limit values laid down in this Annex, a monitoring procedure must be instituted. This procedure must provide for:

- the taking each day of a sample representative of the discharge over a period of 24 hours and the measurement of the mercury concentration of that sample, and

- the measurement of the total flow of the discharge over that period.

The quantity of mercury discharged during a month must be calculated by adding together the quantities of mercury discharged each day during that month. This total must then be divided by the installed chlorine production capacity.

Quality Objectives

For those Member States which apply the exception provided for in Article 6 (3) of Directive 76/464/EEC, the emission standards which Member States must establish and ensure are applied, pursuant to Article 5 of that Directive, shall be fixed so that the appropriate quality objective or objectives from among those listed below is or are complied with in the area affected by discharges of mercury from the chlor-alkali electrolysis industry. The competent authority shall determine the area affected in each case and shall select from among the quality objectives listed in paragraph 1 the objective or objectives that it deems appropriate having regard to the intended use of the area affected, taking account of the fact that the purpose of this Directive is to eliminate all pollution.

1. In order to eliminate pollution in Directive 76/464/EEC, and pursuant to Article 2 of the Directive, the following quality objectives are set:

1.1. The concentration of mercury in a representative sample of fish flesh chosen as an indicator must not exceed 0.3 mg kg^{-1} wet flesh.

1.2. The total concentration of mercury in inland surface waters affected by discharges must not exceed 1 ug l^{-1} as the arithmetic mean of the results obtained over a year.

Table XLVII (cont.)

1.3. The concentration of mercury in solution in estuary waters affected by discharges must not exceed 0.5 ug l^{-1} as the arithmetic mean of the results obtained over a year.

1.4. The concentration of mercury in solution in territorial sea waters and internal coastal waters other than estuary waters affected by discharges must not exceed 0.3 ug l^{-1} as the arithmetic mean of the results obtained over a year.

1.5. The quality of the waters must be sufficient to comply with the requirements of any other Council Directive applicable to such waters as regards the presence of mercury.

2. The concentration of mercury in sediments or in shellfish must not increase significantly with time.

3. Where several quality objectives are applied to waters in an area, the quality of the waters must be sufficient to meet each of them.

4. The numerical values of the quality objectives specified in 1.2., 1.3. and 1.4. may, as an exception and where this is necessary for technical reasons, be multiplied by 1.5 until 30 June 1986, provided that the Commission has been notified beforehand.

Reference Method of Measurements

1. The reference method of analysis for determining the mercury content in waters, the flesh of fish, sediments and shellfish is by flameless atomic absorption spectrophotometry after suitable pretreatment of the sample which takes account in particular of pre-oxidation of the mercury and of successive reduction of the mercury ions Hg (II).

The limits of detection (*) must be such that the mercury concentration can be measured to an accuracy (*) of ± 30% and a precision (*) of ± 30% at the following concentrations:

- in the case of discharges, one tenth of the maximum permitted concentration of mercury specified in the authorization,
- in the case of surface water, one tenth of the mercury concentration specified in the quality objective,
- in the case of the flesh of fish and shellfish, one tenth of the mercury concentration specified in the quality objective,
- in the case of sediments, one tenth of the mercury concentration in the sample or 0.05 mg kg^{-1} dry weight, whichever is the greater.

2. Flow measurement must be carried out to an accuracy of ± 20%.

(*) The definitions of these terms are as given in Council Directive 79/869/EEC of 9 October 1979 concerning the methods of measurement and frequencies of sampling and analysis of surface water intended for the abstraction of drinking water in the member States (OJ No L 271, 29.10.1979, p. 44).

Table XLVII (cont.)

Monitoring Procedure for Quality Objectives

1. For each authorization granted in pursuance of this Directive, the competent authority shall specify the restrictions, the monitoring procedure and deadlines for ensuring compliance with the quality objective or objectives concerned.

2. In accordance with Article 6 (3) of Directive 76/464/EEC, the Member State shall report to the Commission for each quality objective chosen and applied, on:

- the points of discharge and the means of dispersal,
- the area in which the quality objective is applied,
- the location of sampling points,
- the frequency of sampling,
- the methods of sampling and of measurement,
- the results obtained.

3. Samples must be properly representative of the quality of the aquatic environment in the area affected by the discharges, and the frequency of sampling must be sufficient to show any changes in the aquatic environment, taking into account in particular natural variations in the hydrological regime. The salt-water fish analysis must be carried out on a sufficiently representative number of samples and species.

4. With regard to the quality objective in 1.1. above, the competent authority shall choose the species of fish to be adopted as indicators for analysis. For salt waters the species chosen from among those inhabiting coastal waters and caught locally may include cod, whiting, plaice, mackerel, haddock and flounder.

Statement

The Council and the Commission state that the application of the best technical means available makes it possible to limit discharges of mercury from the site of a new industrial plant using the recycled-brine process to less than 0.5 g/tonne of installed chlorine production capacity.

Table XLVIII
Annex I and II of Council Directive of 8 March 1984
Official J. European Communities No. L 74/49-54, 17.3.84

Limit values, time limits by which they must be complied with, and the procedure for monitoring discharges by sectors other than the chlor-alkali electrolysis industry

1. The limit values and the time limits for the industrial sectors concerned are set out together in the table below:

Table XLVIII (cont.)

Industrial sector (*)	Limit value which must be complied with as from: 1 July 1986	1 July 1989	Unit of measurement
1. Chemical industries using mercury catalysts: (a) in the production of vinyl chloride	0.1	0.05	mg l^{-1} effluent
	0.2	0.1	g t^{-1} vinyl choride production capacity
(b) in other processes	0.1	0.05	mg l^{-1} effluent
	10	5	g kg^{-1} mercury processed
2. Manufacture of mercury catalysts used in the production of vinyl chloride	0.1	0.05	mg l^{-1} effluent
	1.4	0.7	g kg^{-1} mercury processed
3. Manufacture of organic and non-organic mercury compounds (except for products referred to in point 2).	0.1	0.05	mg l^{-1} effluent
	0.1	0.05	g kg^{-1} mercury processed
4. Manufacture of primary batteries containing mercury	0.1	0.05	mg l^{-1} effluent
	0.05	0.03	g kg^{-1} mercury processed
5. Non-ferrous metal industry (**) 5.1 Mercury recovery plants	0.1	0.05	mg l^{-1} effluent
5.2 Extraction and refining of non-ferrous metals	0.1	0.05	mg l^{-1} effluent
6. Plants for the treatment of toxic wastes containing mercury	0.1	0.05	mg l^{-1} effluent

(*) Limit values for industrial sectors other than the chlor-alkali electrolysis industry which are not metnioned in this table, such as the paper and steel industries or coal-fired power stations, will, if necessary, be fixed by the Council at a later sage. In the meantime, the Member States will fix emission standards for mercury discharges autonomously in accordance with Directive 76/464/EEC. Such standards must take into account the best technical means available and must not be less stringent than the most nearly comparable limit value in this Table.

(**) see next page

Table XLVIII (cont.)

(**) On the basis of experience gained in the implementation of this Directive the Commision will, pursuant to Article 6 (3), submit to the Council proposals for more stringent limit values to be introduced 10 years after the notification of this Directive.

The limit values given in the table correspond to a monthly average concentration or to a maximum monthly load.

The amounts of mercury discharged are expressed as a function of the amount of mercury used or handled by the industrial plant over the same period or as a function of the installed vinyl chloride production capacity.

2. Limit values expressed as concentrations which in principle must not be exceeded are given in the above table for the industrial sectors 1 to 4. In no instance may limit values expressed as maximum concentrations be greater than those expressed as maximum quantities divided by water requirements per kilogram of mercury handled or per tonne of installed vinyl chloride production capacity.

However, because the concentration of mercury in effluents depends on the volume of water involved, which differs for different processes and plants, the limit values, expressed in terms of the quantity of mercury discharged in relation to the quantity of mercury handled or to the installed vinyl chloride production capacity, given in the above table, must be complied with in all cases.

3. The daily average limit values are twice the corresponding monthly average limit values given in the table.

4. A monitoring procedure must be instituted to check whether the discharges comply with the emission standards which have been fixed in accordance with the limit values laid down in this Table.

This procedure must provide for the taking and analysis of samples and for measurement of the flow of the discharge and, where appropriate, the quantity of mercury handled.

Should the quantity of mercury handled be impossible to determine, the monitoring procedure may be based on the quantity of mercury that may be used in the light of the production capacity on which the authorization was based.

5. A sample representative of the discharge over a period of 24 hours will be taken. The quantity of mercury discharged over a month must be calculated on the basis of the daily quantities of mercury discharged.

However, a simplified monitoring procedure may be instituted in the case of industrial plants which do not discharge more than 7.5 kilograms of mercury per annum.

Quality Objectives

For those Member States which apply the exception referred to in Article 6 (3) of Directive 76/464/EEC, the emission standards which Member States must establish and ensure are applied, pursuant to Aticle 5 of that Directive, will be fixed so that the appropriate quality objective or

Table XLVIII (cont.)

objectives from among those listed in sections 1, 2 and 3 of Annex II to Directive 82/176/EEC is or are complied with in the area affected by discharges of mercury.

The competent authority shall determine the area affected in each case and shall select from among the quality objectives listed in secion 1 of Annex II to Directive 82/176/EEC the objective or objectives that it deems appropriate having reagard to the intended use of the area affected, while taking account of the fact that the purpose of this Directive is to avoid or eliminate all pollution.

The numerical values of the quality objectives specified in 1.2., 1.3. and 1.4. of Annex II of Directive 82/176/EEC may, as an exception and where this is necessary for technical reasons, be multiplied by 1.5 until 1 July 1989, provided that the Commission has been notified beforehand.

10. Scientific rationale for establishing common control measures in the Mediterranean region

10.1 Scientific rationale for establishing intake restrictions and legal limits in seafood for the protection of human health

The equivalent long-term daily intake of mercury as methyl mercury associated with the earliest effects of mercury poisoning in the more sensitive group in the adult population, has been estimated to be 3-7 ug per kg body weight (WHO, 1976). This estimate has been based on data collected during the epidemics of methyl mercury poisoning in Japan (1953-60) and Iraq (1971-72). This long-term daily intake is associated with concentrations of methyl mercury in blood of 200-500 ug l^{-1} and in hair of 50-125 mg kg^{-1}. The above daily intake, with a safety factor of 10, corresponds to a weekly intake of 126-294 ug methyl mercury for a 60 kg person (see also section 7.2). The Joint FAO/WHO Expert Committee on Food Additives (1972) established a Provisional Tolerable Weekly Intake for a 60 kg person of 300 ug total mercury out of which not more than 200 ug can be methyl mercury. These figures correspond to 5 and 3.3 ug per kg body weight. This PTWI has been reconfirmed (WHO, 1980) but with a restriction concerning pregnant and lactating women. The intake of these women should be lower since the brain in the growing foetus and children is very sensitive to methyl mercury.

As has already been explained in section 7.2, the mercury intake does not only depend on the concentration of mercury in seafood but also on the quantity of seafood consumed. As can be seen from Table XLIII, and assuming that 2/3 of the mercury in seafood is in the form of methyl mercury, a 60 kg person does not exceed the PTWI if he eats 3 meals a week (one meal = 150 g) of seafood containing about 0.7 mg kg^{-1} mercury. Legal limits established in certain countries are based on similar calculations. Table XLV shows that these limits in Mediterranean countries generally lie between 0.4 and 1.0 mg kg^{-1}. These estimates are valid for long-term consumption and in addition contain a safety factor of 10. Therefore, effects are only to be expected if an intake of ten times the PTWI is exceeded for periods of ingestion lasting over months and years.

However, the application of legal limits does not solve all the problems. Simple calculations show that heavy consumers of fish and shellfish can still exceed the PTWI by as much as ten times even though the concentration in the fish does not exceed the legal limit. On the other hand a person who eats fish only once a week does not exceed the PTWI even if the mercury concentration in the fish is double that of the higher legal limit.

The above argument indicates that the imposition of maximum permissible legal levels of mercury in seafood does not adequately safeguard the health of heavy consumers whereas people eating low amounts of seafood are not in need of such legal limits. In addition the imposition of legal limits can have adverse affects on the fisheries industry and marketing. Another disadvantage is the high cost for the enforcement of this limit since a monitoring system has to be created. Also, it is almost impossible to enforce the measure for those with direct access to the resource eg. fishermen who constitute a high-risk group.

Table XXXIX (section 6.2) shows that the average consumption of fish and fishery products in the Mediterranean lies between 15 and 300 g live weight per capita and Table XVIII (section 3.5.5) that the mean mercury concentration in the vast majority of fishes is below 600 ug kg^{-1} FW. This value is exceeded only in predatory fishes and in some polluted areas. Based

on the above data it can be considered that the major part of the population has an intake below the PTWI. In these circumstances there does not seem to be any hazard to the population at large and the legal imposition at regional level of an upper limit for mercury concentrations in edible marine organisms would not therefore appear necessary, although such upper limits could possibly be dictated by national or local circumstances.

However, limited population sectors in the Mediterranean area have an intake of methyl mercury through seafood which exceeds the PTWI. The on-going project on evaluation of methyl mercury in Mediterranean populations and related health hazards, currently operational in Greece, Italy and Yugoslavia has so far identified fishermen as having such a high intake, in some cases several times the PTWI, through excessive consumption of fish. Pregnant women also constitute a high-risk group. These groups are not sufficiently protected by normal legal limits on the mercury concentration in seafood in view of their abnormally high consumption, and require separate attention through other measures, involving dietary recommendations and protection through biological monitoring.

10.2 Scientific rationale for control measures to prevent risks to marine organisms and ecosystems

In order to reduce the level of a pollutant in sea water to a concentration that is not harmful to marine organisms and ecosystems, it is necessary to limit the release of pollutants into the marine environment both in quantity per unit time discharged and as concentration of the pollutant in the liquid effluent.

The concentration in the marine environment (environmental quality criterion) must be below that which will not cause significant harm ("minimum risk concentration").

The "minimum risk concentration" can be derived from the lowest effective concentration at which the most sensitive marine organism has shown an effect (section 5). Reducing the lowest effective concentration by a safety factor (usually a factor of 5 to 10), one obtains an estimate of the "minimum risk concentration".

The application of a safety factor of 4 to the effective concentration of 20 ng Hg l^{-1} of the most sensistive phytoplankton species tested (section 7.1) results in 5 ng Hg l^{-1}. This can therefore be taken as the "minimal risk concentration".

Although the sea water concentration of 10 ng Hg-T l^{-1} (Table XLIV), may be considered a typical level for uncontaminated Mediterranean sea water this lower effective concentration is not contradictory because the total concentration of mercury in sea water will not be equal to the "bioeffective concentration". In fact, most of the mercury in sea water is not in a bioavailable form (see section 3.3 and 4.2); the "bioeffective concentration" of natural coastal sea water can be estimated to be less than 10% of the Hg-T, i. e. 1 ng Hg l^{-1}. Likewise, not all mercury discharged in wastes will be in a "bioeffective form", because a certain amount of mercury will react with components contained in the waste and in the marine environment and will, thus, not be "bioavailable".

Assuming that an effluent can be diluted, using jet diffusers employed in sewage disposal, by a factor of 10,000 in the mixing zone adjacent to the outfall of the pipeline, a maximum concentration of 50 ug Hg l^{-1} in such effluent could be tolerated.

In order to avoid excessive amounts of mercury, even at low concentrations in effluents, being released into the marine environment, the total amount per unit time (usually a montly average) to be discharged should also be limited. Such limits are normally linked to production or mercury processing capacity. In the case of the chlor-alkali electrolysis industries, it has been stated that the application of the best technical means available makes it possible to limit discharges of mercury from the site of a new industrial plant using the recycled brine process to less than 0.5 g/tonne of installed chlorine production capacity (EEC, 1982).

It should be pointed out that these limits would hold good only for discharges through pipelines supplied with diffusers or other appropriate devices which guarantee a dilution of 10,000. If the dilution is lower, appropriate reductions would have to be applied. Lagoons and semi-enclosed bays with limited exchange with the open sea cannot be chosen as release sites for new plants. In the case of existing plants, the turnover time of the water contained in the semi-enclosed water body receiving the discharge should be determined, and both the effluent concentration and amount of mercury discharged in such semi-enclosed water bodies reduced accordingly.

Since it is not possible to predict with sufficient precision the distribution of mercury and its chemical species in the marine environment, the effectiveness of the control measures must be checked. This is achieved by monitoring the effluent concentration and the concentration outside the mixing zone (500 m distance from the outfall of the pipeline) regularly. Further monitoring is required to establish the trend of Hg-T in the tissue of sessile or non-migratory biota which should not increase more than 50% above the background concentration. Since mercury increases with the size of the organism and different concentrations are found in different tissues of different biological species (see sections 3.5 and 4.2), the trend of the Hg-T concentration must be determined in the same tissue of specimens of the same species.

Since past experience on the release of mercury from chlor-alkali plants has shown that at a distance of about 20 km from the release point mercury concentrations in sediments and sessile biota return to background (section 3.9), multiple mercury releases into the same marine environment within a range of 10 km must be considered in the total amounts to be released per unit time.

Studies on the reduction of mercury concentrations in an area heavily polluted by mercury wastes from a chlor-alkali plant (section 3.9) have shown that a marked reduction in the amounts of mercury released will only reestablish background concentrations in sediments and biota after several years because the heavily polluted sediment will release mercury only slowly. Monitoring for checking compliance with limitations on mercury discharges by existing plants should result in a trend of decreasing mercury concentrations in sediments and biota. From the limited data available, it may be estimated that the half-time of the concentration of mercury in sediments and biota should be about 5 years. This means that the mercury concentration in wastes released by an existing plant into the adjacent environment with the procedure as specified above should result in a decrease to half the mercury concentration in sediments and biota every 5 years until levels are reached which do not exceed background levels by more than 50%.

Special attention must be paid to the food habits of fishermen and their families which obtain all or large amounts of their seafood from heavily contaminated areas. Surveys to identify these consumers must be carried out in order to guarantee that they do not exceed the PTWI considerably. Limiting fishing activities in such areas could be considered until near background levels have been reached, unless the necessary degree of protection can be guaranteed by other measures.

11. Requirements for control and reduction of pollution effects

11.1 Marine ecosystems

In order to achieve the water quality objective specified in section 10.2, the following measures would be necessary:

(a) an effluent concentration of 50 ug total mercury l^{-1} would have to be set as a limit value.

(b) the discharge of the outfall would have to be placed, and its configuration adapted, in such a way as to guarantee a dilution of 1:10,000 in the mixing zone adjacent to the outfall.

(c) the mercury concentration in sediment and resident biota in an area 5 km away from the outfall should not increase more than 50% above background levels which would have to be determined before the waste discharges from the new plant begin. In the case of an existing plant, concentrations of mercury in sediments and biota should decrease with a half-time of 5 years until levels less than 50% above background are reached. Background levels should be determined in an unpolluted ecologically similar area.

(d) the effectiveness of the control measures should be checked:

- by monitoring the concentration of the effluent; the limit values established in paragraph (a) should not be exceeded by the arithmetic mean of determinations obtained over a year with a monthly frequency. The monthly sample must be representative for the discharge effected over 24 hours.

- by monitoring the mercury concentration in the sea water outside the mixing zone at monthly intervals, to ensure concentrations below 20 ng of mercury l^{-1}.

- by monitoring the mercury concentration in the sediments outside the mixing zone at monthly intervals. Their concentrations must be below 50% of the background levels, or decrease with a half-time of 5 years as specified in paragraph (c).

- by monitoring the mercury concentration in representative resident biological species outside the mixing zone at monthly intervals. In the case of new installations, concentrations should not exceed the background levels by 50% or in the case of existing plants decrease with a half-time of 5 years as specified in paragraph (c).

11.2 Human health

In order to safeguard human health, the following measures would be necessary:

(a) the identification of heavy seafood consumers (irrespective of area), monitoring of seafood consumption patterns, including type and species of seafood consumed through appropriate dietary surveys, and preliminary screening by monitoring concentrations of mercury in hair.

(b) similar monitoring programmes in areas affected by mercury discharges, including moderate seafood consumers.

(c) the formulation and implementation of advisory and recommendatory measures to regulate the type and amount of seafood consumed, for high-risk groups.

12. Measures already approved by the contracting parties

The Contracting Parties approved the following interim Environmental Quality Criteria for mercury at their fourth Ordinary meeting in Genoa (9-13 September 1985) (UNEP/IG.56/5, III, F.5, pages 36-37):

Interim environmental quality criteria for mercury

1) According to the available evidence to date, on the basis of present concentrations of mercury in Mediterranean seafood it appears that the consumption of seafood by the general population does not present any risk.

2) It is considered therefore that, at this stage, the adoption of upper limits for mercury concentrations in seafood on a common regional basis would not be a priori justified.

3) On the basis of the assessment of the quality of Mediterranean seafood with regard to its mercury content prepared by FAO/UNEP, the Contracting Parties:

a) Take note of the interim criterion proposed by the joint FAO/WHO Committee of Experts on food additives. According to this criterion, the Provisional Tolerable Weekly Intake of 0.3 mg of mercury, of which not more than 0.2 mg is methyl mercury, for a person of 60 kg bodyweight, should not be exceeded;

b) Take into consideration this criterion to establish, if national circumstances so require, standards for maximum concentration of mercury in seafoods;

c) Use for the determination of total mercury the Reference Method "Determination of Total Mercury in Selected Marine Organisms by Cold Vapour Atomic Absorption Spectrophotometry" (Reference Methods for Marine Pollution Studies No. 8/Rev. 1, UNEP/FAO/IAEA, 1984) and for the "Determination of Methyl mercury in marine organisms by Gas Chromatography" (Reference Methods No. 13, UNEP/FAO/IAEA, 1984). However, other methods giving comparable results could also be used;

d) Include, to the extent possible, in their National Monitoring Programmes, the sampling and analysis of species of seafood, known to accumulate mercury, in addition to those already monitored in the framework of MED POL - PHASE II;

e) Limit anthropogenic discharges of mercury into the Mediterranean Sea pending the eventual formulation of emission standards for mercury, as a result of the entry into force of the Protocol for the Protecton of the Mediterranean Sea against Pollution from Land-Based Sources, and in terms of article 5 of that Protocol, commence as early as possible, the elaboration of the necessary programmes and measures with respect to mercury;

f) Provide the Secretariat to the Convention with the fullest information possible on:

- present legislation and administrative measures on existing national criteria for levels of mercury in seafood;

- measures taken on b), c), d) and e);

- relevant monitoring data on d) above;

g) Continue to carry out the monitoring and research component of MED POL PHASE II relevant to the assessment of mercury content of Mediterranean seafoods, and the risks affecting all sectors of the population arising from seafood consumption, in particular:

- identification of population groups at risk;

- surveys on seafood consumption patterns among such populations;

- surveys on mercury levels in affected population groups;

- epidemiological studies to obtain the necessary information on the relationship between mercury intake and health effects;

- studies of the relationship between total mercury and methyl mercury conten of seafood, and the effects of cooking on such content;

- studies on biogeochemical cycles of mercury in the Mediterranean;

- studies on the effects of selenium in decreasing mercury toxicity.

13. Additional measures proposed for adoption by the Contracting Parties

On the basis of the present assessment, prepared by FAO/WHO/UNEP and in conformity with paragraph 3(e) of the Interim Environmental Quality criteria for mercury approved by the Contracting Parties at their fourth Ordinary meeting, the following recommendations for additional environmental quality criteria for mercury and limitations on mercury discharges are submitted for the consideration of the Working Group with a view to their transmission by the Secretariat to the next meeting of the Contracting Parties.

The Contracting Parties:

(a) adopt an upper limit (to be calculated as a monthly average) of 50 ug mercury per litre (expressed as total mercury) for all effluent discharges into the Mediterranean sea, in terms of Article 5 and Annex I of the Protocol for the Protection of the Mediterranean sea against pollution from land-based sources.

(b) enforce such limit, for those effluents so demanding, through compulsory monitoring requirements and procedures, including (a) the taking each day of a sample representative of the discharge over 24 hours and the measurement of the mercury concentration of that sample, and (b) the measurement of the total flow of the discharge during this period.

(c) reinforce such measures by appropriate limitations on the total amount of mercury discharged, based on monthly averages and taking into account (a) the production capacity of each relevant industry, and (b) the possible reductions in mercury emissions capable of being achieved by currently available technological processes.

(d) adopt, in principle, an eventual water quality objective of a maximum of 20 ng mercury per litre in marine waters.

(e) for the purposes of progressively reaching the objective, adjust relevant outfall structures in such a way as to achieve a dilution of 1 to 10,000 in the mixing zone adjacent to the outfall and monitor sediments and biota in areas 5 km away from outfall structures to ensure an increase of not more than 50% above background levels in the case of new plants, and achieve a progressive decrease towards the same objective in areas affected by existing plants.

(f) Include, to the extent possible the sampling and analysis of appropriate effluents for mercury within the framework of their national MEP POL monitoring programmes.

(g) Provide the Secretariat to the Convention with the fullest information possible on:

- present legislation and administrative measures on existing national standards and criteria on mercury emissions into the marine environment and water quality regarding mercury

- measures taken relevant to (a), (b), (c), (d) and (e) above

- relevant monitoring data on (f) above

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