REGIONAL SEAS

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# *Mercury in the Mediterranean*

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## PREFACE

Sixteen years ago the United Nations Conference on Human Environment (Stockholm 5-16 June 1972) adopted the Action Plan for the Human Environment, including the General Principles for Assessment and Control of Marine Pollution. In the light of the results of the Stockholm Conference, the United Nations General Assembly decided to establish the United Nations Environment Programme (UNEP) to "serve as a focal point for environmental action and co-ordination within the United Nations system" [General Assembly resolution 2997(XXVII) of 15 December 1972]. The organizations of the United Nations system were invited "to adopt the measures that may be required to undertake concerted and co-ordinated programmes with regard to international environmental problems", and the "intergovernmental and non-governmental organizations that have an interest in the field of the environment" were also invited "to lend their full support and collaboration to the United Nations with a view to achieving the largest possible degree of co-operation and co-ordination". Subsequently, the Governing Council of UNEP chose "oceans" as one of the priority areas in which it would focus efforts to fulfill its catalytic and co-ordinating role.

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans.

The Regional Seas Programme at present includes ten regions 1/ and has over 130 coastal States participating in it. It is conceived as an action-oriented programme having concern not only for the consequences but also for the causes of environmental degradation and encompassing a comprehensive approach to combating environmental problems through the management of marine and coastal areas. Each regional action plan is formulated according to the needs of the region as perceived by the Governments concerned. It is designed to link assessment of the quality of the marine environment and the causes of its deterioration with activities for the management and development of the marine and coastal environment. The action plans promote the parallel development of regional legal agreements and of action-oriented programme activities 2/.

The Mediterranean Action Plan was the first one developed in the framework of the Regional Seas Programme. It was adopted in early 1975 in Barcelona 3/ and since then has shown a remarkable progress.

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1/ Mediterranean, Kuwait Action Plan Region, West and Central Africa, Wider Caribbean, East Asian Seas, South-East Pacific, South Pacific, Red Sea and Gulf of Aden, Eastern AFrica and South Asian Seas.

2/ UNEP: Achievements and planned development of UNEP'S Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No. 1, UNEP, 1982.

3/ UNEP: Mediterranean Action Plan. UNEP, 1985.

A centrally co-ordinated monitoring of the sources, levels and effects of pollutants, as well as research related to this monitoring (MED POL) 4/, 5/ was organized by UNEP as one of the conerstones of the Action Plan. The contamination of the Mediterranean by mercury and the elucidation of the processes governing the mercury was an important target of MED POL.

This publication, prepared by Dr. M. Bernhard, was commissioned by UNEP to review the contamination of the Mediterranean basin by mercury on the basis of results obtained through MED POL and other programmes.

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4/ FAO/UNESCO/IOC/WHO/WMO/IAEA/UNEP: Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL) - Phase I: Programme Description. UNEP Regional Seas Reports and Studies No. 23, UNEP, 1983.

5/ UNEP: Long-term programme for pollution monitoring and research in the Mediterranean (MED POL) - Phase II. UNEP Regional Seas Reports and Studies No. 28, Rev. 1, UNEP, 1986.

C O N T E N T S

## EXECUTIVE SUMMARY

Environmental levels, elements of the biogeochemical cycle, toxic effects of mercucy on marine organisms and potential health effects on humans from mercury intake with marine foods are reviewed. Mainly literature concerning the Mediterranean has been considered, but where data were scarce the Mediterranean data were integrated with information from other regions.

Mercury levels in air, sea water, sediments and biota from the Mediterranean are described and compared with selected levels from other regions. With the exception of Hg levels in biota, due to insufficient quality control, the accuracy of all data is uncertain. In addition, the different Mediterranean regions have been surveyed very unevenly. For some areas, in particular along the southern coast, very little data exist. Therefore, the data reviewed cannot be used to describe the Mediterranean as an entity but they are only characteristic for the region for which the data were collected.

The limited data on the concentrations of "Gaseous Hg" in Ligurian and Tuscan rural areas and near anthropogenic sources are similar to concentrations determined in other regions. Air over land has higher Hg concentrations than air sampled over the sea. High levels were observed near a Hg mine. The air in rural areas of the Mt. Amiata Hg anomaly is higher than the levels in rural areas not influence by Hg geochemical anomalies.

The lack of proper quality control of the sea water determinations makes it difficult to select reliable data. Considering recent data, "open-sea" concentrations range between 7 to 25 ng dissolved total Hg/L. Comparable data from non-Mediterranean regions range between 2 to 14 ng Hg-T/L.

"Open-sea" sediments have Hg levels comparable to those of other regions. Anthropogenic influence is noted near cities and industries. The influence of natural Hg sources is evident in the sediment of the rivers draining the Hg anomalies and in the sediments in the coastal zones adjacent to the river outflows.

In general, Hg levels in fish and shellfish from the Mediterranean are higher than those from the Atlantic. In large bluefin tuna high Hg levels occur in the muscle (up to about 6 mg Hg-T/kg fresh weight), but high concentrations were also observed in other organisms such as the striped mullet and the Norway lobster. The highest concentrations (muscle: up to 40 mg Hg-T/kg fresh weight) were determined in marine mammals. In the same species the Hg concentrations increase with the size (age) of the specimens. In addition, organisms positioned higher in the food chain have higher Hg levels than their prey. Data on several pelagic fish and molluscs and marime mammals show that Mediterranean specimen of the same species have much higher Hg concentrations than specimens of same size from the Atlantic. Interestingly two tuna populations could be identified on the basis of their Hg levels: one Mediterranean with high Hg levels and one Atlantic with about 5 times lower Hg concentrations. The Atlantic tuna migrate into the Mediterranean during March-August only for spawning and leave again through the Strait of Gibraltar. Tuna caught in the Strait of Gibraltar belonged exclusively to the "low-Hg population".

Natural and anthropogenic sources influence the environmental levels. Despite earlier massive Hg contamination by chlor-alkali plants (in one case about 15 MT of Hg/year) the influence of these Hg releases is limited to an area of 10 to 20 kg coast line from the source. After severe reduction in the quantities released the environmental concentrations are slowly decreasing. Natural sources (Hg geochemical anomalies belonging to the Mediterranean-Himalaya geological belt) have a much wider influence. Detailed studies indicate that they are the cause of the high Hg levels in marine organisms in many regions of the Mediterranean.

Few data are so far available on methyl mercury. In plants and plankton the methyl mercury percentage of total mercury is lower than in organisms in higher trophic levels. In higher organisms methyl mercury increases with size (age). The dynamics of uptake and release of inorganic mercury and methyl mercury could be described successfully with a mathematical model. Bivalve molluscs seemed to be an exception in that their methyl mercury percentage decreases with size. At present no explanation can be supplied for these observations. Investigations on the molar ratios of mercury and selenium have shown that seldom this ratio is equal to one.

Few data are published on the elements of Mediterranean biogeochemical cycle. Therefore, selected data from other regions were considered also. The origin of methyl mercury is still uncertain. Model experiments designed to investigate the biological and abiological origin of methyl mercury were carried out under conditions (high additions of Hg) which do not allow an extrapolation to natural conditions. Hence the ecological significance of these data is uncertain. On the other hand there is no doubt that the chemical species of mercury are transformed by organisms and abiotically. Model calculations show, however, that very small amounts in sea water (fractions of ng/L are sufficient to allow an accumulation of high amounts of methyl mercury in marine organisms. Laboratory experiments have shown that the uptake of methyl mercury is very efficient and very little methyl mercury is released after uptake (biological half-time: several years). On the other hand inorganic mercury is taken up to a limited extent and released with a biological half-time of 20 to 30 days. This difference in the dynamics of uptake and release of these two major mercury species results in a relative increase of methyl mercury with age. A mathematical model on the pelagic food chain of tuna illustrates these dynamics. With the exception of autotrophs the uptake of mercury through the food chain is the major path of mercury into biota.

Also in reviewing the effects of mercury on marine organisms non-Mediterranean data have been considered. No data could be found that investigated the toxic effect through the food chain. Only data are available from experiments in which the organisms were exposed to mercury salts added to sea water. Therefore, only data on organisms belonging to the first trophic level have any ecological significance. This explains why some organisms in higher trophic levels can withstand very high mercury concentrations.

The high mercury concentrations observed in many fishes and shellfishes raise the question of possible health risks, especially to heavy consumers of seafoods. A few studies undertaken in Mediterranean regions have shown that persons eating fish many times a week have higher mercury levels in their blood and hair than persons who do not eat fish. Surprisingly it was found that children of fishermen may be the persons most at risk. Pathological symptoms were observed. The legal limits of 0.5 to 1 mg total mercury/kg live weight of seafood in force in many countries do not protect the persons belonging to these "critical groups". To protect the "critical groups" the Provisional Weekly Tolerable Intakes based on recommendations of the World Health Organisation must be taken into consideration. These intake limits are set at a weekly intake of not more than 300 µg total mercury for a person weighing 70 kg of which not more than 200 µg should be methyl mercury. For children and persons weighing less than 70 kg the weekly intake has to be accordingly reduced. Since unborn and young children are more sensitive than adults the intake of mercury by pregnant women and young children must be further reduced. It is proposed that special efforts are made by the competent authorities to identify the "critical persons" and "critical groups" and counsel them on the risk to which they are exposed while consuming large amounts of seafood so that they are induced to reduce their mercury intake from seafoods.

## 1. INTRODUCTION

Following the tragic events of methyl mercury poisoning through seafoods in Japan (Minamata Bay) and the discovery of high mercury (Hg) levels in Swedish fish also in the Mediterranean area high mercury levels were found in several seafoods, especially in tuna and swordfish.

In the early seventies several scientific publications appeared which indicated that certain pelagic fishes had higher mercury levels than specimens of equal size of the same species from the Atlantic. These observations have stimulated the United Nations Environment Programme (UNEP) in co-operation with the relevant specialized United Nations Agencies (FAO, WHO, IOC, IAEA) to propose a Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL) to the Intergovernmental Meeting of Mediterranean countries in Barcelona in 1975. One of the pollutants which received major attention in this proposal was mercury.

In the following literature survey both data generated in the frame of the MED POL programme and data published independently in the scientific literature on the mercury levels in various components of the Mediterranean marine environment will be discussed and where opportune compared with mercury levels from other marine regions. The information available on uptake, release and transformation of different chemical species of mercury by marine biota will be reviewed. Special attention will be given to the question of the biotic and abiotic origin of methyl mercury, since due to its prevalence in seafoods and its elevated toxicity, this mercury species is of special concern.

In order to evaluate the possible effects of mercury introduced into the marine environment on marine organisms, the characteristics of natural and anthropogenic sources of mercury which are released into the sea are described and compared with the effects that mercury compounds have on marine biota. The amounts of seafood eaten by different human populations groups and their mercury intake will be examined and compared with the data on the tolerable intakes.

## 2. GENERAL CHEMISTRY OF MERCURY

Mercury, atomic weight 200.61, belongs to the group IIB of the periodic table together with zinc and cadmium. Air in equilibrium with metallic $Hg^0$ contains 5.5 mg $Hg/m^3$ at $10^oC$ and 13.2 mg $Hg/m^3$ at $20^oC$. Such high levels are never found in the atmosphere and, therefore, Hg in droplet form cannot occur in the environment (Matheson, 1979). Under equilibrium condition the air over inorganic Hg salts can reach considerable concentrations. At equilibrium HgS reaches 100 ng $Hg/m^3$ in dry air and 5000 ng $Hg/m^3$ when the relative humidity is close to 100%. Over HgO dry air contains 2000 ng $Hg/m^3$, and over methyl mercury-chloride solutions (0.04 to 0.08 %) the air concentrations range from 140000 to 900000 ng $Hg/m^3$ (Matheson, 1979).

Knowledge of the chemical forms of inorganic Hg in natural waters is largely due to thermodynamic calculations which predict that in practical terms Hg(I) does not exist. Redox conditions determine the valance state. Mercuric species Hg(II) will predominate in well-aerated, oxygen-containing waters (Eh circa 0.5 V). $Hg^0$ 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). $Hg^0$ is relatively soluble in pure water and in hydrocarbon solvents (Carty and Malone, 1979). Sanemasa (1975) gives its solubility at $20^oC$ in water at as 45 ug/litre and in sea water as 40.6 ug/L. In aqueous solutions $HgCl_2$ exists predominantly as undissociated $HgCl_2$ making it not a good source of $Hg^{++}$ ions, but Hg(II) halides are important species in the environment establishing equilibria shown by Carty and Malone, (1979) as follows:

$HgCl_2 \leftrightarrows HgCl^+ \leftrightarrows Hg^{++} + 2\ Cl^-$

$HgCl_2 + Cl^- \leftrightarrows HgCl_3^-$

$HgCl_3^- + Cl^- \leftrightarrows HgCl_4^{-2}$

$HgCl_2 + H_2O \leftrightarrows HgCl(OH) + H^+ + Cl^-$

In sulfidic marine waters, in interstitial water of sediments and in waste waters sulfidic complexes are to be expected. Hg(II) sulfide, 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 MeHg is not the dominant form of organic Hg in natural waters. $CH_3Hg^+$ occurs in aqueous solutions as an aquo complex $CH_3-Hg-OH_2^+$ with a covalent bond between Hg and O. 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 S, P, O, N, halogens, and C. The rate of the formation of Cl-, Br-, and OH-complexes is extremely fast and is diffusion-controlled (Stumm and Morgan 1981). $CH_3Hg$, 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 MeHg from biological tissues prior to its analytical determination. More details about the chemistry of mercury in biological system can be obtained from the review by Carty and Malone (1979).

The $CH_3Hg^+$ unit itself is kinetically remarkably inert toward decomposition. Therefore, MeHg 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 MeHg (Stumm and Morgan, 1981).

The schemes proposed for the biogeochemical cycle of Hg show the dissolved inorganic and organic Hg as chemical species but in the actual environment the Hg species are associated with various ligands. For example, Andren and Harriss (1975) observed that in water samples from the Mississippi Delta and the Florida Everglades the dissolved mercury was associated with dissolved organic matter. From 46 to 82% of the total dissolved Hg 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 Hg was associated with molecular size fraction of less then 500. Also Wallace (1982) found that 4 to 50% of the total Hg in coastal sea water 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 Hg in sea water was associated with organic matter of a molecular size of 9000.

## 3. MERCURY LEVELS IN AIR, SEA WATER, SEDIMENT AND BIOTA

### 3.0 Data quality

One of the major problems encountered in the determination of Hg 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 Hg in samples of various matrixes but, more important, the exact amounts of different key species of Hg must be determined.

Recognizing that insufficent analytical quality control may jeopardize the success of the MED POL Phase 1 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). This project prepared and distributed sediment samples and samples prepared from various marine organisms for intercalibration exercises ( e.g. Fukai et al. 1978, 1979; IAEA, 1978, 1985). Certified reference standards of the US National Bureau of Standards (NBS) and reference samples from the European Community (EC) were also used by workers from the Mediterranean area. Unfortunately, there are no intercalibration standards which could be used for Hg analysis at the low levels found in sea water, rainwater and air. The two Canadian sea water references (Marine Analytical Chemistry Standards Program, National Research Council of Canada, Ottawa) do not report data for Hg. This is regrettable since, due to the extremely low Hg concentrations in sea water, rainwater and air, the uncertainty of the data available is very high (see also discussion in section 3.2).

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 frame 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%. However, the lower levels of Hg in the two samples of the fourth intercalibration again increased the CV to 33 and 50%. The International Laboratory of Marine Radioactivity (Monaco) distributed several biological intercalibration samples in the frame of the MED POL programme. The CV in the different matrixes ranged from 4 to 40% (Fukai et al. 1978; IAEA, 1978, 1980, 1985).

Results similar to those in the Mediterranean and the ICES areas have been obtained in intercalibrations in other areas. A collaborative study of eight laboratories determining methyl mercury (MeHg) by electron-capture gas-liquid chromatography on blind duplicates of oyster, shrimp, tuna and swordfish samples containing 0.15 to 2.48 mg Hg/kg resulted in a precision of 3 to 13% and an accuracy versus the reference values (established by the Associations Referee Laboratory) ranging from 99 to 120% (Hight and Casper, 1983).

The experiences with intercalibration of sea water samples may also be illustrative for the special difficulties encountered in determining the accuracy at very low levels. Spiked samples showed that a good comparability of the standard solutions examined, but data of the low level unspiked samples (CV about 100%) indicated systematic errors (Olafson, 1982). Similar experiences were made in Japan. Intercomparison by 17 Japanese laboratories showed a wide scatter of data with CVs for some samples as high as 83% (Sugawara, 1978). The scatter was wider in natural water samples than in synthetic solutions indicating difficulties with the natural matrix, i.e. with the determination of different chemical Hg species. Also contamination from sampling devices caused difficulties. Gill and Fitzgerald (1985) report that sea water determinations carried out on water obtained from the PVC sea water samplers attached directly to the usual metal hydrowire resulted in substantially higher (>30 times) Hg concentrations of "reactive Hg". The authors were not sure whether the hydrowire, the PVC sampler or the handling of the samples aboard were the cause of the contamination. These observations are not new, since it is known now for some time that the "usual" sampling gear used on oceanographic vessels is not suitable for trace element analysis (e.g. Betzer and Pilson, 1975; Patterson and Settle, 1976). Also reaction vessels may be the cause of contamination. Baker (1977) found that despite great efforts in cleaning glassware, only quartz vessels were suitable to carry out the oxidation step necessary to transfer all Hg into the analyte species.

The results from these intercomparisons show that the data from different authors are not easily comparable. Only large differences in Hg concentrations may be significant. The uncertainty increases with decreasing Hg concentrations. This means that the uncertainty of the sea water concentrations, which are in the ng/L range, are much greater than that of the much higher levels (µg/kg) in sediments and biota. Nevertheless, large errors can also be committed by experienced laboratories on biological samples (Topping, 1983).

New analytical techniques with increasing sensitivity and specificity make it possible to measure trace elements at very low concentrations. However, at the same time the risk of obtaining wrong results increases also. Examining, for example, the sea water values one gets the impression that the older data are much higher (section 3.2). A greater awareness of the analytical limitations of certain methods and of the risk of contaminating samples have increased the accuracy of the analytical determinations. Nevertheless, it is not possible to state generally that analyses carried out in recent years are necessarily more accurate than older ones and that lower trace element levels are necessarily the more accurate. Often not enough attention has been placed to losses occurring during the analytical procedures and whether the transformation of all Hg species present in the sample into the analyte species was quantitative.

Unfortunately, despite the availabilty of the MED POL intercalibration service and of the reference standards from other agencies not all laboratories used these facilities. Another disadvantage consists in the fact that the results of the MED POL intercalibration exercise remained anonymous and, therefore, it is impossible to say which of the laboratories intercalibrated successfully. This leaves the reviewer in doubt about the validity of the results unless the authors either stated their intercalibration results or give at least the identification number of the MED POL exercise.

For a quality control of biological matrixes and of sediments reference samples and standards now exist and there is, therefore, no excuse for not making use of them. For sea water determinations, direct comparison of samples exchanged between laboratories conveniently located so that the samples can be analysed shortly after sampling, should be encouraged. For air intercalibrations in situ comparison seems to be the only possibility at present.

## 3.1 Levels in air

When evaluating mercury concentrations in air the different behaviour of the various Hg species must be taken into consideration. Although soluble and particulate Hg usually account for less than 1% of the total Hg (Hg-T) (Fitzgerald et al. 1983) these two Hg species are mainly responsible for the transport of Hg from the atmosphere to the earth 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 µm to 50 µm in diameter) found in the marine atmosphere consisting of modified marine and continental source materials.

The number of Hg 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. 1984) compare Hg 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 1). They collected the Hg present in air on small-diameter gold wire eliminating particulate matter with a 0.45 µm pore size filter. The "gaseous Hg" determined by these authors is, therefore, operationally defined. This procedure has shown good collecting efficiency for non-particulate Hg species such as gaseous elemental Hg, MeHg, dimethyl mercury (DiMeHg) and $HgCl_2$ (Braman and Johnson, 1974; Seiler et al. 1980).

Table 1. "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)]

| | number of samples | 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.

From Table 1 it is evident that near the Tuscan coast the air has lower Hg 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 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 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 1 the overall mean is given, but it was not possible for the reviewer to reconstruct the data, so, where possible, the means of Table 1 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 Solvey plant were very localized. Background levels were already restored 4 to 5 km from the plant. Revisiting the site in 1981 showed the Hg 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 system of a cinnabar mine which had been closed two years prior to sampling. The authors were surprised to find that the Hg

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 (Table 1).

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 Hg concentration in urban areas may have a marked diurnal variation, not easily attributable to industrial activities (Figure 1). These authors also report 0.2 to 0.3 ng Hg/$m^3$ in aerosol and rainwater (Table 2) from an urban area. Rainwater collected early in a storm had higher Hg levels than rainwater collected later in the storm because the early rain washes out particles and scavenges Hg. Collecting successively 150 ml fractions during a rainfall showed that after the third sample the dissolved Hg concentration reached a constant value which was 3 to 4 times lower than the first sample (Ferrara et al. 1986c).

Shani and Naccoun (1976) compared air pollution in the city Beer-Sheva (Israel) with an unpolluted desert area at 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 Hg levels are generally a few per cent 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 3). They attributed the high EF to anthropogenic inputs from countries bordering the northern Mediterranean. An increase due to natural degasing from Hg anomalies (see section 4.1.1) was not considered by these authors.

Comparing data from the Mediterranean with data from other areas show that they are of the same order of magnitude (Table 4). Data collected by Slemr et al. (1985) show higher levels in the northern hemisphere than the southern hemisphere (Figure 2). In rural areas levels are definitely lower than in urban areas and higher levels were observed in air over Hg anomalies than in air over rural background areas. The few data (n = 23) so far collected indicate that open ocean atmospheric particulate Hg concentrations vary less than the values observed inshore in the Long Island Sound (Table 4). These inshore variations reflect the dependence of particles on local sources and their short residence time in the atmosphere. Fitzgerald et al. (1983) separated inorganic from organic Hg in the vapour phase, assuming that a silver collection column positioned prior to a gold collection column would selectively remove elemental Hg plus (very probably) any other inorganic forms of Hg while the organic Hg fractions would pass without being adsorbed and be trapped on the following Au collection column. They found at Enewetak that essentially all "gaseous Hg" was trapped on the Ag column and, therefore, all Hg detected must be "inorganic Hg". In the air of their Long Island Sound campus on the other hand, substantial amounts of "gaseous Hg" were also trapped on a gold column indicating that considerable amounts of "organic associated Hg" were present:

| | | |
|---|---|---|
| Total "gaseous Hg" | (n = 108) | 2.9 $\pm$ 0.5 ng/$m^3$ |
| "Organo-Hg species" | (n = 13) | 50% (27 - 82%) of "total gaseous Hg" |

Using a similar technique combined with a gaschromatograph Slemr et al. (1985) found a median of MeHg in marine air masses of <0.1 ng Hg/$m^3$ (= < 5% of gaseous Hg). DiMeHg was <0.02 ng Hg/$m^3$ (< 2%). In rural sites MeHg was 0.41 $\pm$ 0.31 ng Hg/$m^3$ (= 14% of gaseous Hg) and DiMeHg <0.05 ng Hg/$m^3$ (=<14% of gaseous Hg). In urban air the concentrations raised considerably: MeHg: 1.47 $\pm$ 0.5 ng Hg/$m^3$ (= 15% of gaseous Hg); DiMeHg: = 1.67 $\pm$ 1.16 ng Hg/$m^3$ (= 20% of gaseous Hg).

Rain water was determined in Long Island Sound satisfactory only twice during the wet season (1.7 and 2.3 ng Hg/kg rain water). The particulate matter in the air at that time contained 0.002 ng Hg/$m^3$. From these data Fitzgerald et al. (1983) estimated the washout ratio as 1200.

The very few data on Hg concentrations in rainwater from the Mediterranean can be compared with data from other areas (Tables 2 and 5).

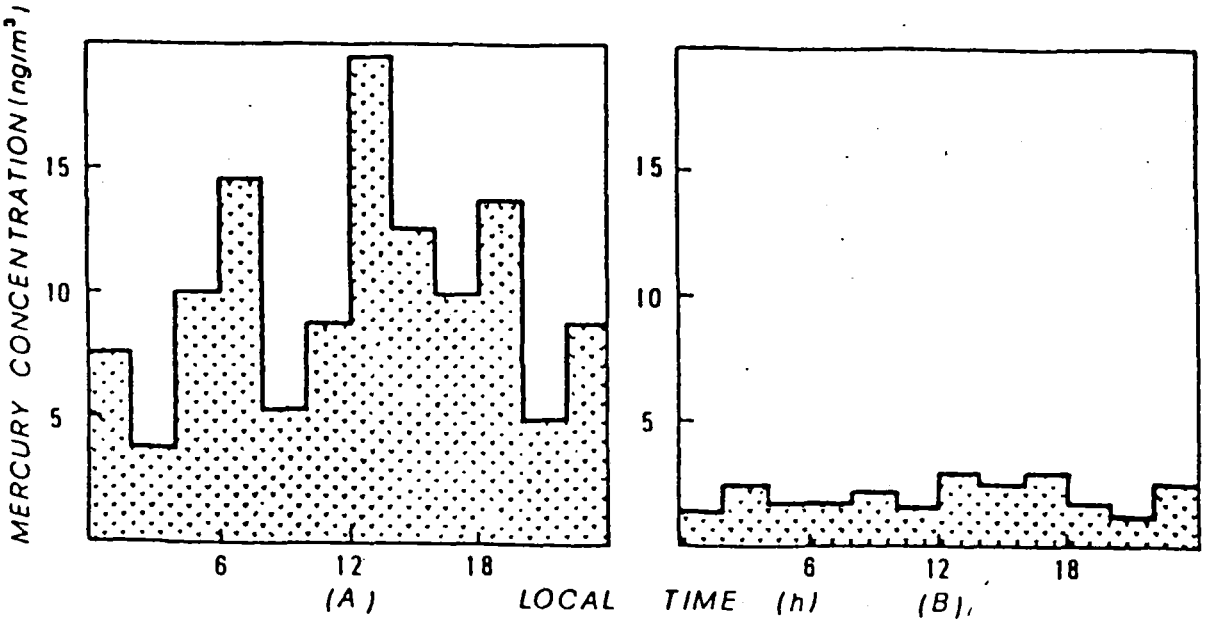


Figure 1. Diurnal variation of mercury concentrations in an urban (A) and a rural (B) area (Ferrara et al. 1982).

Table 2. Mercury concentration (ng/L) 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) |

Table 3. 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)

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

Note: EF denotes enrichment factor. It is defined as:

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

Table 4. Mercury distribution in the atmosphere

| | "Gaseous Hg" ($ng/m^3$) | | | "Particulate Hg" ($pg/m^3$) | | reference |
|---|---|---|---|---|---|---|
| | n | mean | range | n | range | |
| **Marine:** | | | | | | |
| Enewetak, Tropical Pacific | | | | | | |
| dry season (April/May 1979) | 27 | 1.6 | (0.8 - 2.9) | 2 | (0.4 - 0.7) | a |
| wet season (June/Aug 1979) | 67 | 1.7 | (1.1 - 3.2) | 2 | (0.5 - 2 ) | a |
| Atlantic | | | | | | |
| Northern Hemisph. | | 1.96 | (1.0 - 9.4) | | 0.013 ± 0.018 | b (0.7%) |
| Southern Hemisph. | - | 1.33 | (0.8 - 2.1) | | 0.007 ± 0.004 | b (0.5%) |
| NW Atlantic July 1979 | 7 | 1.6 | (1 - 1.9) | 1 | 0.7 | a |
| Long Island S. | 108 | 2.9 | (1.6 - 7.2) | | (8 - 20) | a |
| **Non-marine:** | | | | | | |
| S. Sweden, rural | - | 3.3 | (2 - 6 ) | | | d |
| urban | - | 4 | (0.8 - 13.2) | | | e |
| at 1-3 km height | - | 2.1 | (1.6 - 3.1) | | | c |
| Over remote land | - | | (2 - 9 ) | | | f |
| Mainz, city | - | | (3.5 - 10.0) | | | g |
| Canada, rural | - | 3 | | | | d |
| suburban | - | 8 | | | | d |
| Central Europa 6 to 12 km height | | 2.25 | (1.2 - 3.1) | | | c |

Note: "Gaseous Hg" is operational defined as the Hg species which pass a Gelman Type A-E glass-fibre filter with 0.3 µm pore size.

Ref.: a) Fitzgerald et al. (1983)
b) Slemr et al. (1985)
c) Brosset (1981)
d) Schroeder (1981)
e) Iverfeldt and Olson (1984)
f) Matheson, (1979)
g) Slemr et al. (1979)

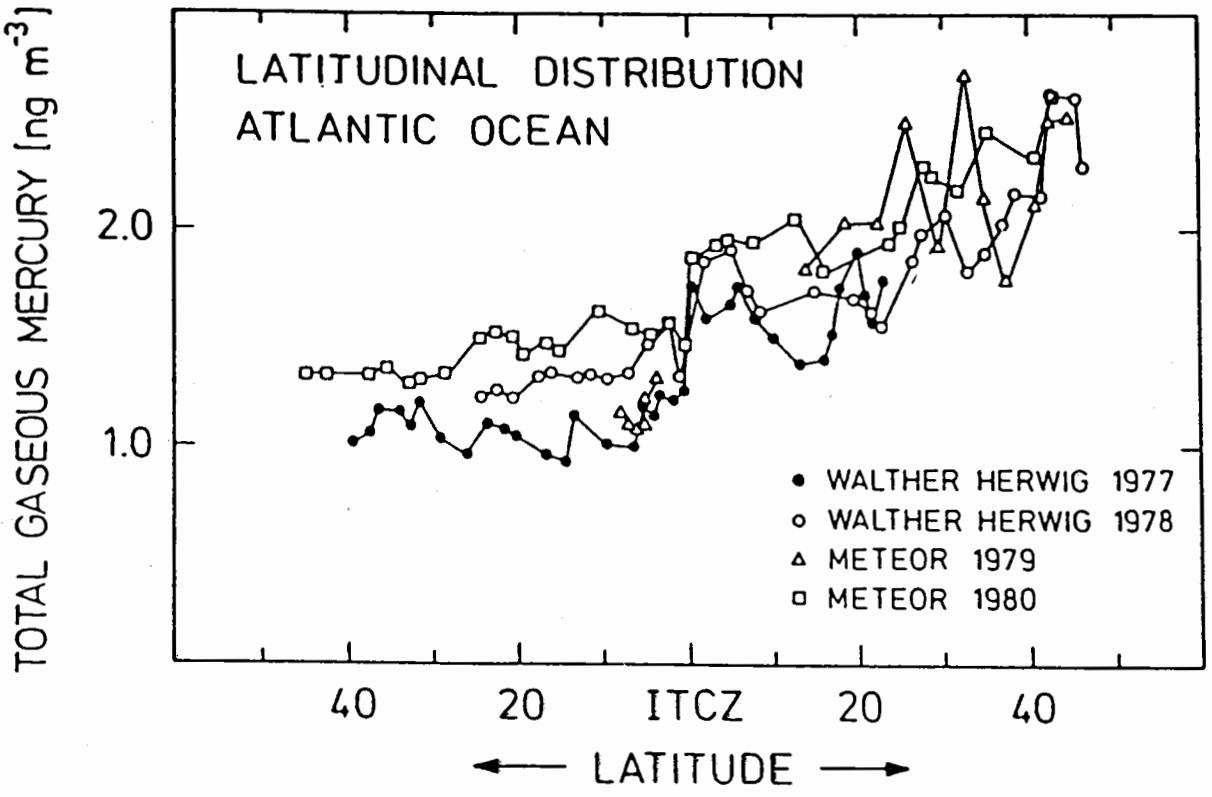


**Figure 2. Latitudinal distribution of total "Gaseous Mercury" in surface air over the Atlantic (Slemr et al., 1985). The midpoint presents the position of the Intertropical Convergence Zone (ITCZ). The Northern Hemisphere is to the right.**

Table 5. Mercury concentrations (ng/L) in rainwater and icecores

| Location | | | | mean | range | reference |
|---|---|---|---|---|---|---|
| Mediterranean: | | | | | | |
| Capraia Isle | Oct 1983/Sep.1984 | rain | dissol. | 8.4 | | s |
| | | | part. | 10.9 | | s |
| S. Pellegrinetto. Mountain area | | rain | dissol. | 7.9 | | s |
| | Oct. 1983/Sep.1984 | | part. | 2.1 | | s |
| Livorno | Oct. 1983/Sep.1984 | | dissol. | 13.4 | | s |
| | | | part. | 13.3 | | s |
| Solvay, chlor-alkali | | | dissol. | 17.0 | | s |
| | Oct. 1983/Sep.1984 | | part. | 9.3 | | s |
| Mt. Amiata, Hg anomaly | | | dissol. | 9.5 | | s |
| | Oct. 1983/Sep.1984 | | part. | 9.3 | | s |
| idem near vapour springs | | | dissol. | 14.4 | | s |
| | Oct. 1983/Sep.1984 | | part. | 6.7 | | s |
| Non-Mediterranean: | | | | | | |
| Atlantic Ocean | Jan/Febr 1979 | rain | | | (4.3 - 3.1) | j |
| Onsala, Sweden | Aug | rain | | 20 | (10 - 75 ) | a |
| | Nov | rain | | 37 | (21 - 52 ) | b |
| Gothenburg, Sweden | Nov | rain | | - | (10 - 25 ) | b |
| Vendalen, Fredrika Sweden (2 samples) | Nov | snow | | 1 | | b |
| Vindeln, N. Sweden | | | | 4 | ( 2 - 10 ) | e |
| Denmark, rural sites | whole year | rain | | 80 | ( 5 - 300 ) | c |
| Greenland | | icecores | | - | ( 7 - 13 ) | q |
| | | icecores | | 10 | ( 2 - 17 ) | r |
| Liverpool, UK | | rain | | 17 | ( 6 - 30 ) | d |
| North Sea | | rain | | 30 | ( 17 - 50 ) | m |
| Goettingen, FRG | | early rain | | - | ( 23 - 75 ) | f |
| Hokkaido, Japan | May-Aug | rain | | 1 | ( 0.7 - 1.5) | g |
| (coastal site) | Dec | rain | | 1 | ( 1 - 1.5) | g |
| | Dec-March | snow | | 1 | ( 0.6 - 3.4) | g |
| Canada, several sites | | snow | | - | ( 20 - 200 ) | k |
| Quebec, Canada | | rain + snow | | - | ( 20 - 100 ) | l |
| Southern New England (coastal site) | Sept-Nov | rain | | 10.5 | ( 2 - 21 ) | h |
| Northern New England (mountain site) | March | rain | | 60 | | i |
| North Pacific Ocean | | rain | | - | (10 - 50 ) | n |
| Alaska | | snow | | - | (<5 - 26 ) | p |
| Tropical Pacific | July | rain | | 2.0 | ( 1.7 - 2.3) | o |
| Samoa Island | Nov | rain | | - | ( 0.8 - 0.2) | h |

References:


a) Brosset (1981)
b) Brosset (1982)
c) Anonymous (1979)
d) Airey (1982)
e) Brosset (1983)
f) Ruppert (1975)
g) Matsunaga and Goto (1976)
h) Fogg and Fitzgerald (1979)
i) Schlesinger et al. (1974)
k) quoted by Matheson (1979)
l) Tomlinson et al. (1980)
m) Cambray et al. (1979)
n) Nishimura (1979)
o) Fitzgerald et al. (1983)
p) Weiss et al. (1975)
q) Appelqvist et al. (1978)
r) Boutron and Delmas (1980)
s) Ferrara et al. (1986c)

## 3.2 Mercury concentration in 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 MeHg predominates in marine organisms, it is the most important Hg species from the biological and health protection point of view. Unfortunately only very few MeHg data for sea water exist (Yamamoto et al. 1983; Egawa et al. 1982; Fujita and Iwashima, 1981). Their values range from <0.03 to 6% of the Hg-T present (Table 6). No MeHg data exist for the Mediterranean.

Several authors have determined "reactive mercury" i.e. the mercury which reacts with the reagents of flameless Hg determination (in general after the sea water sample has been acidified with HCl for conservation during storage). "Reactive Hg" represents those Hg species that are readily reducible with $SnCl_2$ at the sample pH. These species include dissolved inorganic Hg species, labile organo-Hg associations and Hg that is readily leachable from any particulate matter present (Gill and Fitzgerald, 1985). Obviously, "reactive Hg" data cannot be compared with the concentrations obtained with analytical procedures that determine Hg-T which include also stable organo-Hg associations and Hg in particulate matter. The Hg species in sea water are only operationally defined and more work on the actual species present in sea water are urgently needed.

Data of Hg concentrations in the 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 Hg species or groups of Hg species have been determined. Furthermore, several different methods have been used for which it is not clear which fraction of the Hg species present in the sea water were 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 Hg 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 Hg concentrations determined. In Table 6 an attempt has been made to characterize to some extent the "operational species" involved and to illustrate the analytical difference in the methods used.

It is now believed that the Hg concentrations in open sea will range from fractions of ng Hg-T/L to ng/L (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 Hg adsorbs easily to surfaces. In addition, many Hg 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 levels allows no estimation on the accuracy of the data presented and makes a comparison of data from different authors practically impossible.

The sea water concentrations reported for the Mediterranean vary over a wide range (Table 6). 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 Hg (Hg-T) of different authors range from 7 to 25 ng Hg-T/L with ranges from 1 to 30 ng Hg-T/L. For many areas, especially of the eastern and southern Mediterranean no data exist. The different operationally defined Hg species have also wide ranges. It may be worthwhile noting that it is general pratice to acidify sea water samples for storage. This means that if unfiltered open-sea samples are analysed the acidified sample most likely have concentrations near total Hg concentrations. Means of Hg-T in "open sea" samples from non-Mediterranean areas range from 2 to 14 ng/L with some values up to 24 ng Hg-T/L. Also the levels reported for other operational defined Hg forms vary widely both in the Mediterranean and in other regions. So even if one is willing to accept these Hg levels as valid, no differences between Mediterranean and non-Mediterranean Hg 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.

Table 6. Selected mercury concentration (ng/L) in sea water from the Mediterranean and other regions

| | n | mean | range | location | sampling depth (m) | 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. (1986b) |
| 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. (1986b) |
| 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. (1986b) |
| 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. (1986b) |
| 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 & |
| Hg-E | 4 | 340 M | 210 - 370 | Kavala Gulf | 0 | Vasilikoitis (1983) |
| 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. (1986b) |

**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. (1981) |
| 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) |
| 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 et al. (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 Creselius (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) |

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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-isotbutyl-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 [Stroeppler (1984), pers. com.]
?: data unknown
#: range of means
±: standard deviation

The vertical distributions of "reactive Hg" in the Strait of Gibraltar and other stations of the western Mediterranean are interesting (Figure 3). In the Strait of Gibraltar the salinity wedge at about 90 m depth corresponds to a Hg maximum. Does this mean that high salinity Mediterranean sea water has a higher Hg concentration than low salinity Atlantic water? In all three figures, stations SRG1, SRG2, SRT and SRS1 have high surface Hg concentrations. The meaning of these high surface concentrations is not clear. The authors suggest that the Hg levels in the Atlantic are higher than in the Mediterranean because of these high surface levels. These observations do not agree with the lower Hg levels observed in pelagic fishes from the Strait of Gibraltar (section 3.4.5) which would indicate low Hg concentrations in surface sea water and in the food of these fishes. Recently, Ferrara et al. (1986a) have determined dissolved Hg in sea water from the area around Gibraltar. These authors could not find an increase in Hg concentration towards the surface as shown in Figure 3 nor an increase of the Hg concentrations in sea water of higher salinity. Unfortunately, only few depths were sampled in the different water masses.

Levels in coastal areas are strongly influenced by natural and anthropogenic sources (section 3.5 and 3.6). The data from Barghigiani et al. (1981) and Seritti et al. (1982) may give an idea of the possible (operationally defined) species of Hg in different areas (Table 7):

(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); and

(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 exceptional high values of soluble Hg were not observed and also the same high Hg levels were not found at both sampling times. Particulate Hg was high at the mouth of the Arno river. Clearly, sea water concentrations are less indicative for pollution sources than sediments (section 3.5 and 3.6).

The input of Hg (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 Hg concentrations ranged from not detected to 26 µg/L with a mean of 1.7 µg/L (the Dese river) and from 45 to 410 µg/L with a mean of 170 µg/L (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 for calculating the mean". Certainly, if the data on the water concentrations are correct, the input of Hg through the Silone Canal must be enormous. From September 1982 to August 1983 Bernardi et al. (1985) determined again the Hg in several outlets they found the following values: Silone 0.7 ug Hg/L, Dese 1.4 µg/L, Lova 0.9 µg/L, Montalbano 1.8 µg/L, and Trezze 2.5 µg/L. For the other outlet the authors did not give concentrations because the mean values were again considered to be obtained under extreme conditions.

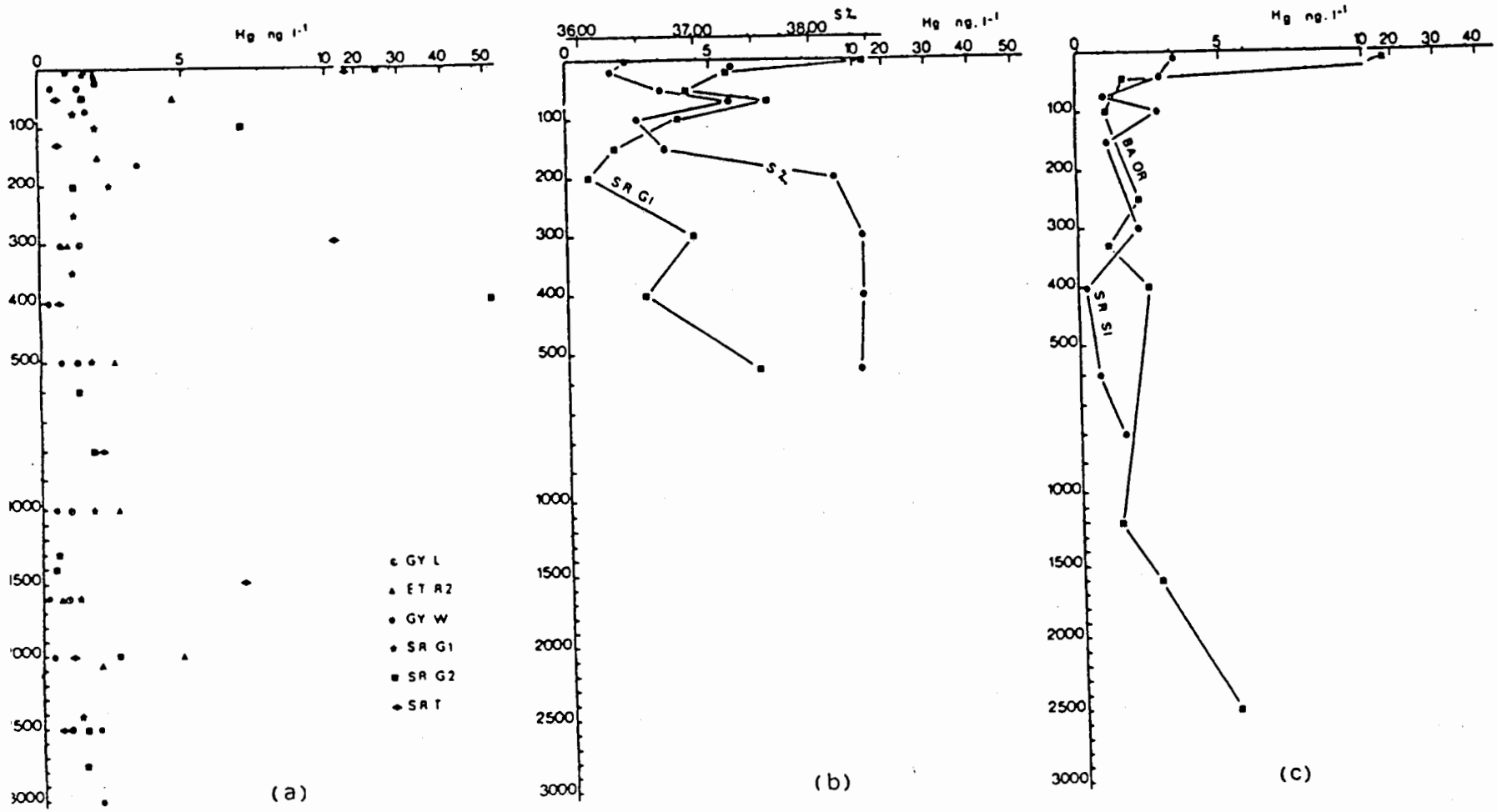



Figure 3. Vertical distribution of mercury. (a) in the western Mediterranean basin; (b) in the Straits of Gibraltar; (c) in the Straits of Sicily and eastern basin (Copin-Montegut et al. 1986).

Table 7. Concentrations (ng/L) 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 | Albegna, 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 |
| | | 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 soluble Hg
Hg-R: reactive soluble Hg

### 3.3 Mercury in sediments

Not many data on open-sea sediment concentrations have been collected in the Mediterranean Sea (Table 8). 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, NBS 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 DW (dry weight) may be considered a typical background value for the Mediterranean. Industrial sources (see section 3.6) and the frequent natural geochemical anomalies in the Mediterranean (see section 3.5) influence the Hg 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 countre clockwise around the Mediterranean coast.

Obiols and Peiro (1981) investigated the Hg levels in sediments off the Ebro delta. Later Peiro et al. (1983) studied, among other elements, the distribution of Hg in more than 70 sediment samples between Barcelona and the Gulf of San Jorge. Off the Ebro mouth and off Tarragona high Hg levels were observed showing concentations higher than 1 mg Hg/kg DW offshore Taragona. Between the Ebro delta and Taragona concentrations vary between background levels and 1 mg Hg/kg DW. Where investigated, a decreasing gradient toward northeast was observed in front of the Ebro delta and one decreasing from Taragona southeastwards. The Hg content in sediments north of Barcelona, near the mouth of the river Besos and near the Barcelona sewage outfall, showed high levels of Hg only in the surface layers near the sewage outfall (Cros Miguel and Grancia Rey, 1980). These high concentrations decrease in the deeper layers of the sediments and at greater distance from the coast.

Table 8. Selected mercury concentrations (mg/kg DW) in "open-sea" sediments

| depth (m) | 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. (1983b) |
| ? | 43 | 0.11 | 0.01 - 0.27 | W-Gulf Lions | Arnoux et al. (1983b) |
| 1380 - 2720 | 14 | 0.22M | 0.12 - 0.57 | NW Mediterranean | Arnoux et al. (1983a) |
| 2535 - 2795 | 17 | 0.12M | 0.07 - 0.23 | SW Mediterranean | Arnoux et al. (1983a) |
| 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. (1978) |
| 2360 | 1 | <0.3 | | S off Crete | Robertson et al. (1972) |

The French Mediterranean coast has received considerable attention. Hg concentrations were studied in the Marseilles area (Figure 4) and in the adjacent open-sea region (Arnoux et al. 1981, 1983a,b). The Etang de Berre, especially in the southern part where most industrial plants are located showed high Hg concentrations (Figure 5). The highest levels were detected in 1981 in the north (up to 3.8 mg Hg/kg DW). In the Gulf of Fos the <63 $\mu$ fraction of the sediments contained concentrations of up to 6 mg Hg/kg DW, but the highest levels were observed near the sewage outfall of Marseilles at Cortiou where concentrations up to 16 mg Hg/kg DW have been found. These concentrations, however, level off to less than 1 mg Hg/kg DW at $\sim$3 km from the outfall. The Hg gradient from the mouth of the Rhone to the ports north of Marseilles show a considerable increase in Hg concentrations towards Marseilles. These high sediment levels probably are caused in part by wastes discharged into the Rhone and in part by pollution caused by the industries located in and around Marseilles. For comparison, the highest levels observed in the Gulf of Lions had 0.63 mg Hg/kg DW (mean 0.175 mg Hg/kg DW) and the BIOMEDE cruises in the western Mediterranean showed that the maximum concentration was 0.57 mg Hg/kg DW with a mean of 0.18 mg Hg/kg DW (Figure 6).

Rapin et al. (1979) investigated the Hg levels in the fraction <63 $\mu$ of coastal sediments from St. Tropez to Cap Ferrat. High levels up to 12.6 mg Hg/kg DW were observed in the ports of Cannes and Villefranche, while offshore levels were background or near background. Flatau et al. (1983), determining the Hg levels in unfractionated sediments between 10 and 100 m depth, found values ranging from <0.01 to 0.052 mg Hg/kg DW with a median of 0.014 mg Hg/kg 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 3.5 and 3.6.

The Hg 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 (Figure 7). The vertical Hg distribution in the cores showed higher Hg levels in the surface layers of the sediments (Figure 8) indicating continuous releases of Hg into the marine environment. It is noteworthy that near Cuma where the main sewage outfall of Naples is located the Hg levels in the sediments are near background. This is certainly a remarkable difference to the high Hg concentrations observed near Taragona, Barcelona, Marseillse, 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 Hg levels in sediments from the Gulf of Venice (Figure 9). 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 is discussed in section 3.5.

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

Salihoglu and Yemenicioglu (1986) determined Hg and MeHg in river deltas and harbours along the Turkish Levantine coast. The Hg concentrations in samples collected near Mercin and in the harbour of Mercin were at background levels, and 5 to 20 % of the Hg-T were MeHg.

Amiel and Navrot (1978) investigated the Hg 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 Hg were found in the sediments. The Hg concentrations decreased from about 0.5 mg Hg/kg DW to background levels ( $\sim$ 0.1 mg Hg/kg DW) at a distance of about 1700 m. Hornung et al. (1984) studied the influence of Hg releases from a chlor-alkali plant situated in the Bay of Haifa. These data and the influence of Hg sources near Alexandria are discussed in section 3.6.

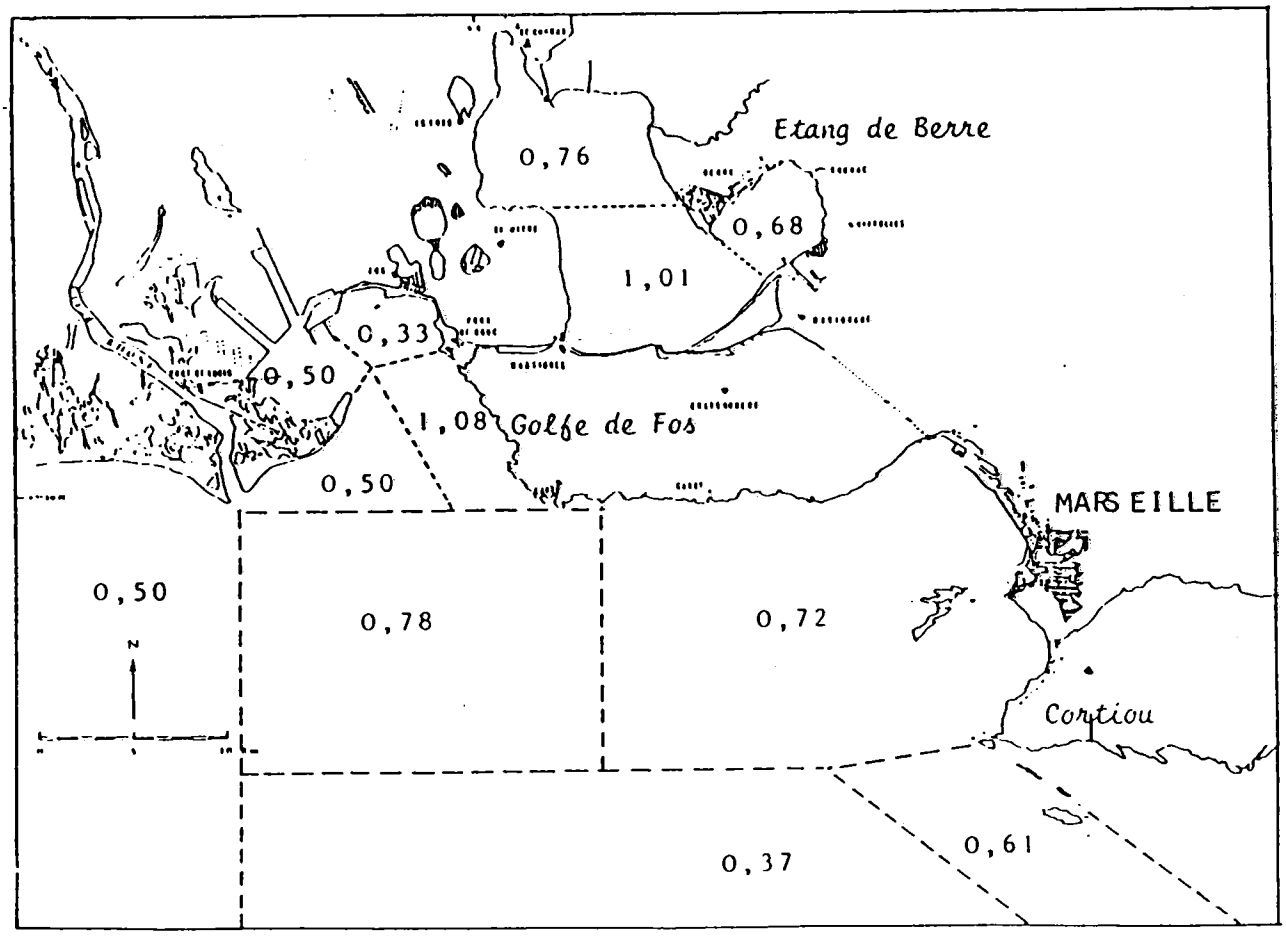



Figure 4. Mean mercury concentrations (mg/kg DW) in sediments near Marseilles (Arnoux et al. 1983).

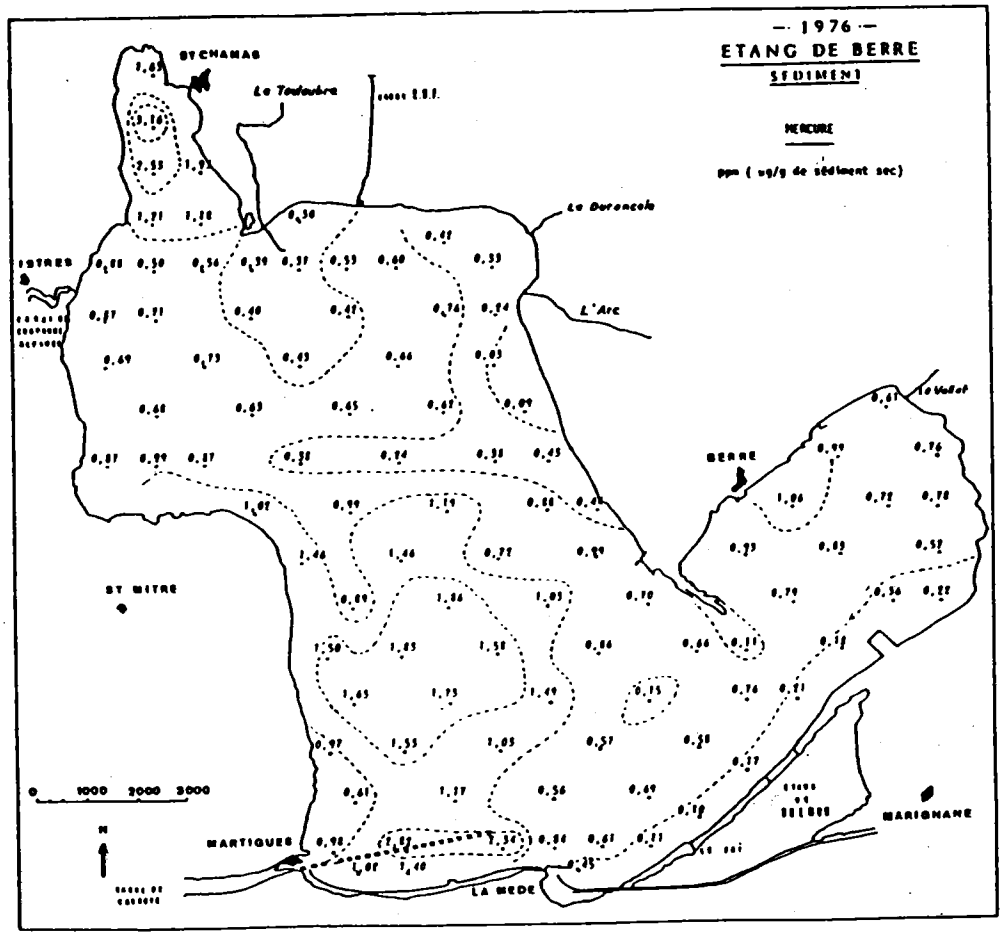



Figure 5. Mercury concentrations in the Etang de Berre (Arnoux et al. 1981).

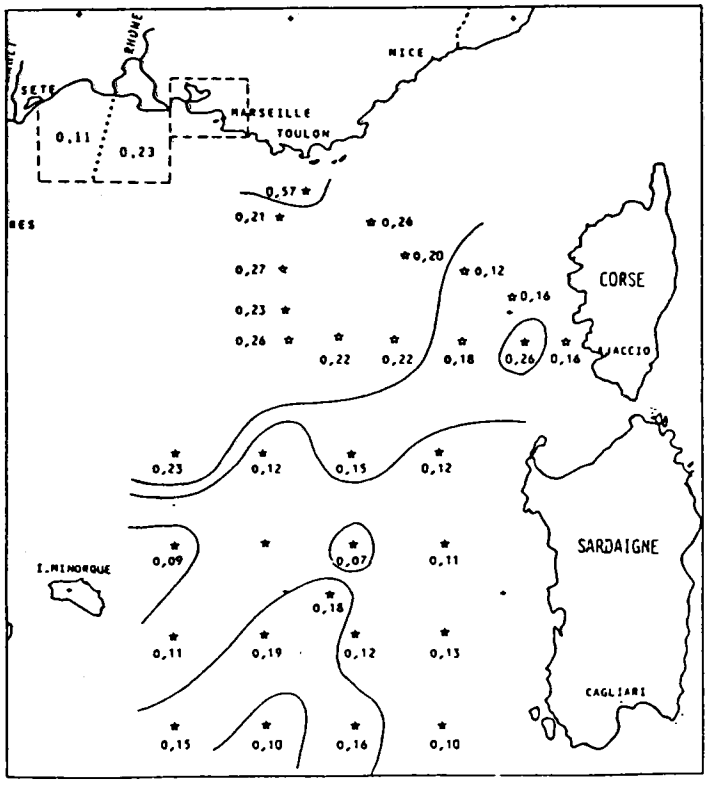



Figure 6. Mercury levels in sediments (mg/kg DW) in the Western Mediterranean (Arnoux et al.

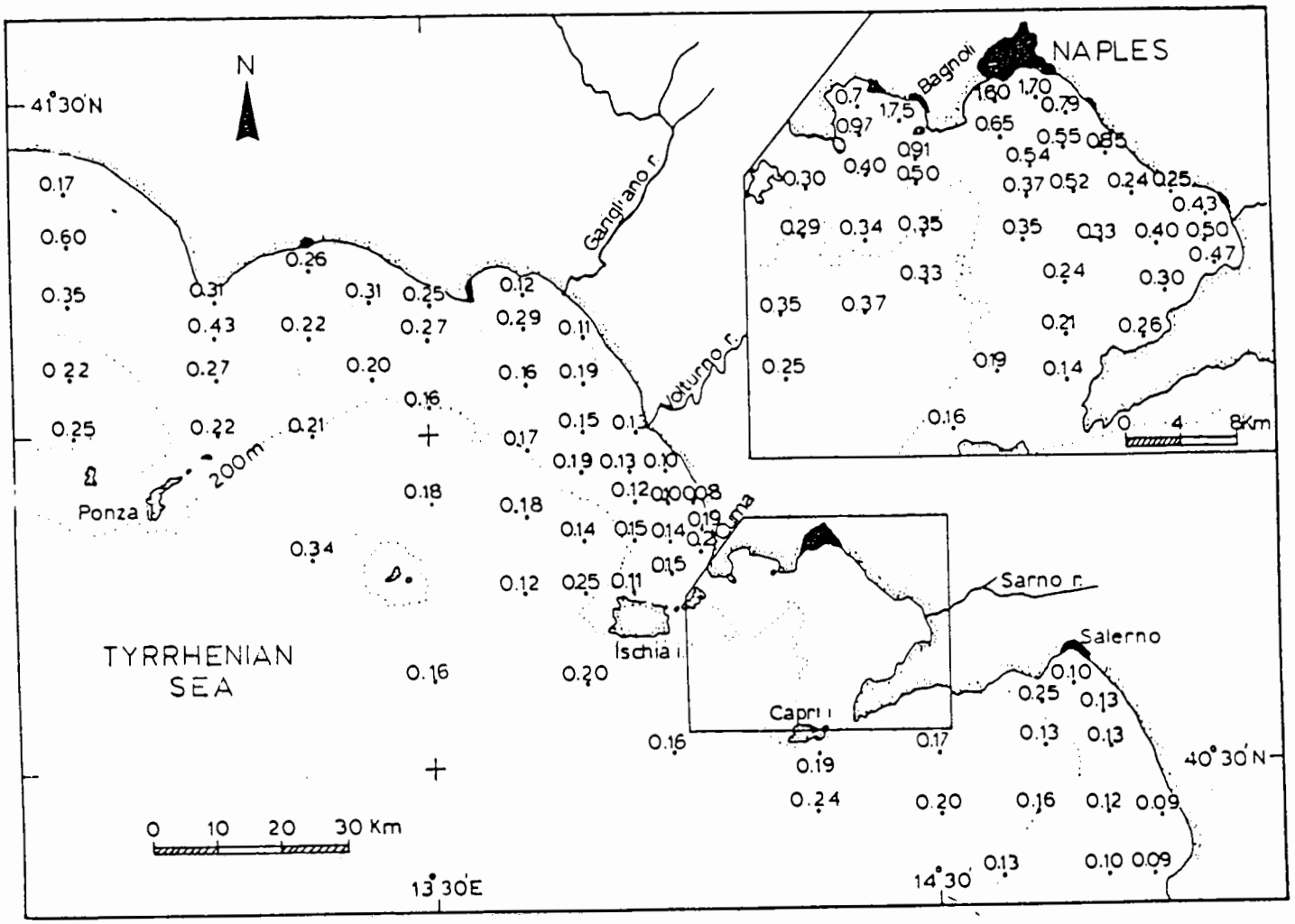



Figure 7. Mercury concentrations (mg/kg DW) in the top 3 cm of sediments in the Gulf of Naples (Baldi et al. 1983)

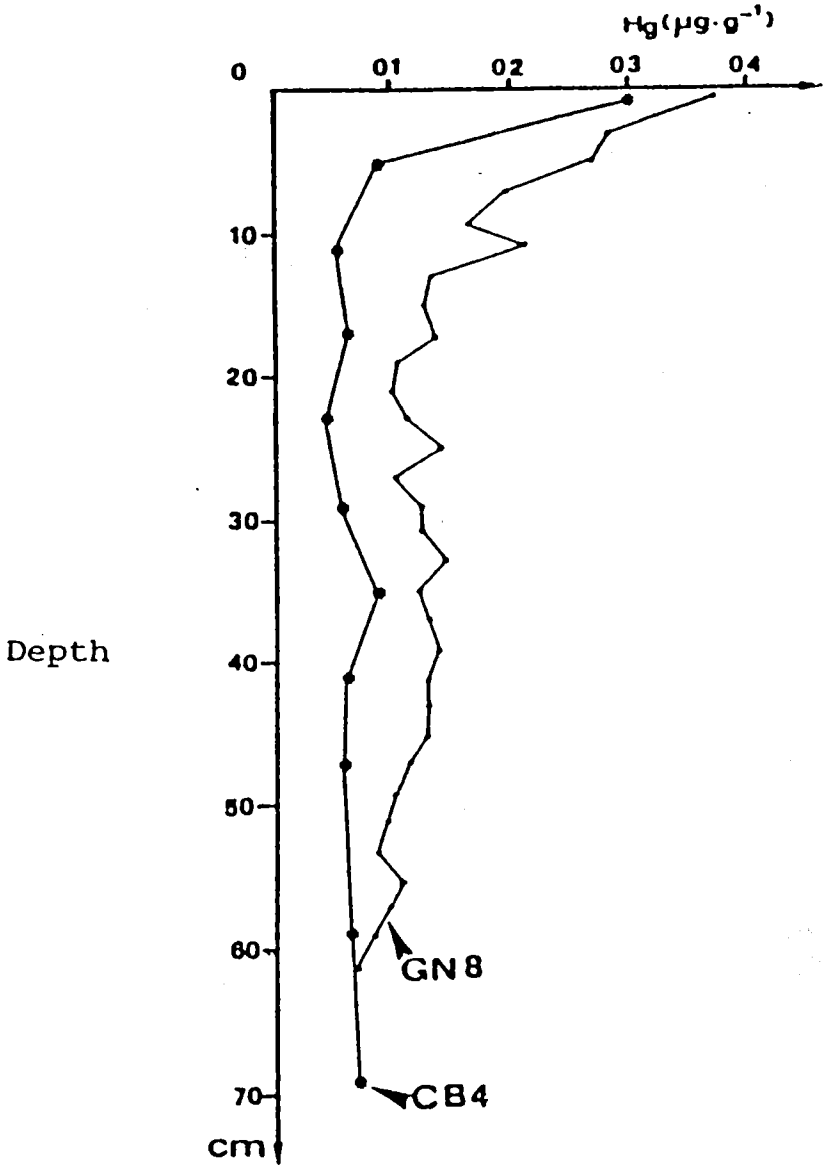



Figure 8. Mercury in the cores from the Gulf of Naples (GN8) and coast of the Tuscan coast (CB4) (Baldi, 1986).

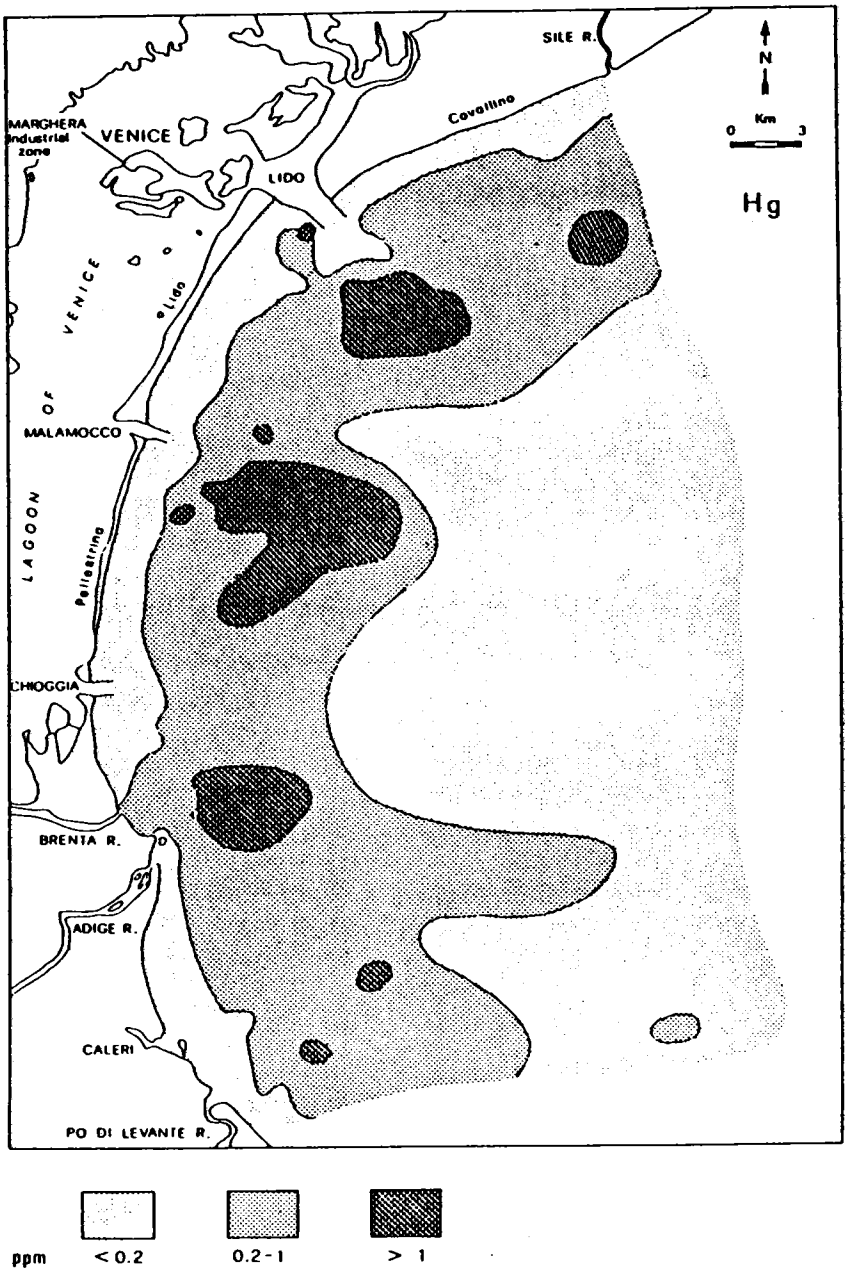



Figure 9. Mercury concentrations in sediments along the coastline of Venice. (Angela et al. 1981).

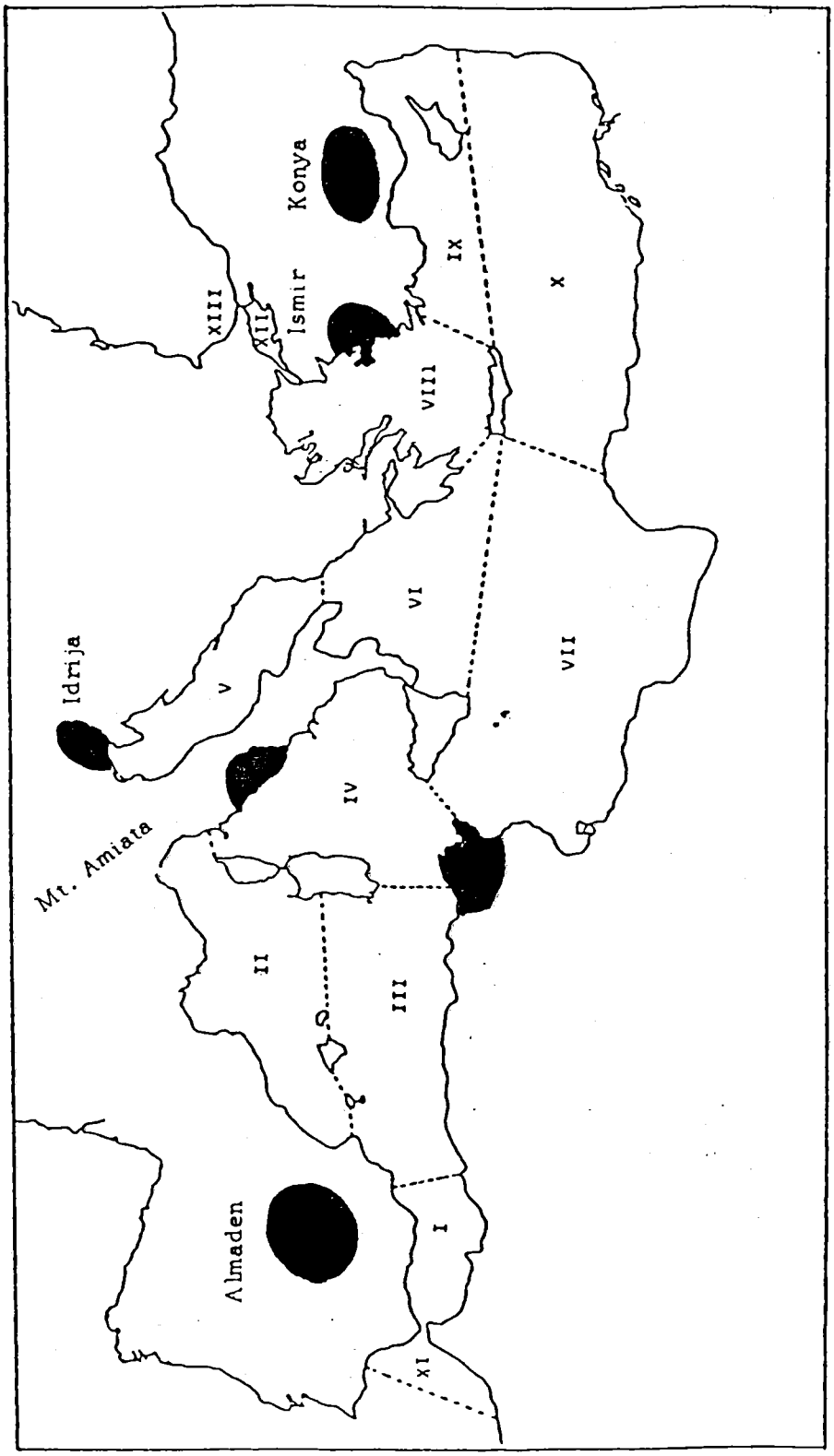



Figure 10. MED-POL areas and major mercury mining areas.

## 3.4 Mercury in marine 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. The Hg concentrations in an organism depend on environmental factors such as the concentration of Hg in sea water and its food-chain position and, in particular, on the chemical species of Hg to which the organism is exposed (see section 4.3). Various biological species may have different Hg concentrations and also different biological tissues of the same species have different Hg concentrations. In addition, the relative distribution of various chemical species of Hg differ between biological species and their tissues and organs. This means that it is difficult to compare the Hg concentration of different biological species. An efficient comparison of Hg concentrations in marine organisms can only be carried out on the relation between Hg concentration and size (age) in the specimens of the same biological species and the same tissues. Data on the Hg 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 Hg concentration in the marine foods consumed, but rarely have samples been selected with this purpose in mind (Paccagnella et al. 1973).

Due to the difficulties in determining exact Hg 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 (Figure 11), but also other marine organisms of different taxonomic groups show similar size-Hg concentration relationships (Figures 12 to 18). Further examples can be seen in other figures (see below and in sections 3.5 and 3.6). The only exceptions so far reported concern mussels (see section 3.4.2). With few exceptions, only total Hg (Hg-T) concentrations are reported. However, recently a few data on MeHg concentrations in Mediterranean marine organisms have been published (see below and section 3.7). Because the physiological behaviour of various Hg species is very different (see section 4.3), for a more precise prediction of the Hg levels in marine foods detailed information on the chemical species of Hg in marine organisms is urgently needed.

The largest uniform data base on Hg-T concentrations in the Mediterranean were collected in the framework of the UNEP/FAO monitoring programmes of the MED POL Phase 1 pilot project (FAO/UNEP 1975). The participants in this project were aware that certain criteria had to be established in order to make the survey effective. First of all, all participants had to intercalibrate with the reference materials distributed by IAEA (see section 3.0). 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 Hg concentrations the results of the monitoring exercise can only be comparable if the size range and the tissues analysed were specified. A wide geographical distribution in the Mediterranean and edible tissues were the characteristics for selecting the species and the tissues 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

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

Since high Hg concentration 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 "Hg concentrations versus size" relationships, because, the differences in Hg levels are much easier to establish if their "Hg concentration-size" relationship is compared rather than the levels in specimens of the same size.

Stimulated by the MED POL pilot project many other species of marine organisms also have been analysed for mercury (Table 9) and in many cases their "Hg concentration-size" relationship was established. The data of these analyses were transmitted to FAO and are preliminarily summarized by UNEP (Nauen et al. 1980a). 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 Hg concentrations without data on size can only give a very approximate idea of the Hg levels present in the marine organisms, the reviewer has preferred to use the tables already prepared by UNEP and to treat individual data published in scientific journals only if they contain collateral biological or ecological data which can explain phenomena of the Hg accumuation, retention and release.

For this reason also the data from Eisler (1981) will not be considered. Unfortunately, Eisler has compiled an enormous number of single data on element concentrations in marine organisms, but without any indication on size of the specimens analysed and without any indication, whether the authors had analysed the sample under an adequate quality control.

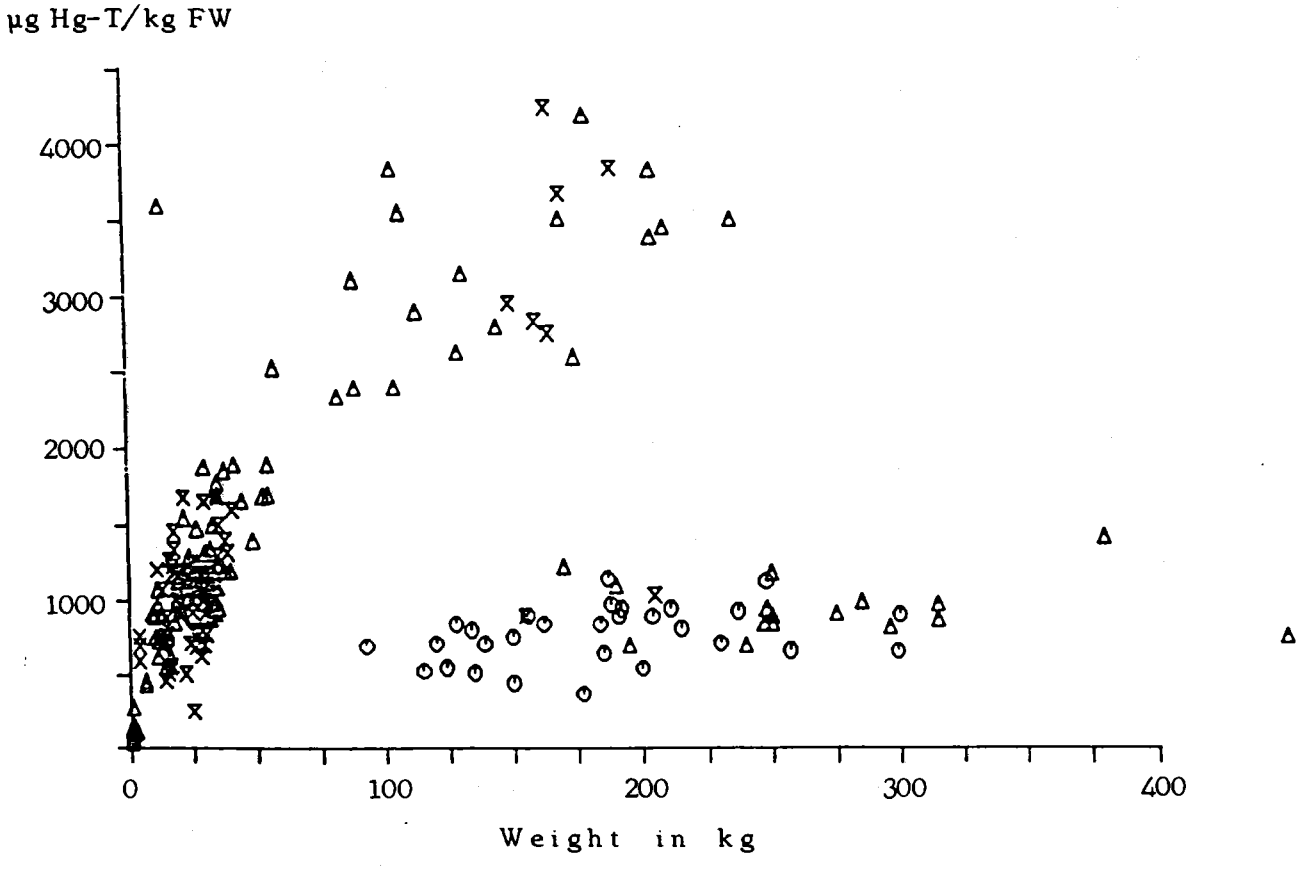



Figure 11. Total mercury concentrations in Thunnus thynnus from the Strait of Gibraltar (⊙), Spanish coast (x), the French coast (⊼) and Tyrrhenian Sea (△). The term FW denotes fresh weight. (Data from Renzoni et al. 1979; Establier, 1972, 1973, Ballister et al., 1978; and Thibaud and Gouygou, 1979)

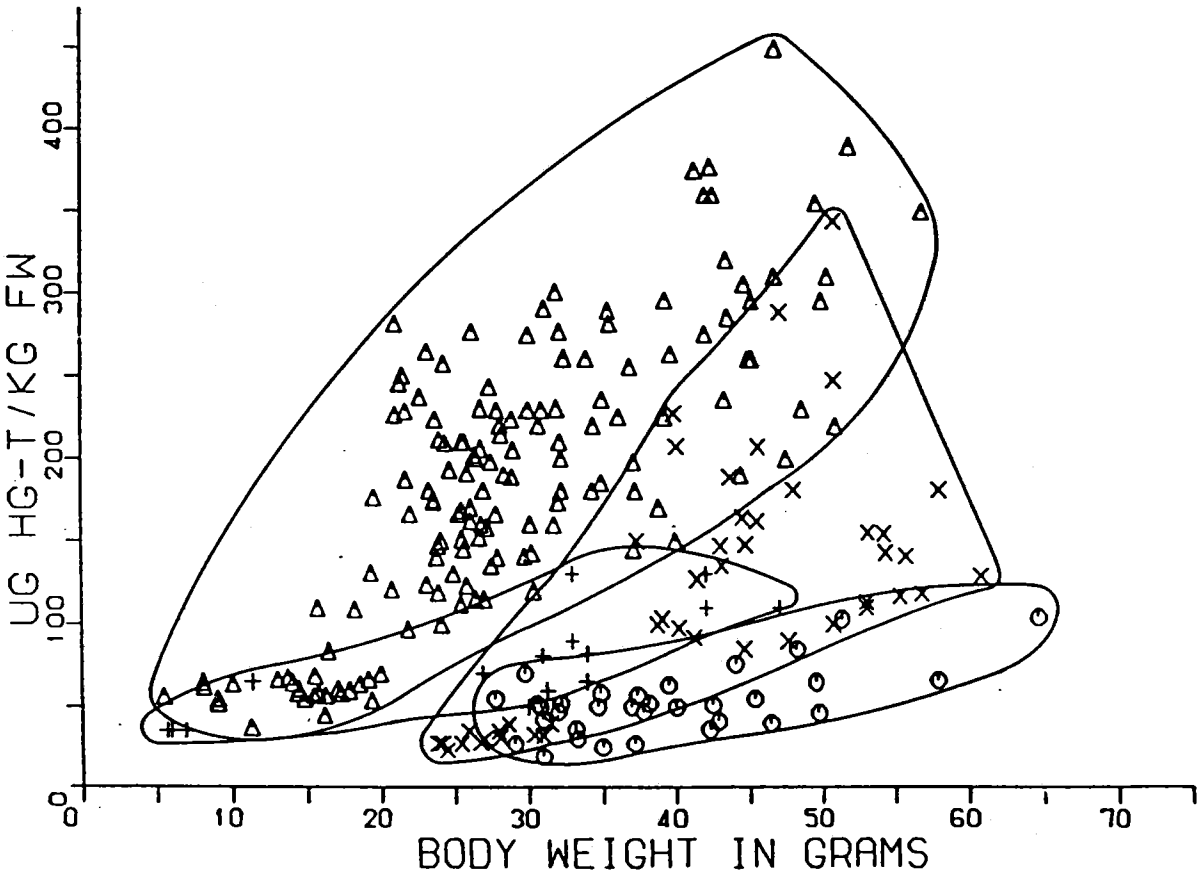



Figure 12. Total mercury concentrations in Sardina pilchardus fromthe Strait of Gibraltar (○), Tyrrhenian Sea (△), Sanremo (+) and Fano (x). The term FW denotes fresh weight. (Data from Stoeppler et al. 1979; Baldi et al. 1979).

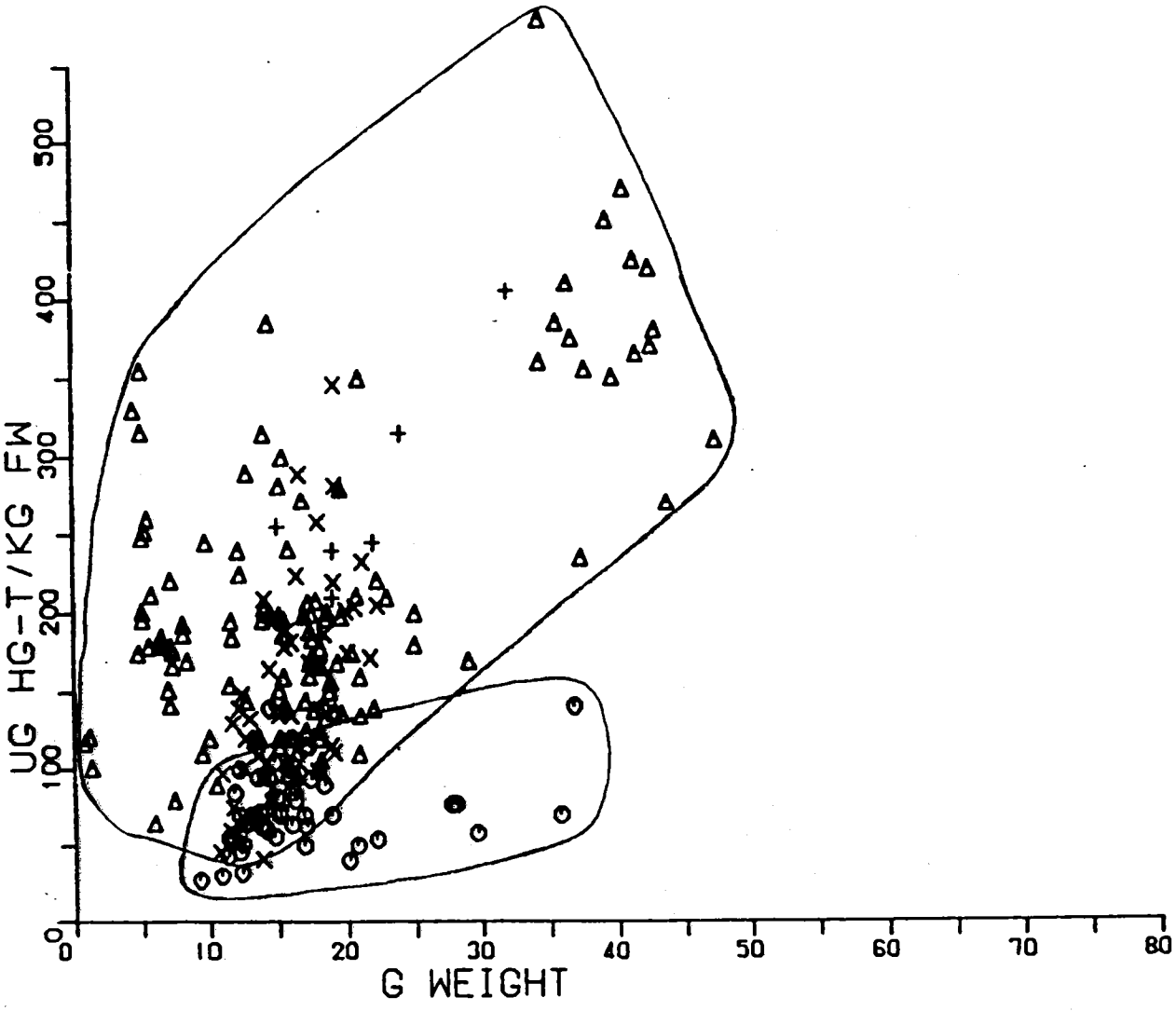



Figure 13. Total mercury concentrations in Engraulis encrasicholus from the Strait of Gibraltar (○), Tyrrhenian Sea (Δ), Sanremo(+) and Fano (x). The term FW denotes fresh weight. (Data from Stoeppler et al. 1979, Baldi et al. 1979).

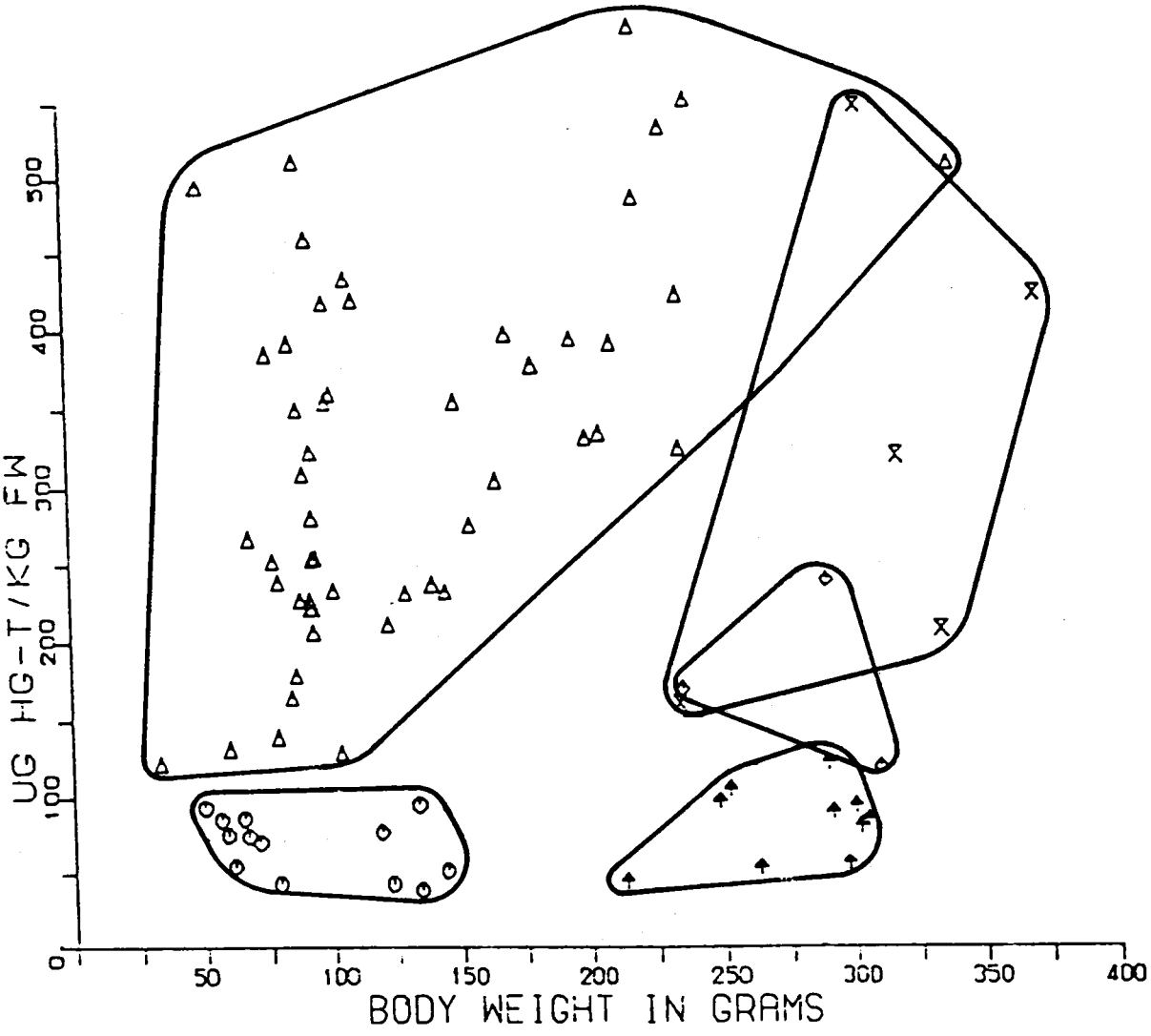



Figure 14. Total mercury concentrations in Scomber scomber and S. japonicus from the Strait of Gibraltar (○), Tyrrhenian Sea (△), Ostend (✕) and Schevingen (↑). The term FW denotes fresh weight. (Data from Stoeppler et al. 1979).

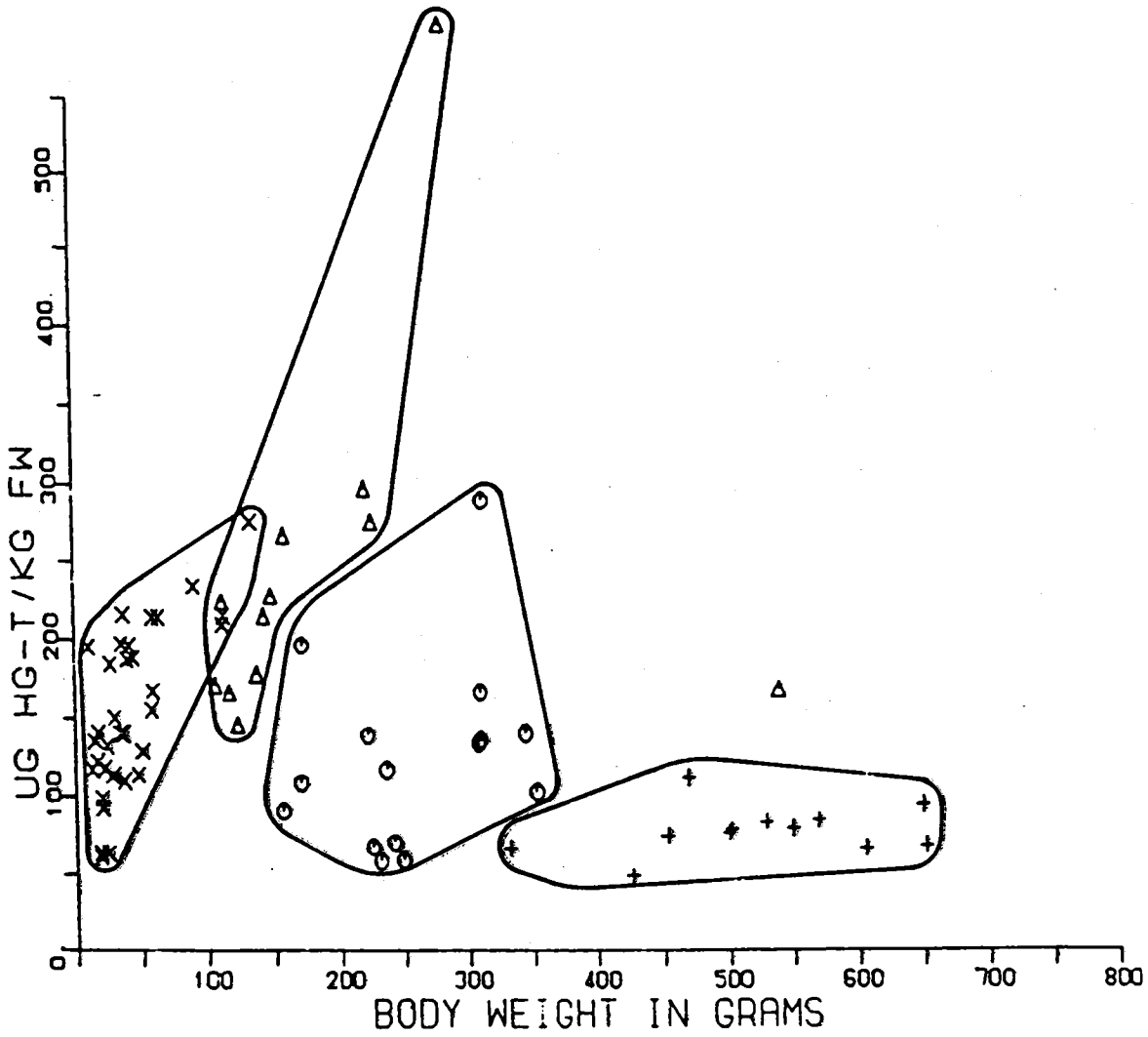



Figure 15. Total mercury concentrations in Sepia vulgaris from the Ostend (Ø), Chioggia (x), Tyrrhenian Sea (Δ) and Schevingen (+). The term FW denotes fresh weight. (Data from Stoeppler et al. 1979).

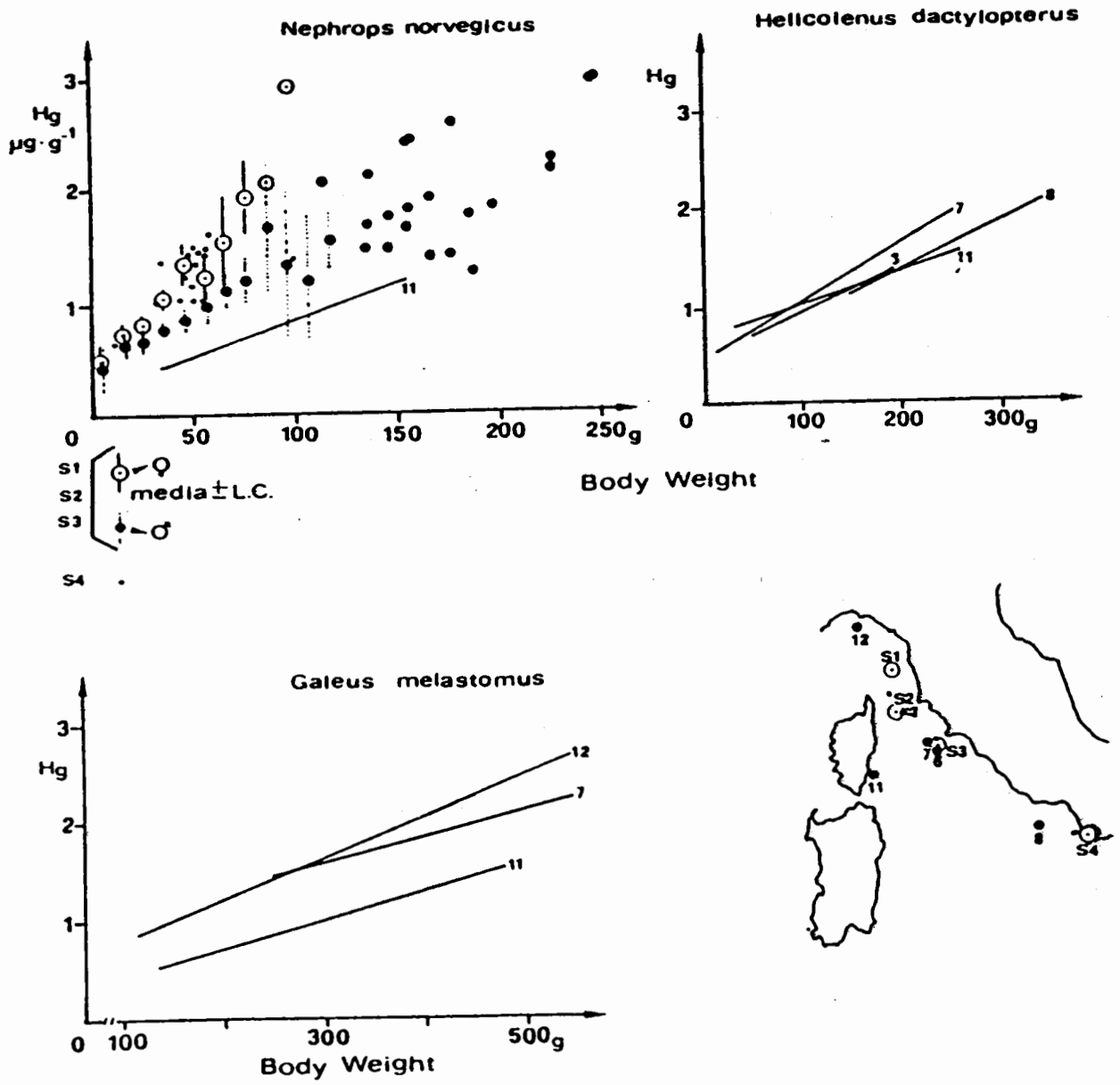



Figure 16. Hg concentration vs. size in benthic crustaceans from remote sampling areas in the Ligurian and Tyrrhenian Seas (Baldi, 1986). Numbers in the graphs indicate sampling stations in the map. The data points the figure for N. norvegicus refer to in sample location S1 to S3. Full circle = male; open circle with dot = female.

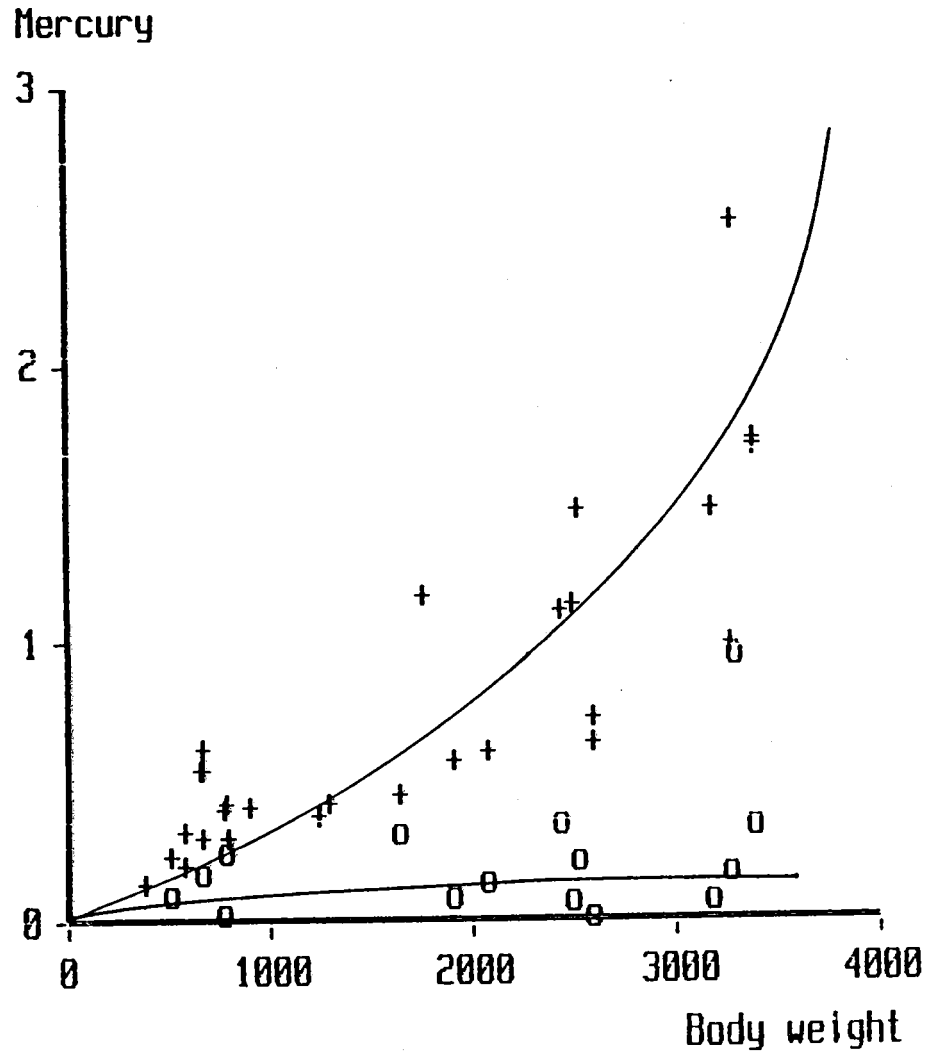



Figure 17. Total (o) and inorganic (+) mercury (mg) in dark muscle of Sarda sarda versus body weight in grams (Capelli et al. 1986).

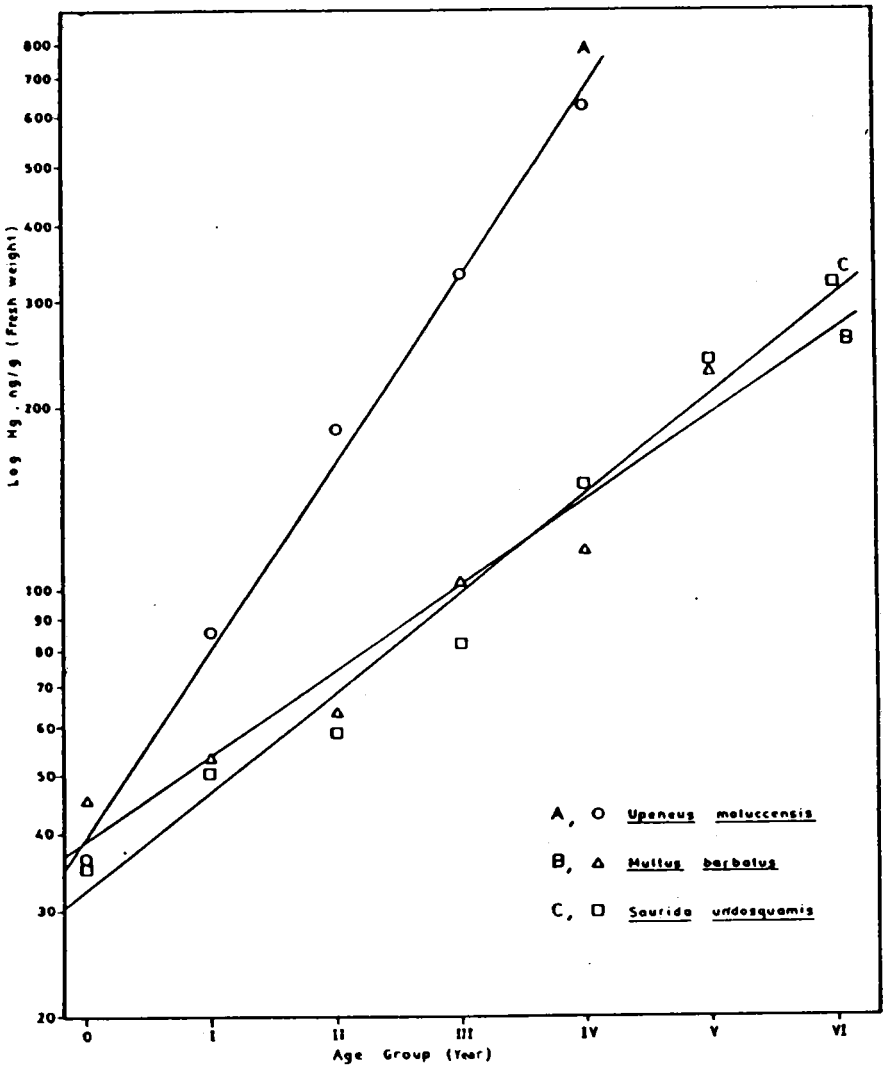



Figure 18. Mercury concentration vs. age in Upeneus moluccensis, Mullus barbatus and Saurida undosquamis (Aydogdu et al. 1983).

Table 9. Mercury levels in various Mediterranean marine organisms (Nauen et al. 1980a).

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 General Fisheries Council Mediterranean (GFCM) classification.

| Species | Number of data (number of samples analyzed) | 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) | 128 | 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 9 (cont'd).

| Species | Number of data (number of samples analyzed) | | 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 lesus | 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 |

### 3.4.1 Plankton

Few data have been published on Hg concentrations in plankton organisms (Tables 10 and 11). The samples in Table 10 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): 19 samples from the Aegean Sea to Gibraltar with pore size 60 μ and 13 samples over the same distance with pore size 132 μ. In other areas nets with other pore-sizes have been used (60 to 500 mμ). All Hg concentrations are given without data on the taxonomic species composition. Depending on the pore size of the net, samples contain a varying mixture of phytoplankton and zooplankton species. In samples collected with small pore size nets more phytoplankton is collected than in samples with larger pore size. In the largest pore size nets phytoplankton is present only if the nets clog. In addition, many factors (e.g. clogging, towing speed, net avoidance) not controllable in hauls with normal plankton nets, determine how many individuals and which are plankton species present in the sea water actually collected. Therefore, samples taken with the commonly used plankton nets will not be representative for 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 μ in diameter. But also zooplankton is misrepresented because nauplii and copepods will pass through the 180 μ pore size nets and many species can avoid the slowly towed nets (Bernhard et al. 1973). Obviously the species composition of net samples taken with different pore size nets will vary widely and, therefore, Hg concentrations in samples taken with nets of different pore size are not comparable. This great variability is reflected in the wide variation of the Hg concentrations which range from 15 to 560 μg Hg-T/kg DW in the samples from the Mediterranean and from about 100 to 1100 μg Hg-T/kg DW in selected samples from other areas, excluding the high levels from the Adriatic and the Minamata Bay. This means that the Hg-T averages vary by a factor of about 40 in the Mediterranean and by a factor of 10 in the data from the other areas. Even comparing plankton samples taken with nets having the same pore size shows ranges varying by factors from 4 to 9.

It is unfortunate that so little attention has been given to the Hg 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 Hg 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 Hg concentration versus developmental stages are needed to evaluate the dynamics of the accumulation and release of Hg species by these organisms which present the first levels of the marine food-chain. Some species like euphausids have a life span of four to five years (Mauchline, 1980) which is comparable to that of sardines and Anchovy. Data on the relative distribution between inorganic Hg and MeHg are needed to understand their role in the dynamics of the accumulation and release of Hg species in the marine food-chain of which they are part (see section 4.4).

The very few data, seldom with information on the size of the specimens, available on individual plankton species are shown in table 11. The data in this and previous Table 10 show that plankton enriches the Hg concentrations from sea water (Table 6) by a factor of 1000 to 5000 and that, albeit on very limited data, the Hg concentrations increases with size of the plankton organisms. Euphausids of one cm length contain on the average 80 μg Hg-T/kg DW, those of 1.5 - 2 cm length 175 and euphausids longer than 2 cm contain 240 μg Hg-T/kg DW.

Fowler and his colleagues (Fowler, 1985a, 1985b; Aston and Fowler, 1985b; Aston et al. 1986) have recently maintained that no difference exists between Hg concentrations in plankton from the Mediterranean and plankton from other oceans. In fact the published data do not show any difference between Mediterranean plankton and plankton from other oceans (Table 10). This is primarily due to the great variability of the data obtained. In order to compare plankton organisms it is not sufficient to compare mixed plankton samples but, like in larger marine organisms, size versus Hg concentration relationships must be compared. In fact, Fowler (1985a) has shown, albeit with some very limited data, that the Hg concentration of euphausids, as to be expected, increases with size (Table 11). Nevertheless, he and his co-authors (Fowler 1985a, 1985b; Aston and Fowler, 1985; Aston et al. 1986) insist that the Hg level in euphausids without any indication on size and that undefined entities such as mixed plankton samples can be used to compare Hg levels in planktonic organisms from different oceans. Only a comparison between Hg concentration-size relationships from different areas, similar to the comparisons carried out with larger pelagic organisms (see section 3.4.4), will be able to settle the question whether Hg levels in Mediterranean planktonic species are different from that of other oceans.

The only data on organic mercury in plankton from the Mediterranean 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%). The Hg-T of the 32 plankton samples analysed had a mean of 132 µg Hg-T/kg FW with a range from 70 to 235 µg Hg-T/kg FW (Table 10).

Table 10. Selected mercury concentrations (µg Hg-T/kg) in mixed plankton samples

| pore size (in µ) | n | fresh weight mean | fresh weight min | fresh weight max | dry weight mean | dry weight min | dry weight max | location | reference |
|---|---|---|---|---|---|---|---|---|---|
| Mediterranean: | | | | | | | | | |
| 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 | 37 | | | | 170 | 20 | 680 | Adriatic | b |
| 333 | 3 | | | | 2860 | 1860 | 4230 | Adriatic, open | d |
| 250 | 7 | | | | 290 | 160 | 440 | Aegean, coast | c |
| ? | 32 | 132 | 70 | 235 | | | | Alexandria, coast | k |
| Non-Mediterranean: | | | | | | | | | |
| 400 | 57 | | | | | 70 | 910 | N-Atlantic, shelf | e |
| 153 | 3 | | | | 140 | 110 | 190 | W-Atlantic, estuar. | f |
| 360 | 18 | | | | 1100 | 70 | 3800 | Caribbean | k |
| 76 | 34 | 10 | 5 | 30 | 207 | 105 | 490 | Monterey Canyon | f |
| 76 | 7 | 20 | 10 | 52 | 410 | 115 | 705 | Hawaii-Monterey | f |
| 76 | 5 | 5.5M | 4.7 | 15.2 | | | | Monterey Bay | f |
| 76 | 5 | 2.0 | nd | 4.5 Me | | | | Monterey Bay | f |
| 360 | 25 | 10 | 2 | 20 | 110 | 50 | 180 | Monterey Canyon | i |
| 360 | 14 | 10 | 4 | 35 | 130 | 40 | 4450 | Hawaii-Monterey | i |
| 360 | 2 | | 65 | 170 | | | | Monterey Bay | i |
| 360 | 3 | 28 | 5.3 | 50 Me | | | | Monterey Bay | i |
| 360 | 9 | (8.5 ± 3.5) | | | 90 ± 35 | | | Monterey Bay | i |
| 360 | 2 | | | | | 75 | 160 | Off Pacific Grove | j |
| 76 | 7 | | | | 250 | 170 | 320 | Pacific Gr. Calif. | g |
| 95 | 3 | | | | 12400M | 6300 | 16800 | Minamata Bay | h |
| 95 | 2 | | | | | 150 | 750 | Yatsushiro Sea | h |
| 328 | 3 | | | | 26400M | 18500 | 47300 | Minamata Bay | h |
| 328 | 2 | | | | | 570 | 1770 | Yatsushiro Sea | h |

Note: M: median; Me: methyl mercury; ± : standard deviation; nd: not detected.

References:

a: Fowler (1985a)
b: Kosta et al. (1978)
c: Zafiropoulos and Grimanis (1977)
d: Vucetic et al. (1974)
e: Windom et al. (1973)
f: Knauer and Martin (1972)
g: Robertson et al. (1972)
h: Kumagai and Nishimura (1978)
i: Martin and Knauer (1973)
j: Robertson et al. (1972)
k: Aboul-Dahab et al. (1986)

Table 11. Mercury concentration in plankton species

| Species | length (cm) | sample n | µg Hg-T/kg DW mean | min | max | location | reference |
|---|---|---|---|---|---|---|---|
| Arcatia clausi | ? | 8 | 190 | 30 | 240 | Elefsis B. (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 |
| Meganychtiphanes norvegica | ? | 1 | 310 | | | Ligurian Sea | d |

a: Zafiropoulous and Grimanis (1977)
b: Fowler et al. (1976b)
c: Fowler (1985a)
d: Belloni et al. (1978)

### 3.4.2 Macrophytes

Very few Hg levels are available on seaweeds. Capone et al. (1986) found concentrations in several zones of a contaminated site to vary from about 10 to 550 µg Hg-T/kg FW in Ulva, Enteromorpha, Cladophora, Graciliaris and in Ruppia (Table 30). In Cladophora, 40% of the Hg-T was MeHg. Salihoglu and Yemenicioglu (1986) determined Hg-T and MeHg in the macro-algae Caulerpa prolifera. They found a mean (n = 17) of 67 µg Hg-T/kg DW (FW/DW circa 10) with a standard deviation of about 17. MeHg made up about 10% of Hg-T.

Posidonia oceanica from Corsica had Hg concentrations ranging from 3 to 30 µg Hg-T/kg FW. Near the Solvay chlor-alkali plant the concentrations in the various parts of the seagrass increase about 10 times (Maserti and Ferrara, 1986).

### 3.4.3 Crustaceans

The Hg levels observed in crustaceans from the Mediterranean (Table 12) are surprisingly high when compared with other crustacean species from the ICES areas (Table 13). In the Mediterranean areas II and IV mean levels of about 1100 µg Hg-T/kg FW have been observed in Nephrops norvegicus (Norway lobster). In the other areas for which data exist, the means are already much lower. The uneven distribution of samples over the Mediterranean, most samples having been taken near the Hg anomaly of the 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, similar to other marine organisms, N. norvegicus also exhibits the typical "Hg concentration-size" relationship (Figure 16). Females have higher Hg levels than males of the same weight. These crustaceans are sampled at depths between 300 and 700 m. Also Capelli et al. (1983) found in the Gulf of Genoa that in N. norvegicus Hg levels increase with length. Interesting, too, are the high Hg levels in benthic crustaceans collected in remote areas from industrial sources. For example, 35 km west of the Isle of Giglio corresponds to about 50 km from the Tuscan coast at about 500 m depth (Table 14). Very similar "Hg concentration-size" relationships to those of N. norvegicus were observed in some of these species (H. dactylopterus and G. melastomus in Figure 16). Penaeus kerathurus from the coastal waters of Alexandria had slightly lower Hg concentrations for females [mean 150 (40-250) µg Hg-T/kg FW] than for males [(mean 175 (30-315)], but since the ranges overlapped the difference is not significant. Organic Hg varied from 55 to 75% of Hg-T (About-Dahab et al. 1986). Neptunus pelagicus from the same area had similar concentrations [mean 165 (70-325) µg Hg-T/kg FW]. Organic Hg ranged from 50 to 70% of Hg-T. Both species had positive Hg-T-size correlations.

Table 12. Average total mercury levels (µg Hg-T/kg FW) in samples (n) of crustaceans. Data from MED POL I pilot project (Nauen et al. 1980a)

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

(!): value above 500 ug Hg-T/kg FW
Sampling areas are shown in Figure 10.

Table 13. Mercury concentrations (µg/kg FW) in crustaceans (whole body) from ICES areas (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) |
| brown shrimp | 80 | ± 20 | Belgian coast | ICES (1984) |
| deep sea shrimp | 25 | <20 - 30 | W. Greenland | ICES (1977a) |

Table 14. Mercury concentrations (µg Hg-T/kg FW) in benthic organisms from remote areas at about 500 m depth (Renzoni and Baldi, 1973)

| sampling area / species | n | body weight (g) mean | body weight (g) range | µg Hg-T/kg FW mean | µg Hg-T/kg FW range | Hg-weight correlation |
|---|---|---|---|---|---|---|
| 35 km west of Isle Giglio | | | | | | |
| Aristeus antennatus | 12 | 5.1 | 2.5 - 7.5 | 750 | 400 - 800 | + |
| Helicolenus dactylop. | 15 | 130 | 20 - 280 | 1100 | 500 - 1800 | + |
| 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 | 980 M | 460 - 1150 | 1100M | 800 - 2100 | |
| Lophius budegassa | 3 | 660 M | 580 - 740 | 930 | 670 - 1000 | |
| NW Isle Asinara (NW Sardinia) | | | | | | |
| Aristeus antennatus | 10 | 27 M | 12 - 80 | 560 | 190 - 1200 | |
| Galeus melastomus | 4 | 300 M | M185 - 450 | 800 | 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

### 3.4.4 Molluscs

Mytilus galloprovincialis, or in the few locations where not available, other mussels of the same genera (Modiolus barbatus, Perna perna), were the "obligatory monitoring species" of the MED POL Monitoring Programme (section 3.4). As can be seen from Table 15 the Hg-T concentration vary widely. This is due to the fact that sessile filter-feeder mussels are exposed to local environmental Hg concentrations which are easily influenced by natural or anthropogenic sources. In fact, the great variation in Hg concentrations within a distance of only 92 meters (Figure 19) shows that the Hg concentration in a sessile organisms can change considerably within very small distances (Leonzio et al. 1981). In using mussels for monitoring of trace elements this must be taken into consideration and a composite sample must be taken from various sites located at some distance from each other to be representative for an area. Even greater variability would probably be observed if the concentration of single mussels and not those of composite sample had been reported. The Hg level determined in a homogeneous composite sample is equal to the mean value of single samples. Therefore, in Table 15 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 (and other trace metals) to the same extent. As can be seen from Table 16, 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 Hg levels, while Mytilus and Ostrea, living in the intralittoral 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 intralittoral 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.

The Hg-T values shown in Table 15 can be compared with the Mytilus edulis Hg determinations carried out in the framework of the ICES monitoring exercises (Table 17). Examining the data in these two tables show that the ranges of Hg 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 µg Hg-T/kg FW and the maximum is 7000 µg Hg-T/kg FW.

Interesting are recent data (Figure 20) on mussels (M. galloprovincialis) and on oysters (Ostrea sp) which show that the methyl mercury (Najdek and Bazulic, 1986) and total mercury (Tusnik and Planinc 1986) in mussels from the Yugoslav coast decreased with increasing dry weight of the specimens. These observations are different from those made in other marine organisms where generally the Hg concentrations increase with weight. Also Hornung and Oren (1980/81) found a negative correlation between Hg-T in the soft parts and shell length in Donax trunculus from Haifa Bay. So far no explanation can be given.

For Sepia officinalis Hg-T concentration increase with size and the concentrations in specimens from the Tyrrhenian Sea are higher than concentrations in specimens from Ostend and Schevingen (Figure 15). Comparable levels of sepias from the Chioggia (Adriatic Sea) are higher than the ones from the Tyrrhenian.

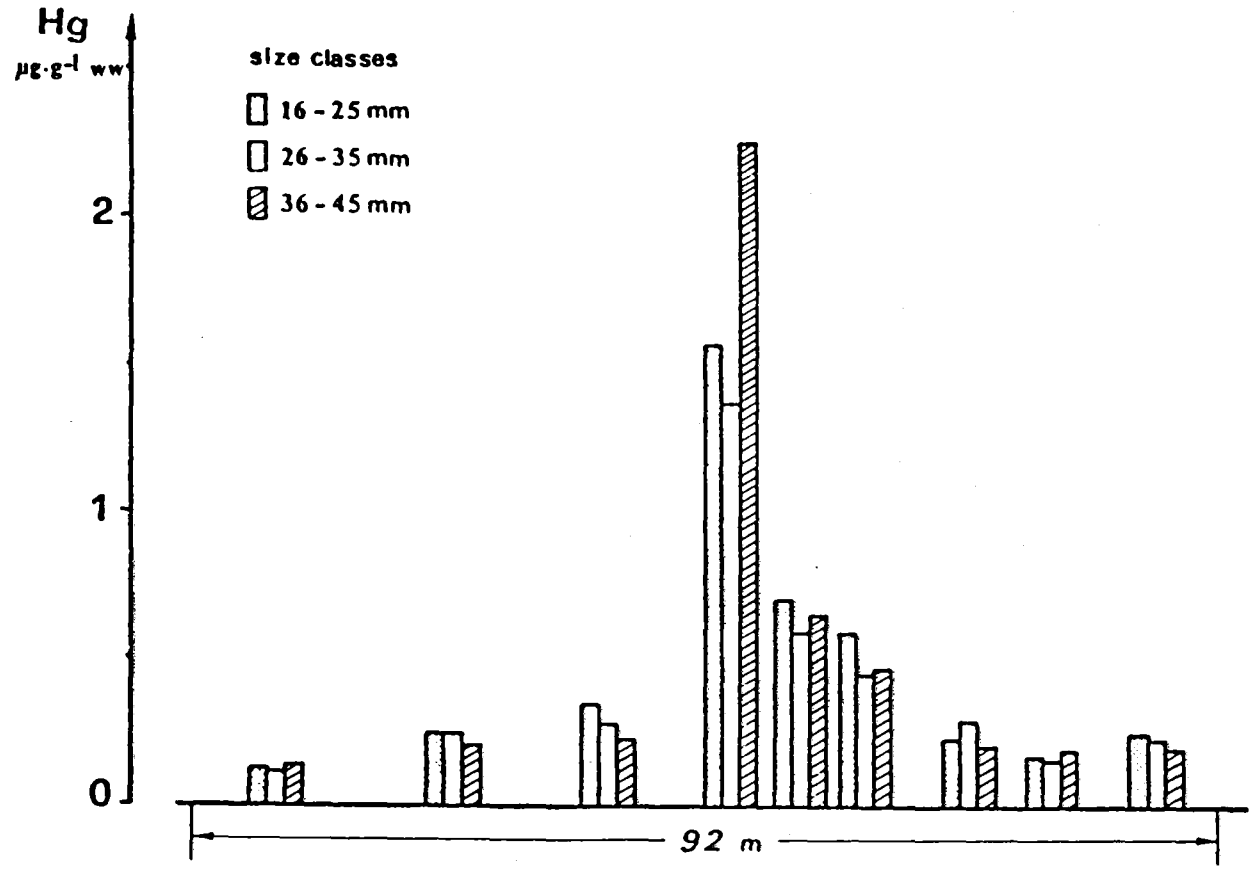



Figure 19. Variation in mercury concentration in Mytilus galloprovincialis specimens collected within a distance of 92 m according to size classes (Leonzio et al. 1981).

Table 15. Overall averages of levels of mercury in composite samples (n) of molluscs. Data from MED POL I pilot project, (data from Nauen et al. 1980a).

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

(!): value above 500 µg Hg-T/kg FW
Sampling areas are shown in Figure 10.

Table 16. Mercury concentrations (µg/kg DW) of the soft part of molluscs from the coastal waters of the western part of the Saronikos Gulf between Megara and Slamis Island. All samples were collected between 0 and 12 m depth. (Papadopoulou and Kanias, 1976)

| species | concentration |
|---|---|
| Mytilus galloprovincialis | 210 |
| Venus verricosa | 22 |
| Glycymeris glycymeris | 15 |
| Ensis ensis | 2350 |
| Meretrix chionae | 73 |
| Ostrea edulis | 320 |
| Tapes decussatus | 290 |

Coefficient of variance 10%

Table 17. Mercury concentrations (µg Hg-T/kg 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) |
| 60 | 40 - 120 | Wales/England | ICES (1984) |
| 130 | ± 30 | Belgian coast | ICES (1984) |
| 170 | 90 - 300 | French coast | ICES (1984) |

M: median

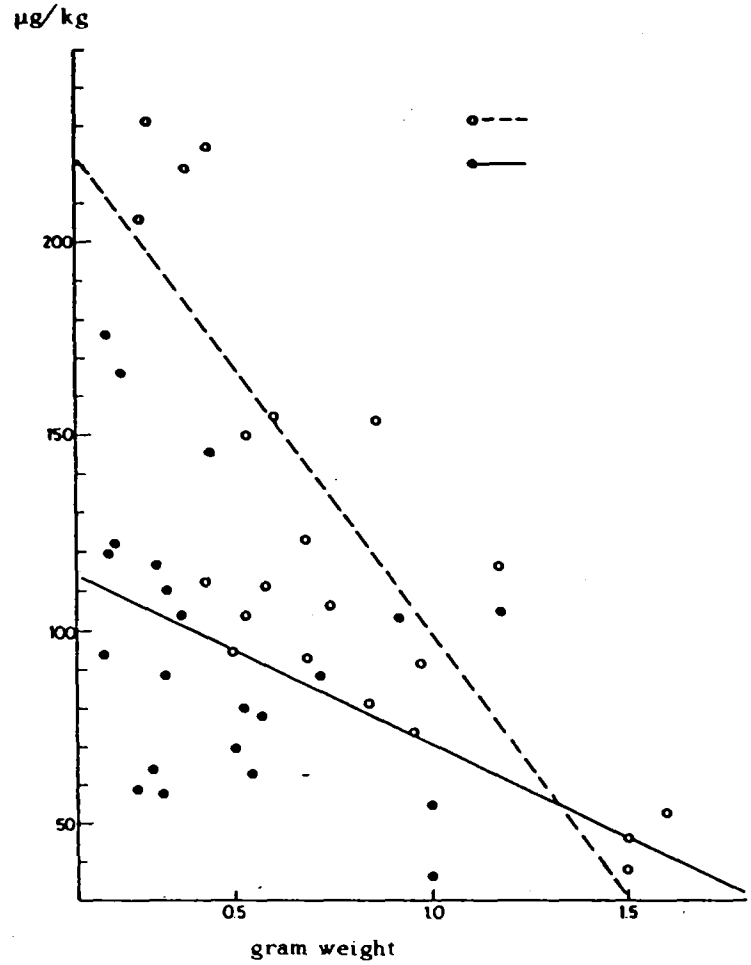



Figure 20. Relationship between methyl mercury and dry weight in oyster (open circle, dashed line) and mussels (full circle, continuous line) (Najdek and Bazulic, 1986).

### 3.4.5 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 (see section 3.4). Since its Hg 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 Phase I project not all participants reported only on M. barbatus of the prescribed size and hence the data shown in Table 18 are not strictly comparable. From these data it appears that the M. barbatus of areas II and IV have higher Hg levels than those of other areas. These results are similar to those already observed for N. norvegicus (Table 12). Data published before MED POL I and summarized by Bernhard and Renzoni (1977) have already shown that M. barbatus can have high Hg levels (Table 19).

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 on both Mediterranean and Atlantic specimens in a collaboration between the Istituto di Biologia Ambientale (Siena), Institut fuer Angewandte Physikalische Chemie (Juelich, RFT) and the Centre for Marine Studies (ENEA, La Spezia) (Baldi et al. 1979b; Renzoni et al. 1979; Stoeppler et al. 1979) and integrated with data on either regions from other authors (Table 20). The three groups intercalibrated with each other and in addition made extensive use of reference materials supplied by NBS and IAEA (Stoeppler et al. 1979). Comparing general data from the North Atlantic with those from the Mediterranean show that in general Mediterranean fishes have higher Hg levels (Tables 18 and 21). In fact, only the means of the Hg levels in plaice from the Atlantic are higher than 500 µg Hg-T/kg FW, while several of the Mediterranean species do exceed this level. Note that Table 21 reports on median and range of means while the other tables give means and ranges of individual values (individual specimens and composite samples)

Table 18. Averages of mercury concentrations (µg Hg-T/kg FW) according to UNEP sampling areas (Nauen et al. 1980a, 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 (!) |
| | T. 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 (!) |
| | 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. gobbosus | 12 | 140 | 100 - 180 |
| | Epinephelus aenus | 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 |
| | T. 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 |
| | T. mediterraneus | 3 | 345 | 340 - 350 |

(!) = levels above 500 ug Hg-T/kg FW
sampling areas are shown in Figure 10.

Table 19. Mercury concentrations (µg Hg-T/kg FW) and length (cm), in Mullus barbatus and M. surmuletus from the Mediterranean. (Bernhard and Renzoni, 1977)

| sample location | n | Hg concentration mean | Hg concentration range | fork length mean | fork length range | reference |
|---|---|---|---|---|---|---|
| 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 |
| Off Pescara | 2n | | 55 - 145 | | 9 - 14 | e |
| 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 | f |
| 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 µg Hg-T/kg FW

References: a: Stoeppler et al. (1979)
b: Ballester et al. (1978)
c: Renzoni and Baldi (1973)
d: Ciusa et al. (1973)
e: Caracciolo et al. (1972)
f: Establier (1978)
g: Roth and Hornung (1977)

Table 20. Mercury concentrations (µg/kg FW) in some pelagic fishes from the Mediterranean and the Atlantic (Bernhard and Renzoni, 1977)

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

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

References: a: Establier (1972)
b: Establier (1973)
c: Ciusa et al. (1973)
d: Riolfatti (1977)
e: Majori et al. (1967)
f: Perna et al. (1972)
g: Caracciolo et al. (1972)
h: Ballester et al. (1978)
i: Gilmartin & Revelante (1975)
k: Roth and Hornung (1977)
l: Paccagnella et al. (1973)

Table 21. Mercury concentrations (µg Hg-T/kg FW) in some fish (muscle). Selected data from ICES areas and Mediterranean.

| | median* | range** | location | references |
|---|---|---|---|---|
| plankton feeder: | | | | |
| herring | 40 | 20-240 | N.Sea | ICES (1974) |
| herring | 20 | 10-35 | N.Atl. | ICES (1977a) |
| herring | 40 | 10-230 | 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) |
| cod | 170 | 130-340 | Wales/England | ICES (1984) |
| "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) |
| plaice | 260 | 50-430 | Wales/England | ICES (1984) |
| plaice | 50 | 30-160 | France | ICES (1984) |
| "typical" | 100 | | | |
| sole | 150 | 50-320 | N.Atlantic | ICES (1977a) |

* median of means

** range of means

There exist now data for several species which allow the comparison of Hg concentrations versus weight of specimens. The clearest evidence comes from the Hg concentrations in bluefin tunas. Figure 11 shows two distinct populations: a "high-mercury" and a "low-mercury" population. The small tunas collected north of Sicily, medium size tunas from the French Mediterranean, the Italian Adriatic and from the Ligurian Sea as well as a part of the large tunas caught in the tuna traps situated in Sicily and Sardinia belonged to the "high-mercury" population. Another group of tunas belong to the "low-mercury" population. Note that these "low-mercury" 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 (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-mercury" tunas and "high-mercury" 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. Confirming thus that only "low-mercury" tunas enter and leave the Mediterranean. Also additional data published in the literature confirmed our 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). Thibaud and Gouygou (1979) have analysed several hundred tunas from the French Mediterranean coast and found that, with two exceptions which belonged to the "low-Hg-population", all belonged to the "high-Hg-population". It may be worthwhile noting that these two tuna populations are well separated from each other and no specimens have "intermediate" Hg levels between the two groups.

Similar, but not so clear cut, differences in Hg levels have been observed in anchovy, mackerel and sardine (Figures 12 to 14). These species are also pelagic. In all three species the specimens from Gibraltar, and for the mackerel also those from the North Sea (from Schevingen and Helgoland), have lower concentrations than the specimens from the Mediterranean. In the Adriatic Sea near Fano lower Hg concentrations have been observed than in the Tyrrhenian Sea. The levels in specimens from Sanremo-Monaco lie between the Fano and the Tyrrhenian Sea samples. Similar differences were observed for the mollusc Sepia officinalis (Figure 15).

As already mentioned above, this review limits the discussion of Hg levels to the lists compiled by FAO(GFCM)/UNEP, because it is impossible to identify single Hg concentrations in scientific publications and separate them from the FAO(GFCM)/UNEP list (Table 18). Therefore, only a few data which have some significance for the general understanding of the biogeochemical cycle of Hg will be discussed below.

Studying the concentrations of total and organic Hg, Capelli et al. (1983, 1986) found that in the fish S. sarda, total Hg correlates significantly with weight and length and that the accumulation of inorganic Hg increase in the S. sarda until the fish reaches a certain length and then remains constant while the MeHg continues to increase with size of the specimens (Figure 17).

Aydogdu et al. (1983) investigated Hg concentrations in the fishes Upeneus moluccensis, Saurida undosquamis and M. barbatus. No difference in Hg content between males and females of the same size were detected. For all three species a significant correlation of Hg level with size was observed (Figure 18). The authors point out that the Hg levels increased more with size in U. meluccensis than in S. undosquamis, although S. undosquamis feeds on U. moluccensis. Certainly the food-chain of S. undisquamis needs checking. According to FAO species identification sheets S. undisquamis "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. undisquamis residues of E. encrasicholus (anchovy), Sardinella aurita and Macrura species (decapods) have been found. U. moluccensis is not mentioned although the areas investigated by Aydogdu et al. (1983) and Zismann are relatively near to each other. A seasonal fluctuation of the Hg levels was observed in U. moluccensis which is brought into association with Hg 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 Hg level in this fish.

### 3.4.6 Marine birds

The data on Hg levels in marine birds are still very few and very unevenly distributed over the Mediterranean area. The Hg levels determined in tissues of sea birds from different sites in the Mediterranean are shown in Tables 22, 23 and 25. Additional Hg levels are shown together with Se levels in Table 35. The birds caught in the highly polluted Lagoon of St. Gilla near Cagliari 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 Hg levels only in the St. Gilla Lagoon but in the Lagoon of Marano the Hg concentrations in the diversified feeder P. nigricollis (black-necked grebe) were higher (see below the influence of food-chain position on Hg levels). The different ages of the birds may be one reason. Also the time of sampling has an influence on the Hg concentrations observed.

Birds collected shortly before their departure (April) from the Lagoon of Marano to their breeding areas in northern and central Europe had higher Hg levels (and chlorinated hydrocarbons levels) in the tissues than birds collected shortly in September and October after their return into the lagoon (Table 23). During the half year of their absence from the lagoon they had lost various percentages of the Hg previously accumulated in the various tissues and then regained approximately the original levels during the next six months of their presence in the lagoon. The data are not strictly comparable because the birds analysed before departure and after return were obviously not the same specimens. This is also illustrated by the fact that the departure levels and the arrival levels are not the same at different departures and arrivals, but the data show, nevertheless, that the biological half-time of Hg in these birds must be relatively short, much shorter than that of fishes.

Renzoni and his collaborators have grouped all their previous data according to the birds' food-chain relationships (Leonzio et al. 1986b). 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 24). The results show that both in eggs and liver, tertiary consumers have higher Hg levels than secondary consumers which in turn have higher levels than primary consumers (Table 25). The lowest levels are observed in the liver of 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 3.6). The Hg anomaly of Mt. Amiata influenced the levels in the birds from Elba, as it does those of fishes (section 3.5). The birds from Marano (Grado) could be influenced by the Idrija Hg anomaly, but, in the other locations also, high Hg levels have been observed. A comparison of the Hg 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 influenced by fluctuations in the Hg intake. Furthermore, it would have had the advantage that data on birds could be compared with the Hg levels in the muscle of other marine organisms. Where data of the same species and tissues are available the specimens from the non-Mediterranean site had much lower concentrations than the Mediterranean specimens (Figure 22).

Table 22. Mercury concentrations (ug Hg-T/kg 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 23. Mercury concentrations (mean and standard deviation in mg Hg-T/Kg DW) in migratory birds collected in the Lagoon of Marano (North-East Italy) before departure to and after arrival from Northern and Central Europe (Leonzio et al. 1986a)

| | Departures | | | Arrivals | | |
|---|---|---|---|---|---|---|
| Muscle | April 83 | 11.85 ± | 3.85 | Sept 83 | 3.7 ± | 1.55 |
| | April 84 | 6.0 ± | 1.7 | Oct 84 | 4.2 ± | 1.3 |
| | April 85 | 10.75 ± | 3.5 | | | |
| Brain | April 83 | 14.90 ± | 3.7 | Sept 83 | 3.6 ± | 2.45 |
| | April 84 | 14.75 ± | 3.9 | Oct 84 | 3.7 ± | 1.4 |
| | April 85 | 13.45 ± | 3.2 | | | |
| Liver | April 83 | 57.9 ± | 9.95 | Sept 83 | 9.35 ± | 2.25 |
| | April 84 | 48.5 ± | 9.05 | Oct 84 | 16.55 ± | 7.7 |
| | April 85 | 42.4 ± | 5.75 | | | |
| Kidney | April 83 | 35.05 ± | 7.0 | Sept 83 | 7.65 ± | 1.55 |
| | April 84 | 14.8 ± | 4.55 | Oct 84 | 10.75 ± | 5.35 |
| | April 85 | 28.5 ± | 2.95 | | | |
| Fat | April 83 | 1.15 ± | 0.25 | Sept 83 | 0.55 ± | 0.2 |
| | April 84 | 1.5 ± | 0.75 | Oct 84 | 0.85 ± | 0.35 |
| | April 85 | 0.8 ± | 0.45 | | | |
| Uropygial gland | April 83 | 10.25 ± | 3.5 | Sept 83 | 3.75 ± | 2.3 |
| | April 84 | 9.85 ± | 3.1 | Oct 84 | 4.15 ± | 0.7 |
| | April 85 | 10.0 ± | 1.6 | | | |

Table 24. 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 25. Mercury concentrations (ug Hg-T/kg FW) in eggs and liver of marine birds from the Atlantic and the Mediterranean (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 35. The sample locations are shown in Figure 21.

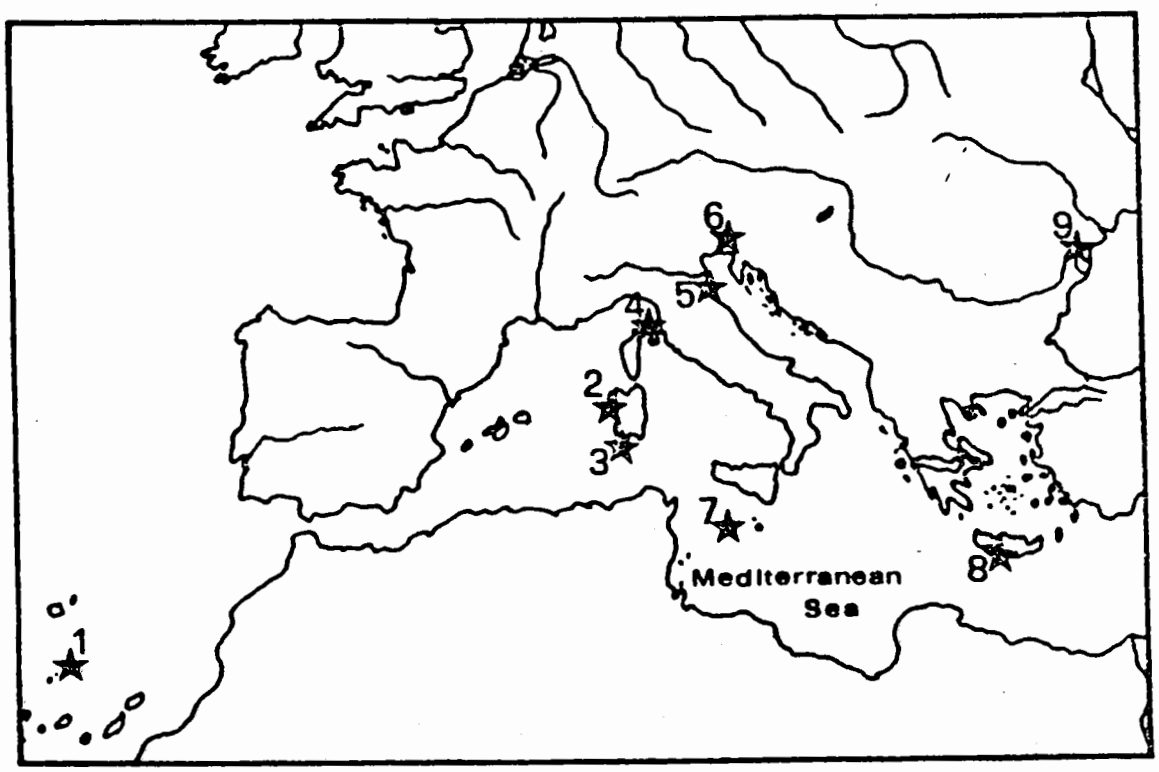



Figure 21. Sampling locations of marine birds collected by Renzoni's group. (Leonzio et al. 1986).

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

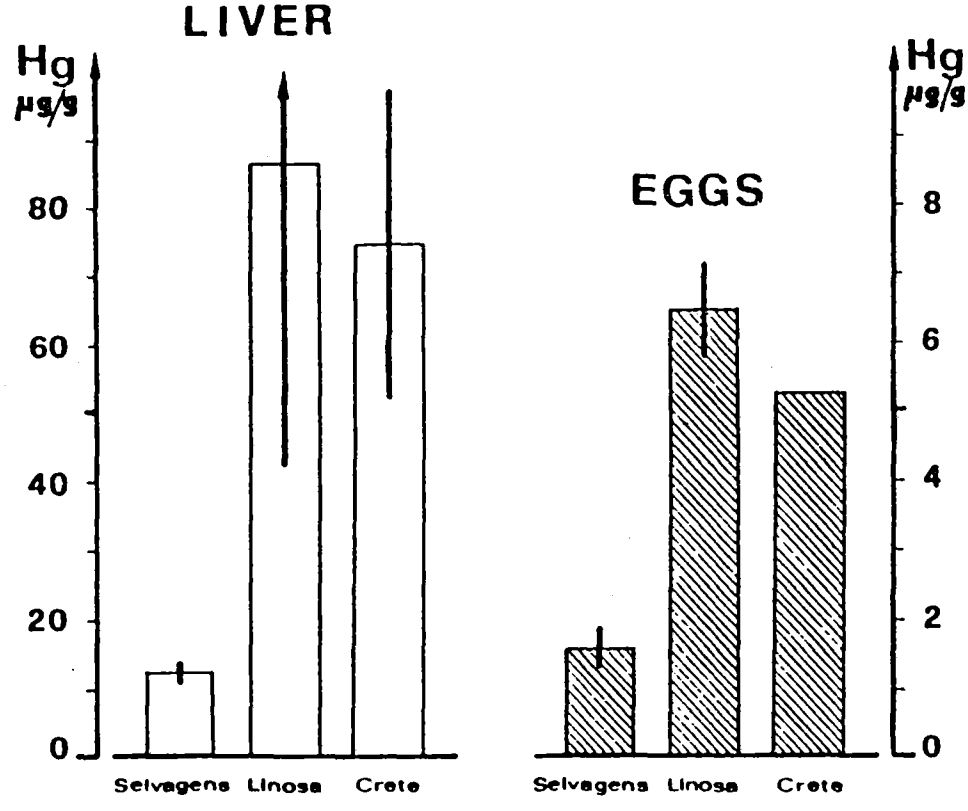



Figure 22. Mercury concentrations in liver and eggs of C. diomedia from Madeira (Selvagens), the Isle of Linosa (Sicilian Channel) and Crete. (Leonzio et al. 1986). For locations see Figure 21

3.4.7 Marine mammals

Remarkably high Hg concentrations were observed in dolphins, porpoises and whales from the Mediterranean and the Atlantic (Table 26). The concentrations in the liver are especially impressive (maximum value: circa 1 g Hg/kg FW). Here also smaller animals of the same species have lower concentrations. The Hg concentrations in muscle tissue are higher than in fats. 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, as in many other oganisms, the Hg concentrations in Mediterranean specimens are higher than in the specimens from the Atlantic. In the liver of marine mammals with high mercury concentrations low MeHg percentages are found. This may indicate a demethylation in the liver.

Table 26. Mercury concentrations (ug Hg-T/kg FW) in pelagic mammals from the Mediterranean and Atlantic (Bernhard and Renzoni, 1977)

| Species | sex | age | size cm | muscle | | fat | | liver | | sample location and date |
|---|---|---|---|---|---|---|---|---|---|---|
| Atlantic: | | | | | | | | | | |
| Phocaena phocaena | M | adult | 172 | 6750 | | 770 | | 61000 | | Rochelle (V/1972) |
| Delphinus delphis | F | young | 125 | 890 | | 710 | | 900 | | Ile de Re (VII/1972) |
| 1) | F | adult | 140 | 600 | (100) | 20 | (100) | 980 | (70) | Pyrenees Atl.(VII/1973) |
| | F | adult | 165 | 910 | | 27 | | 1430 | | Pyrenees Atl. (IV/1973) |
| 2) | M | adult | 185 | 1840 | ( 77) | 220 | (100) | 20000 | ( 7) | Landes (VII/1973) |
| | F | adult | 210 | 6250 | | 2650 | | 4850 | | Gironde (V/1972) |
| | M | >15 y | 220 | 2180 | | 2780 | | 66700 | | Tropic Atl. 1975 |
| 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) |
| 3) | M | adult | 210 | 23800 | ( 13) | 6000 | ( 30) | 344000 | ( 2) | Lavandou (Var)(IV/1973) |
| Grampus griseus 4) | F | adult | 300 | 16000 | ( 21) | 1700 | ( 70) | 905000 | (1.5) | Cacalastre (Var) (VII/1973) |
| 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 5) | M | adult | 490 | 5300 | ( 29) | 860 | ( 38) | 860 | ( 1) | 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) |

Note: Data in brackets give the percentage of MeHg
Additional data for specimens marked with numbers:

1) brain: 400 µg Hg-T/kg FW (100% MeHg), kidney: 980 µg Hg-T/kg FW (70% MeHg)
2) brain: 890 µg Hg-T/kg FW (77% MeHg), kidney: 4300 µg Hg-T/kg FW (23% HeHg), testicles: 1000 µg Hg-T/kg FW
3) testicles: 15600 µg Hg-T/kg FW (19% He Hg), spleen: 530000 ug Hg-T/kg FW (1.5% MeHg), kidney: 39200 µg Hg-T/kg FW (<2.5% MeHg)
4) spleen: 905000 µg Hg-T/Kg FW (2.2% MeHg), kidney: 6000 µg Hg-T/kg FW (63% MeHg),
5) blood: 3000 µg Hg-T/kg FW (73%)
*) 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)]

### 3.5 Influences of natural mercury sources on environmental levels

Higher than background levels were observed in various components of the marine environment near the well-known Hg 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 Hg levels (Figure 23). The water of these rivers had high Hg concentrations only near the mining area:

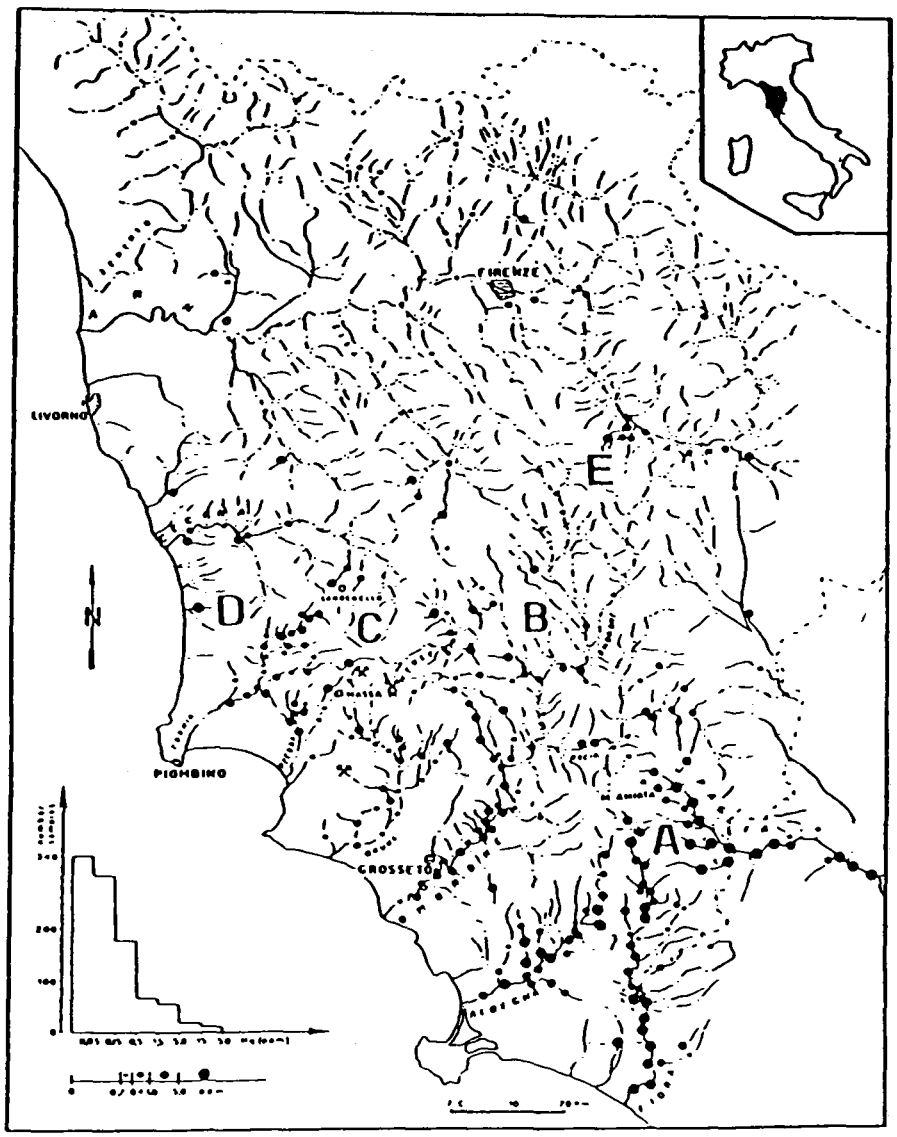



Figure 23. Distribution of mercury in river sediments around the mercuryanomaly of Mt. Amiata (Tuscany) (Dall'Aglio, 1974).

for example in the water of the upper part of Paglia river which flows into the Tiber. Downstream from the mining area the Hg concentration in the river water diminished rapidly, because the dissolved Hg is readily absorbed by sediment and suspended matter. Near the coastline the Hg concentrations in the river water fell below 0.05 µg Hg/L, the detection limit of Dall'Aglio's method. Contrary to the river water concentrations, the Hg concentrations in the river sediments remain high right down to the coast: often over 5 mg Hg/kg DW of sediment. All rivers south of Livorno and north of Civitavecchia showed similar high Hg concentrations in their sediments. Much less Hg is contained in the sediments of the rivers Arno and its tributary Serchio. The high Hg levels observed in the upper part of the Serchio river are caused by Hg contaminations from the felt and leather industry situated there. The Hg concentrations along the Tuscan and Ligurian coast have been investigated by Baldi and Bargagli (1982, 1984). Figures 24 and 25 show clearly the input of Hg-rich sediments into the coastal zone and their subsequent mixing with marine sediments low in Hg. The plumes of the rivers draining the cinnabar deposits 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. In part, 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 may be due to industrial activities around Rome (Melchiorri et al. 1983). The Hg concentrations in the sediments of the river mouths along the Ligurian-Tuscan coast have been confirmed by Breder et al. (1981).

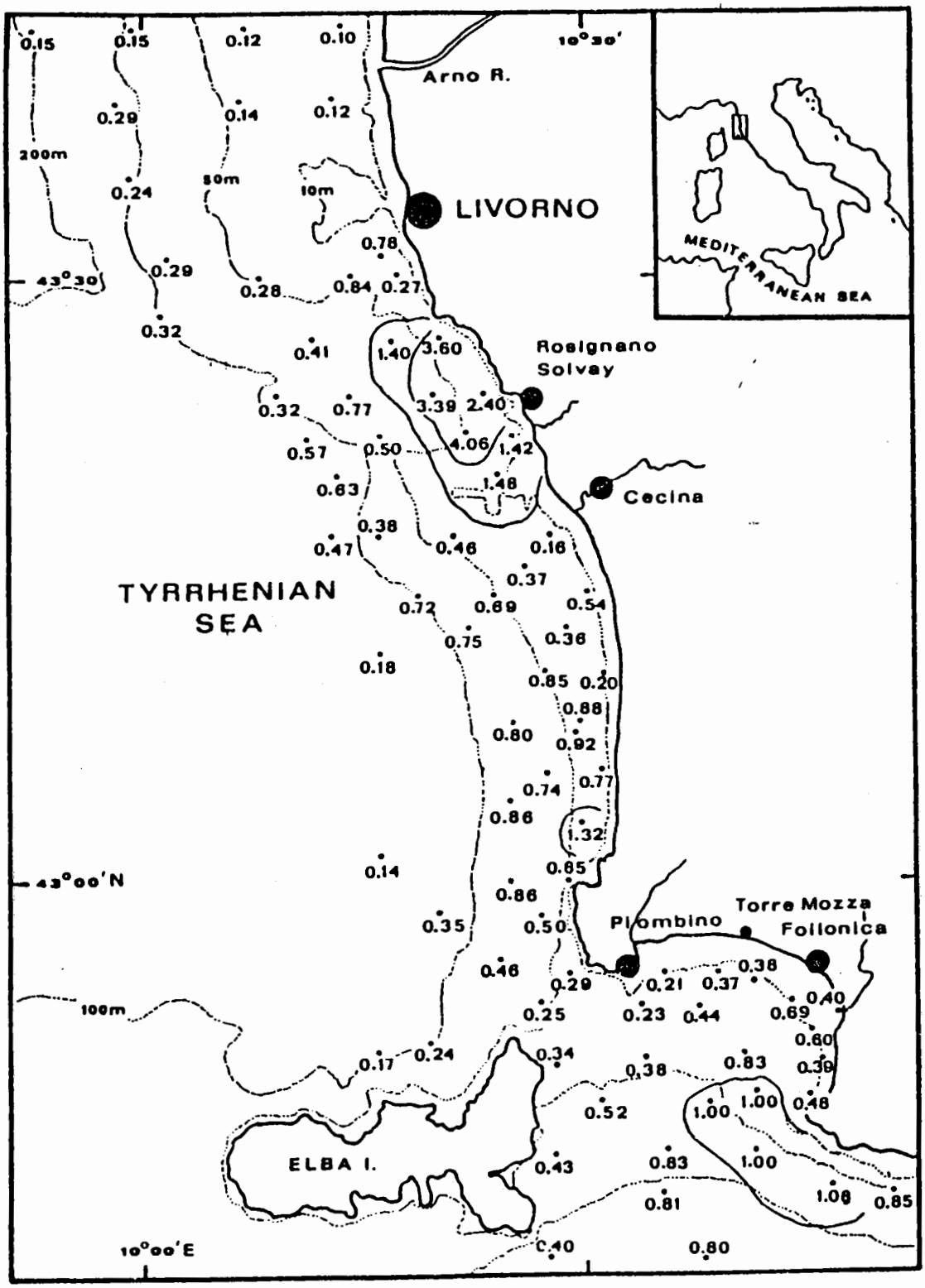



Figure 24. Distribution of mercury (mg Hg-T/kg DW) in surficial sediments from the western Italian coastline from the Arno to Follonica. (Baldi and Bargagli, 1984).

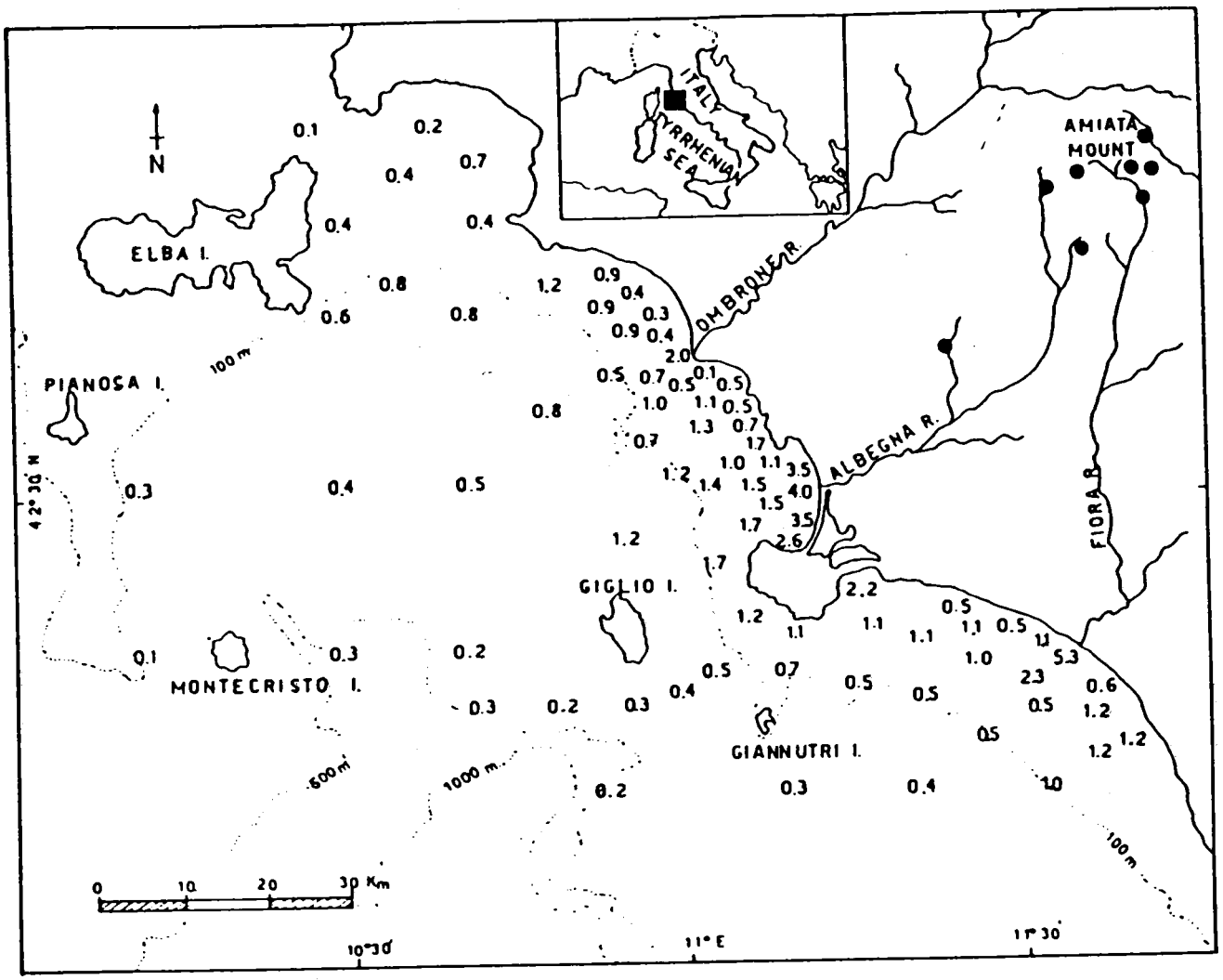



Figure 25. Distribution of mercury (mg Hg-T/kg DW) in surficial sediments from the western Italian coastline from Elba to the river Fiora. (Baldi and Bargagli, 1982).
Note: the locations of the cinnabar mines (●).

The vertical Hg distribution within the sediments from the Mt. Amiato area and the Gulf of Naples in two cores shows higher Hg concentrations in the upper 10 cm of the cores than below (Figure 8).

Different extracting methods yielded different Hg concentrations, but did not change the horizontal Hg distribution pattern significantly (Baldi and Bargagli, 1982). Interestingly, the Hg is more leachable (applying acid extraction) in the river mouths, and 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 (Figure 26). In fact, near the shoreline the sediments, which are not influenced by the river plumes, contained only up to about 4% of leachable Hg. At depths greater than 40 metres the leachability increased greatly to reach 30 to 70%.

The influence of elevated Hg sediment levels and the bioavailability of Hg present in these sediments have been investigated surveying the concentration of Hg in M. barbatus. M. barbatus feeds mostly on small bottom-living invertebrates (worms and crabs). While doing so, it burrows through the sediment ingesting part of the sediment on its way. Often its stomach and intestine are found containing mud and sand. Comparing the Hg concentrations versus size distribution in the fillet of M. barbatus caught along the Tuscan coastline showed that the Hg concentrations increases greater 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 (Figure 27A). At the same time the authors observed that in a transect from the mouth of the Arno river to the Gorgona Island the Hg concentrations in specimens of the same size increased with depth (Figure 27B). Apparently two parameters are causing the Hg enrichment in the fish: one is the distance from the coast and the other the distance from the Hg anomaly. The higher Hg levels in the fish with distance from the coast could result from the greater availability (leachability) of Hg in sediments from greater depths (see above). Also the relatively low Hg concentrations in the fish near the Talamone river may be due to scarce availability (leachability) of Hg 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 had a different Hg distribution pattern. S. porcus 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). The Hg 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 (Figure 28). Probably the different food-chains of M. barbatus and S. porcus may supply an explanation.

Much higher than background levels have been observed near another Hg anomaly. The Idrija anomaly drains through the Isonzo (Soca) River into the Gulf of Trieste (Figures 29 and 30). In the river sediments concentrations as high as 76.5 mg Hg-T/kg 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 DW were observed, the Hg concentrations in the sediments decreased rapidly towards the city of Trieste (2 mg Hg-T/kg DW) and the open Adriatic Sea. In the inner port of Trieste the Hg levels were slightly above background. Higher sea water concentrations were also observed in the mouth of the river (0.16 to 0.2 µg Hg/L) than in the open Adriatic (0.01 to 0.21 µg Hg/L). However, in the light of recent ideas on true sea water concentrations these values must be considered with caution (see section 3.2).

In the Gulf of Trieste the anticlockwise current carries the Hg discharged from the Isonzo River towards the Italian coast. Mussels on the Yugoslav coast have significantly lower Hg levels than mussels from the Italian coast (Figures 29 and 30). However, the influence is limited to about 100 km west of the river mouth of the Isonzo. Mussels from the lido of Venice have background levels again. Majori et al. (1967) verified this observation with an in situ experiment (Figure 31). Mytilus grown in the low level area of Lazzaretto were transplanted to the higher level area, Bocca di Primero. After the transplantation Hg 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 slower Hg decrease (loss and "biological dilution") over a

period of five to six months. The difference in the chemical species of Hg 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 Hg anomalies (Figures 10 and 46).

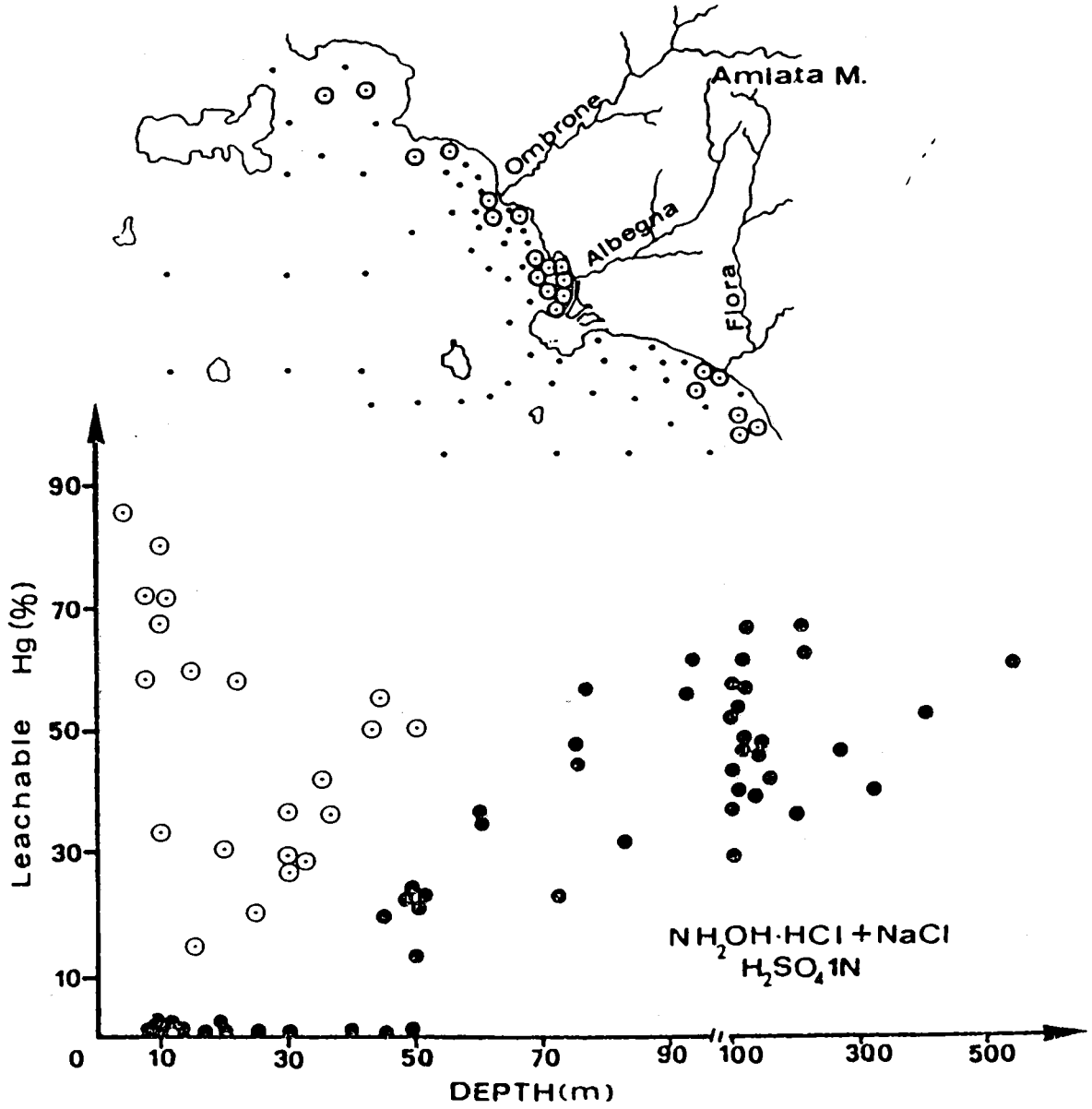



Figure 26. Percentage of acid-leachable (weakly bound) mercury in sediments affected by the Hg anomaly of the Mt. Amiata region (Baldi, 1986). The leaching solution used was $NH_2OH.HCl+NaCl$ in 1 $NH_2SO_4$.

Note: circles with a dot mark sediments which have been collected in Posidonia beds and had an unusually high content of organic matter.

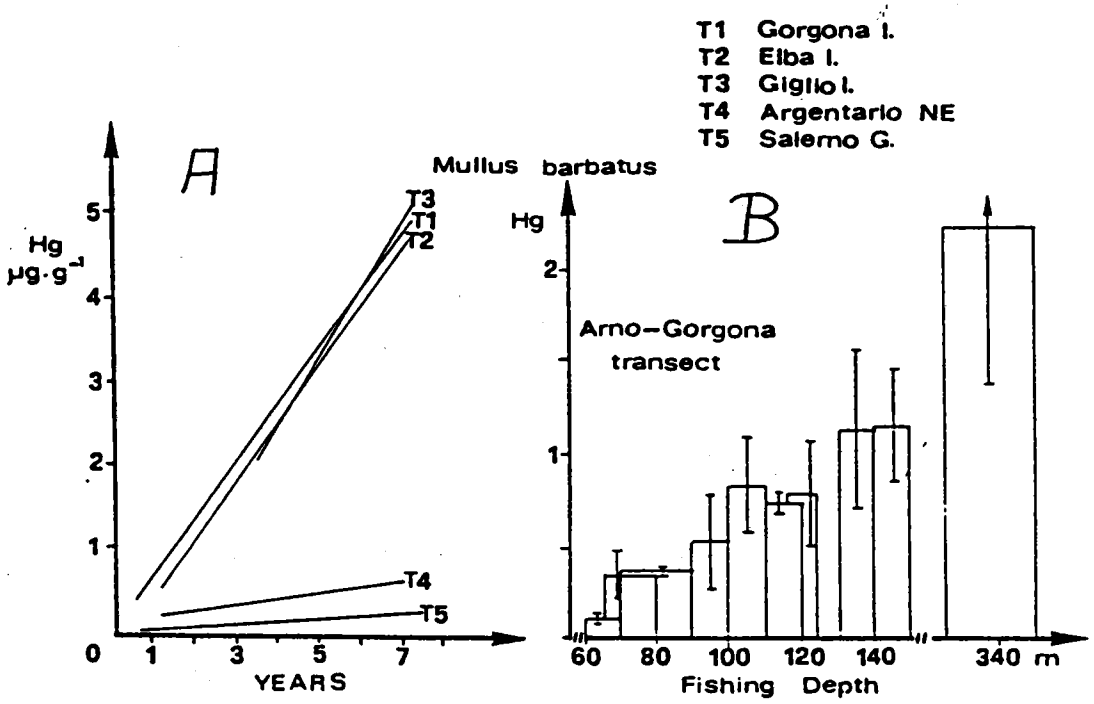



Figure 27. (A): Mercury concentrations versus age (years) correlations in Mullus barbatus from different locations of the western Italian coast and (B): mercury concentrations in specimens of the same size versus fishing depth along a transect offshore of the river Arno (B). (Baldi, 1986).
Locations: T1: offshore Arno river mouth; T2: north of Elba; T3: west of Isle Giglio; T4: offshore Albenga River mouth; T5: Gulf of Salerno.

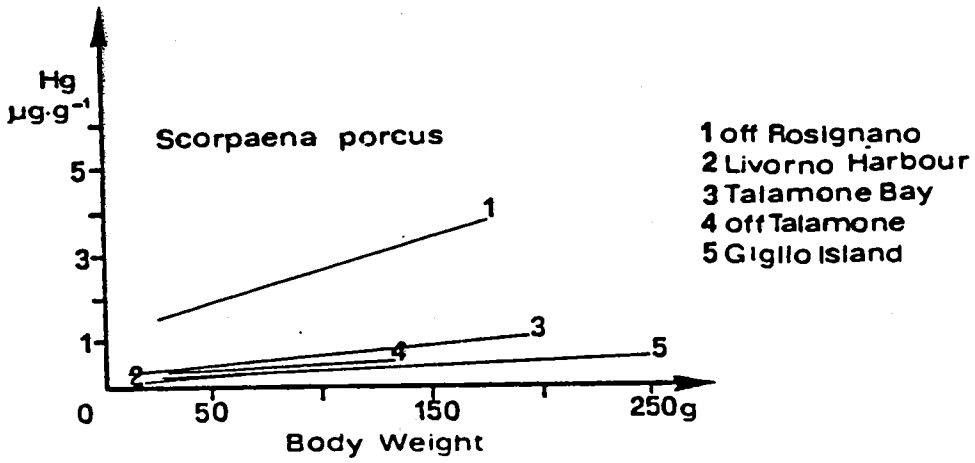



Figure 28. Mercury concentrations (mg Hg-T/kg FW) in Scorpaena porcus from the western Italian coast (Baldi, 1986) versus body weight (g).

Note: curve 1 corresponds to curve 1973 in Figure 33.

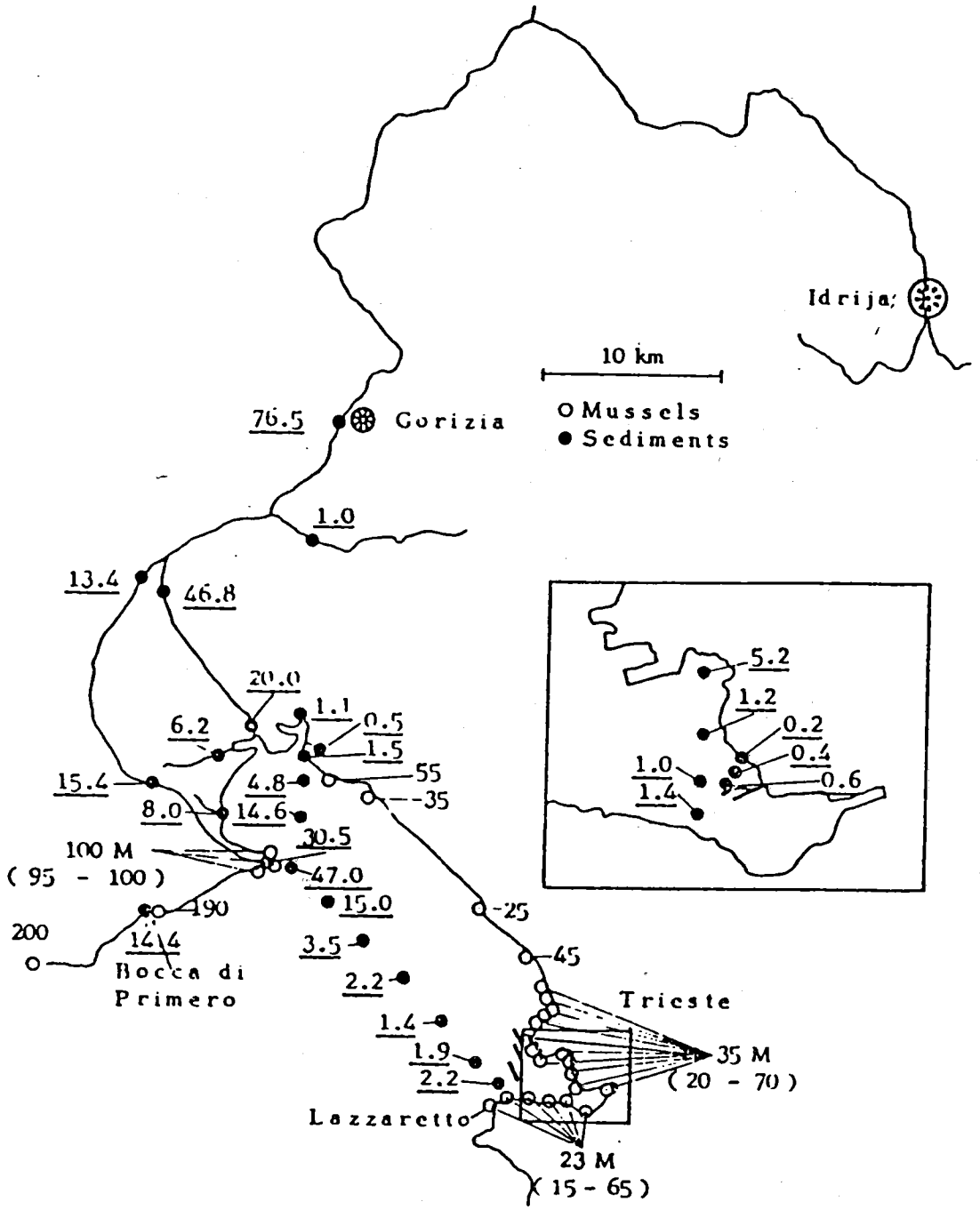



Figure 29. Mercury concentrations (µg Hg-T/kg DW) in sediments of the river Isonzo (Soca) and in marine sediments (underlined values) and in Mytilus (µg Hg-T/kg FW) from the Gulf of Trieste (Majori et al. 1967, modified).

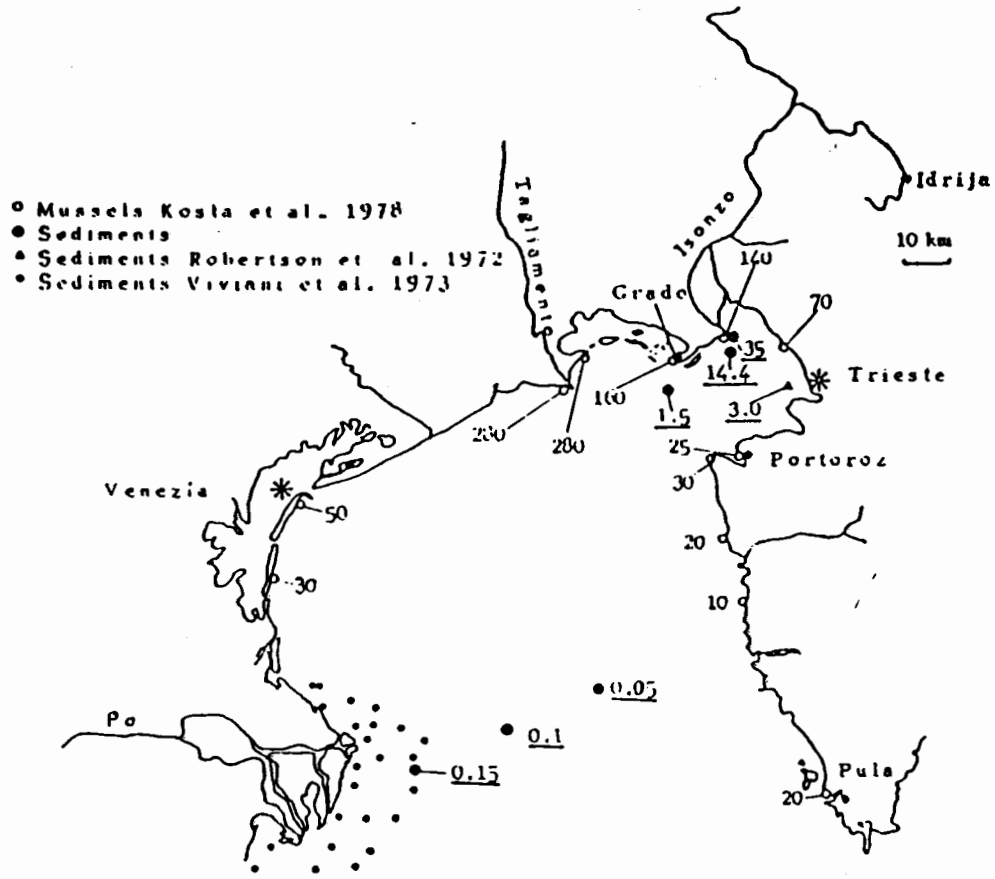



Figure 30. Mercury concentrations (µg Hg-T/kg DW) in sediments of the River Isonzo (Soca and in marine sediments (underlined values) and in Mytilus (µg Hg-T/kg FW) from the Gulf of Trieste. Sediment levels in the Po Delta: 0.4 (0.07 to 0.97) mg Hg-T/kg DW. Data from Kosta et al. 1978; Robertson et al. 1972; Viviani et al. 1973).

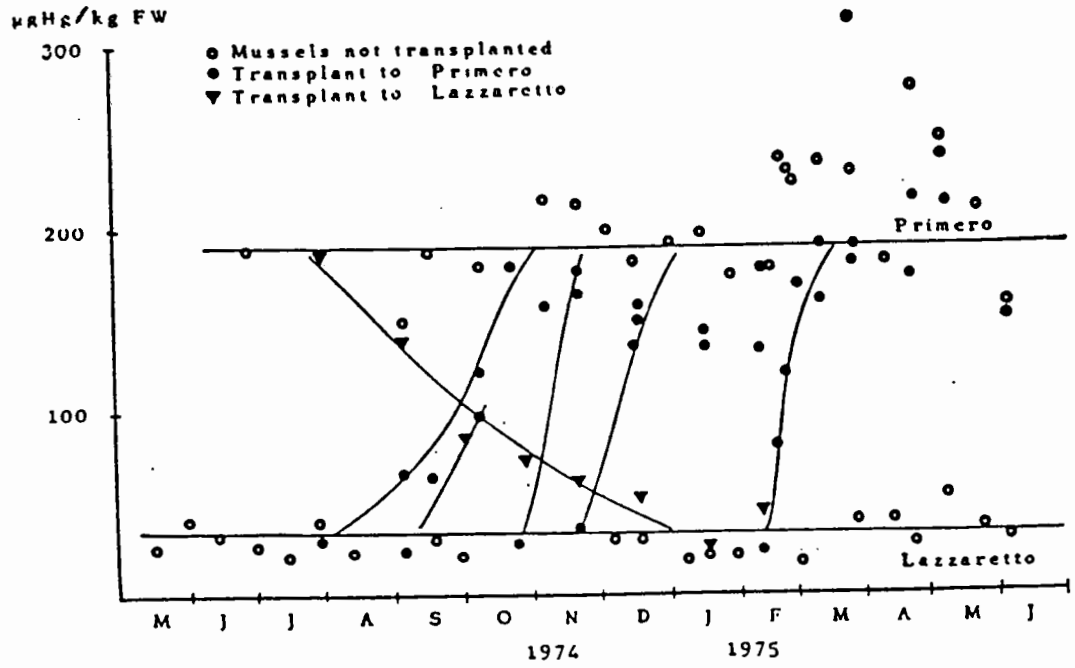



Figure 31. Accumulation and loss of mercury versus time by Mytilus transplanted from a high-Hg-environment (Primero) to a low-Hg-environment (Lassaretto) and vice-versa in the Gulf of Trieste (Majori et al. 1967, modified).

### 3.6 Influences of anthropogenic mercury sources on environmental

Anthropogenic releases have been investigated in several areas of the Mediterranean. Beginning in 1973 Renzoni and collaborators studied the influence of the Hg releases from the outfall of the Solvay chlor-alkali plant situated about 20 km south of Livorno near Rosignano (see Figure 24 for location). They investigated the Hg levels in sea water, sediment and biota and in humans consuming seafoods 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 Hg in wastes together with about $10^5$ MT/y of white solids, mainly carbonates. This means that in the first 30 years of the plant's activity several hundred MT of Hg 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 instead of releasing about 15 MT/y the release was reduced to first 300 to 400 kg Hg/y in the years 1975/1976 and later to the present levels of about 3 kg Hg/y (Bacci et al. 1986).

Figure 32 summarizes the results obtained in 1973, i.e. before the effluent treatment. The highest concentrations for sea water, sediments, limpids (Patella) and crabs (Pachygrapsus) were observed 2.5 km south of the outfall (station R 4). The Hg concentrations in the water and crab of stations R 4 were much lower in the next stations but those in the sand and limpids were only slightly lower. At about 10 km north and south (stations R 1 and R 6) of the outfall of the Solvay plant the sediment (sand) and the limpids contained only slightly higher concentrations than the background levels (stations R 7 to R 10) sea water and Pachygrapsus had there still higher than background levels. In April-May 1975 and May-June 1976 (i.e. 15 to 16 months and 28 to 29 months after the beginning of the effluent treatment, respectively) the body levels in the limpet, in the crab and in two fish species were again examined. As can be seen from Table 27 the Hg concentration in the crab decreased more (80%) than in the other marine organisms (20 to 30%). Also the Hg concentration-size relationship in the fish S. porcus illustrates clearly the reduced level in the environment of the Solvey plant after effluent treatment (Figure 33 and the curves 1 for 1973 in Figure 28). Note the different inclination of the regression curve of 1973 from the inclination of 1975 and 1976. This shows that specimens collected in 1975 and 1976 had lower Hg concentrations than specimens of the same size collected in 1973.

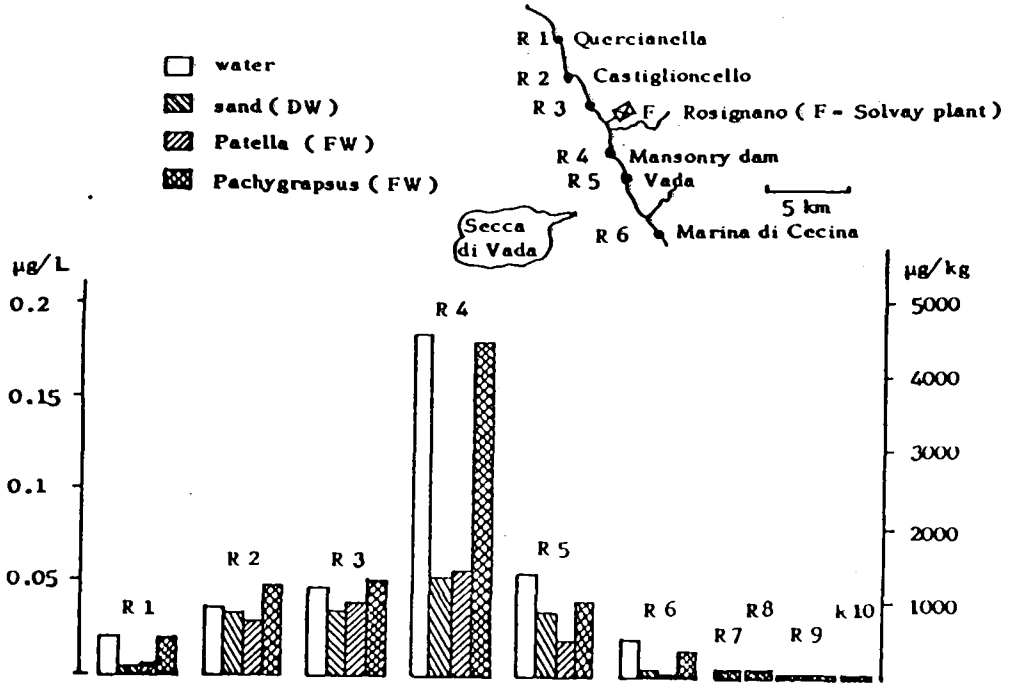



Figure 32. Mercury concentrations in sea water, sediments, Patella sp. and Pachygrapsus from the outfall area of the Solvay chlor-alkali plant in 1973 before the installation of a mercury waste treatment and in Patella and Pachygrapsus from several other Mediterranean sites as controls (R 7: Fiumicino, R 8: Montecarlo, R 9: S. Stefano, R 10: Talamone) (Bernhard and Renzoni, 1977).

Table 27. Mercury concentration (µg Hg-T/kg 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 |

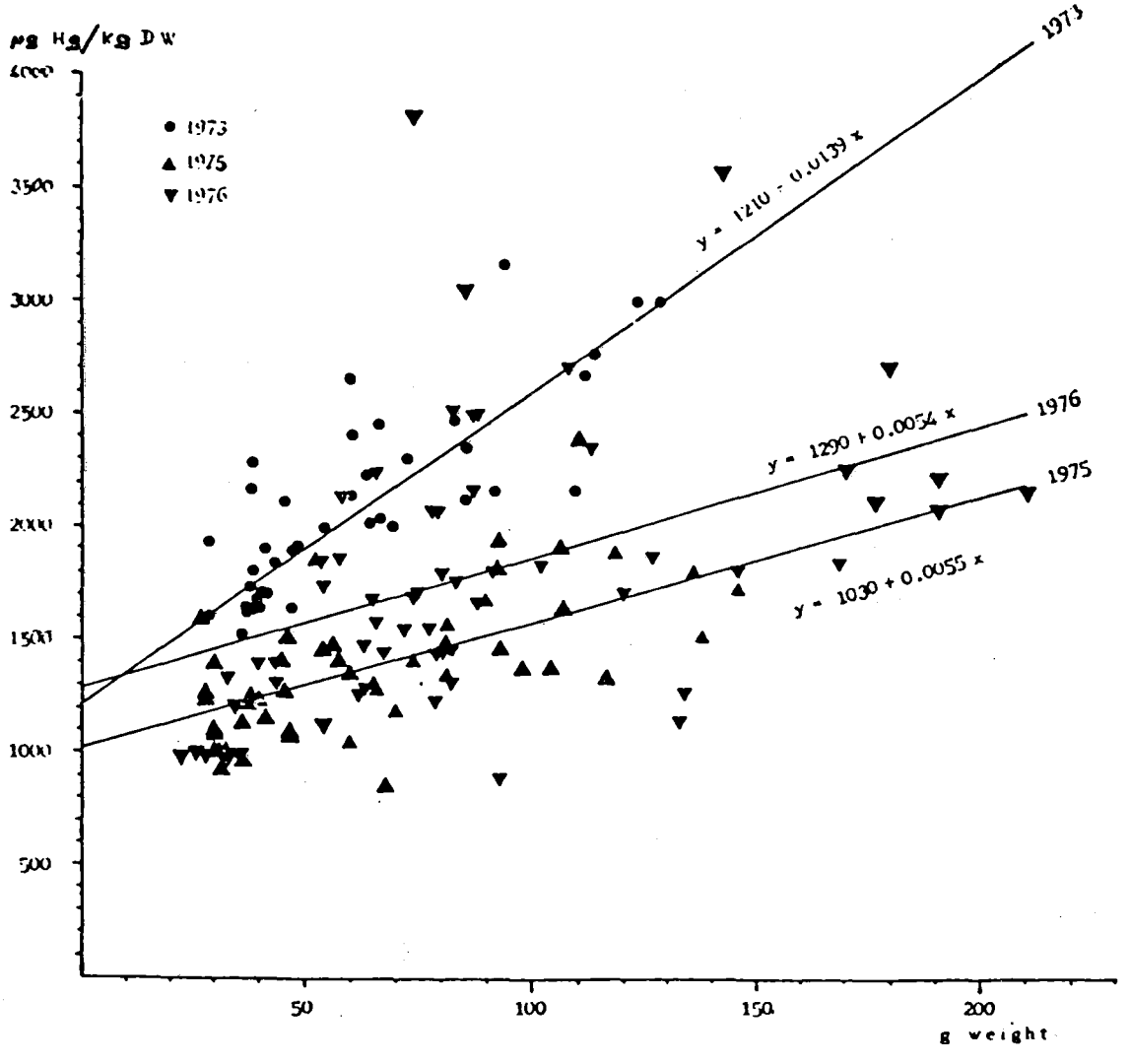



Figure 33. Mercury concentration versus weight in Scorpaena porcus from the banks of Vada before (1973) and after (1975 and 1976) waste treatment began in the Solvay chlor-alkali plant (Renzoni, 1977).

A recent survey (1981-82) of the area still showed high Hg levels in sediments around the Solvay plant (Figure 24). 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 $CaCO_3$ and Hg-T (Figure 34). The depth profiles show interesting vertical distributions of both parameters (for comparison see Figure 8). Taking into consideration the operational data of the Solvay plant and assuming a constant sedimentation rate, the authors explain the changes in vertical distribution of Hg and $CaCO_3$ with different intensities of the industrial activity in the Solvay plant. The lower part of the profile shows background levels both of $CaCO_3$ and Hg. A first increase in the $CaCO_3$ content of the sediment core is associated with the beginning of the ammonia production of the plant in 1914. The first Hg 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 large amounts of Hg-containing wastes. The waste treatment started in 1974 which is reflected in the reduced Hg concentrations in the sediments. If one compares the reduction of the Hg released, first by a factor of about 40 and then later by 5000 (see above), with the reduction of Hg concentration in the upper part of the sediment core, one sees that the sediment in the upper layer still contains relatively high amounts of Hg. In fact, the most recent determinations show a reduction by a factor of 2.5 from the peak concentration in the early seventies. This small reduction may be explained by a redistribution with the older sediment layers. It is interesting to note that the $CaCO_3$ concentration remained about constant in the upper layer of the sediment core. Using the Hg 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 28; Figure 35). The high "recovery time" derived from the two fish is explained by the authors by assuming that the fish contain higher amounts of MeHg than the invertebrates. The biological half-time of inorganic Hg is about 30 days while the biological half-time of MeHg is in the order of years (see section 4.3).

Four similar cases are under study in Sardinia, Yugoslavia, Israel and Egypt. Several authors investigated the Hg contamination of the lagoon of S. Gilla (Cagliari). The S. Gilla Lagoon receives industrial wastes from a chlor-alkali and petrochemical plants ("Pet" in Figure 36), 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 particulate and in flakes of inorganic sulphide from the chlor-alkali plant. Sarritzu (1983) found in all sediment samples from the lagoon Hg levels above 1 mg Hg-T/kg DW and near the outfall of the petrochemical plant an enormously high 300 mg Hg-T/kg DW. The Hg concentration was still at 5 mg Hg-T/kg DW at 1 km distance from the outfall showing that quite a large area has been highly contaminated with mercury. Cottiglia and collaborators (Cottiglia et al. 1985, 1986; Capone et al. 1986; Porcu and Masala, 1983) investigated the Hg levels in sediments of the lagoon and in the Gulf of Cagliari and the Hg concentrations in various marine organisms, including birds (see section 3.4.6). The authors 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) (Figure 36). Contu et al. (1985) have investigated the remobilization of Hg in these sediments using different extraction procedures. As can be seen from Table 29 only very strong extraction methods can liberate more than 1 to 5% of the Hg present in the sediments. Of interest is the great difference between samples taken during the two sample collections in January and April 1981. Despite the fact that only a few Hg percentages can be mobilized, on examining the data of Table 30 one is surprised to see how little the high Hg levels in the sediments of the different zones influence the concentrations in the various biota. The levels in the biota collected in area (R) are higher than in the other areas, but certainly not as high as one would expect from the sediment levels. Bioavailability is without doubt a major factor as already suggested for the data observed in the Gulf of Trieste (section 3.5). The greatest effect of the Hg pollution is seen in the birds. In Table 25 their body levels are compared with that of birds from other areas. The influence of sediment concentrations and levels in marine organisms was also studied in four experimental tanks filled with sediments containing different amounts of Hg: one with sediments and biota from an uncontaminated lagoon (S. Giusta) and three with sediments from the S. Gilla Lagoon containing different Hg concentrations. The results obtained after 18 months clearly showed the influence of the Hg 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 (Figure 37).

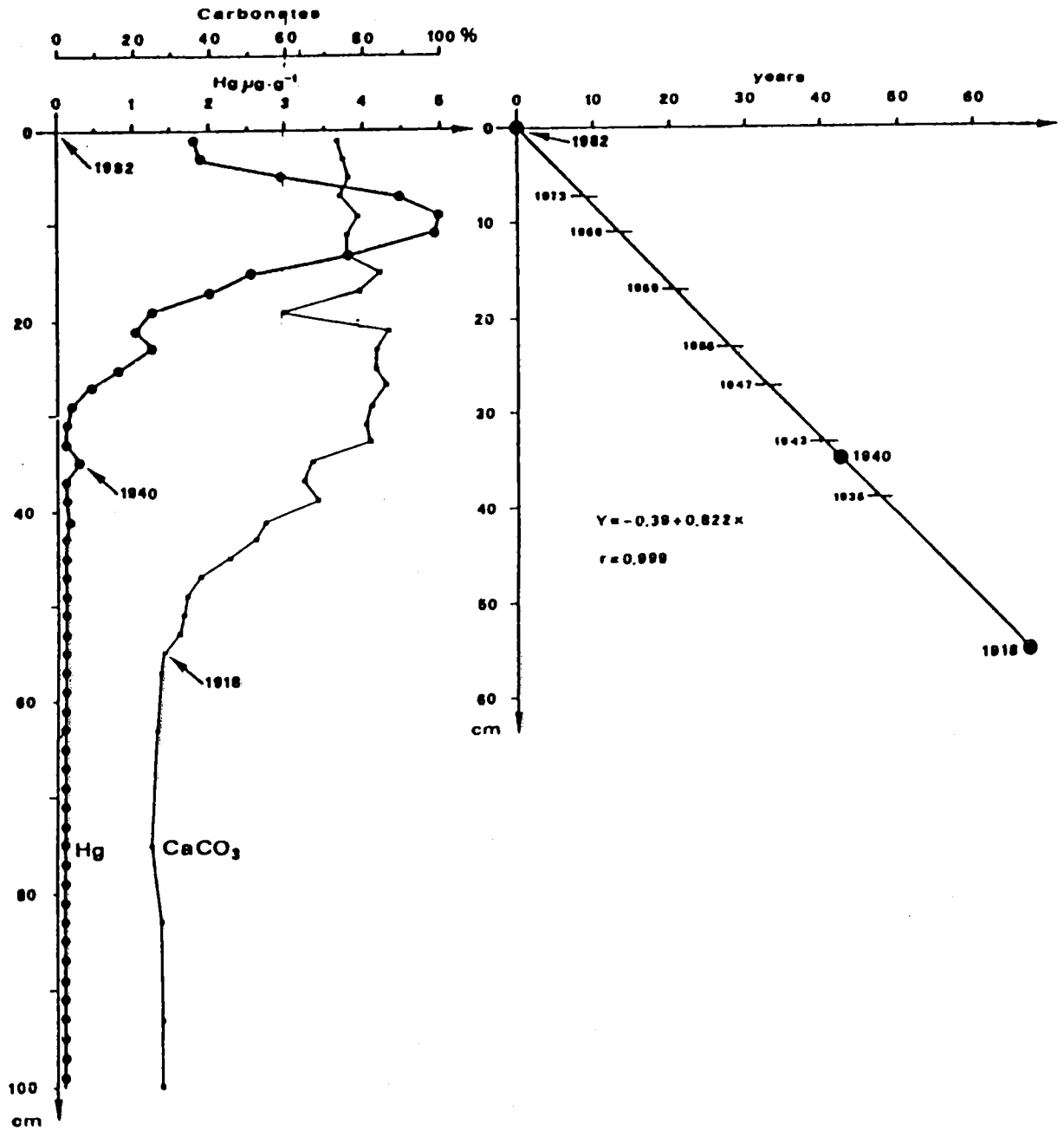



Figure 34. Profiles of mercury and carbonate concentrations in a sediment core taken near the Solvay chlor-alkali and estimation of the sedimentation rate. (Bacci et al. 1986).

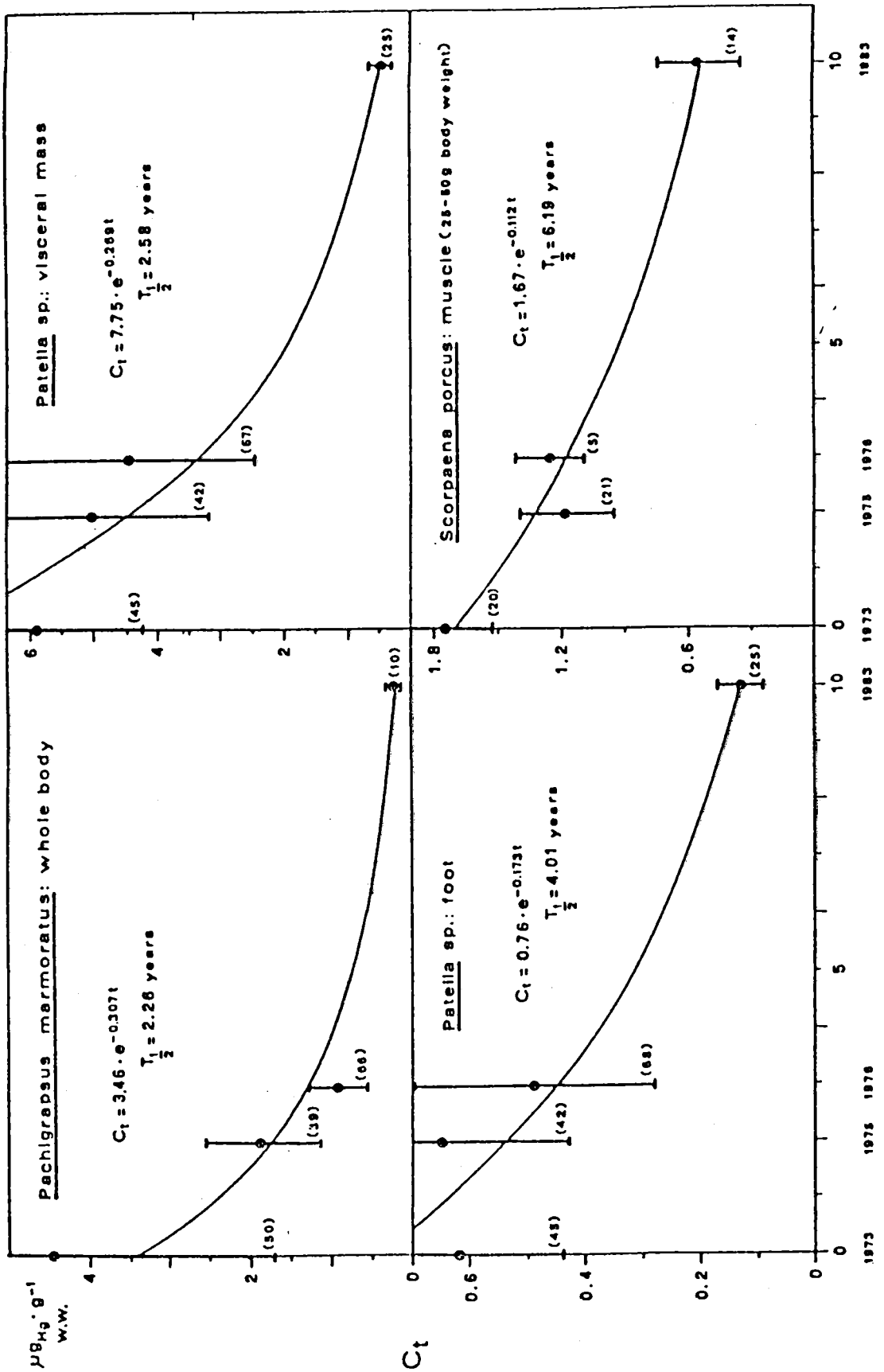



Figure 35. Recovery trends estimated from different "bioindicators" in Solvay outfall area (Bacci et al. 1986). $C_t$ represents the Hg concentration in the indicator organisms according to a one compartment model, and T1/2 biological half-time of mercury in organisms.

Table 28. Reference area level (µg Hg-T/kg FW) 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 | SD | recovery time (year) |
|---|---|---|---|---|
| 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 |

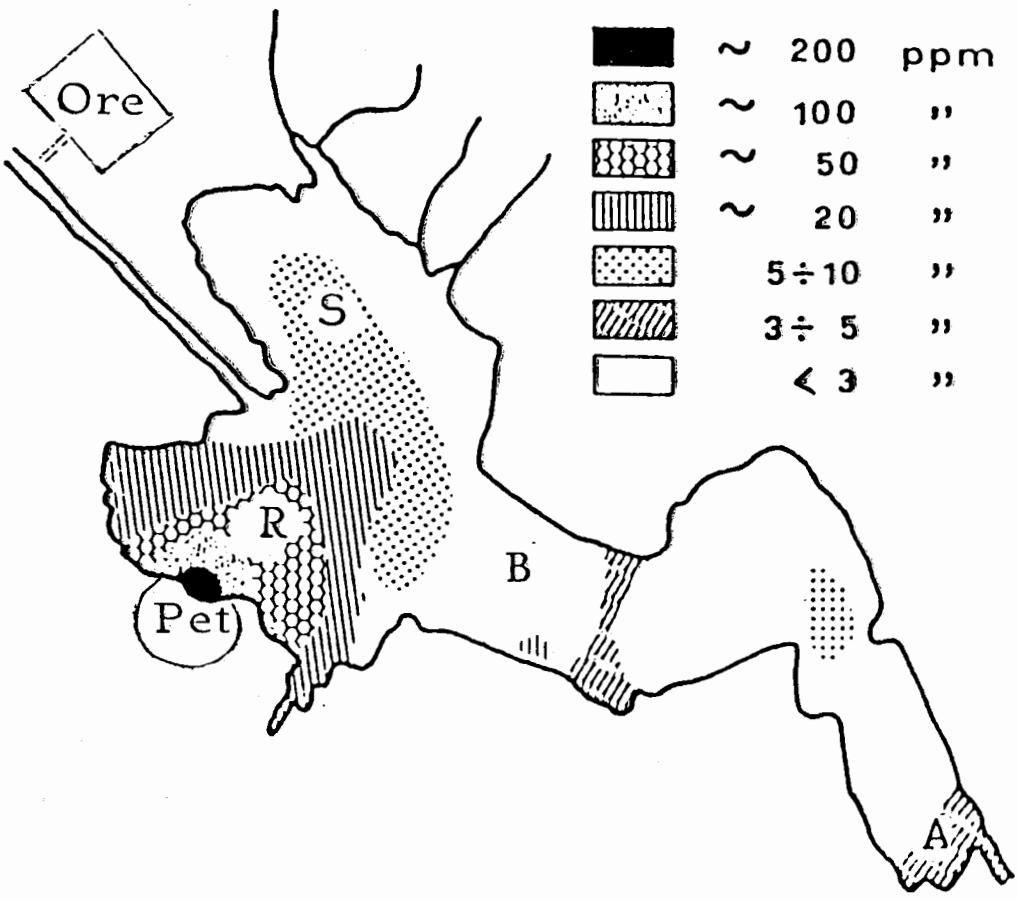



Figure 36. Mercury concentration in the surficial sediments of the S. Gilla Lagoon (Cagliari). A: entrance from the Gulf of Cagliari; Pet: petrochemical industry; Ore: ore processing industry; B, S, R: different zones in the lagoon (Porcu and Masala, 1983, modified).

Table 29. Mercury extracted with different extraction procedure from the top one-cm layer of sediment samples (<100 mesh) collected in the S. Gilla Lagoon in January and April 1981 in per cent of an extraction with $HF/HNO_3/HClO_4$. (Contu et al., 1985)

| station | 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 |

Table 30. Average mercury concentration (µg Hg-T/kg FW) in some benthic macrophytes, crustaceans, molluscs and fishes from various areas of the S. Gilla Lagoon. Data are from Porcu and Masala (1983) and Capone et al. (1986). For the location of the areas see Figure 36.

| species | Area | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 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 | | - |

Also the relative influence of mercury released from another industrial complex (refinery and petrochemical plant) into the Gulf of Cagliari is limited (Cottiglia et al., 1984). The sediments are enriched in Hg near the industrial complex but not near the outlet of the lagoon. On the other hand the Hg in the total suspended matter is higher near the outlet of the lagoon. Four fish species (C. juis, S. scriba, S. cabrilla and D. annularis), all from the 7th to 8th year classes, showed up 2.4 times higher Hg concentrations than background near the industrial complex (station 10), but also here the influence of the release was restricted to the area near the industrial outfall. The author estimated the input of Hg into the Gulf of Cagliari from the S. Gilla Lagoon and the industrial complex in the gulf. Suspended matter of all kinds (suspended sediment, organic detritus, plankton, etc.) would have transported annually not less than 200 kg Hg-T into the gulf, mostly in particulate insoluble form. The annual transport of Hg associated with living biota was estimated at some 100 g Hg-T. The release from the refinery was more difficult to estimate. The concentration of the outflow was sampled only once resulting in 7.5 ug soluble Hg (membrane-filtered)/L and 70 ppm Hg-T in suspended matter (Cottiglia et al. 1984). If one follows the authors, assuming that the plant discharges several $m^3$/sec with a load of solid suspended matter containing 0.5 mg Hg/$m^3$, one arrives only at some 10 to 100 kg of Hg a year.

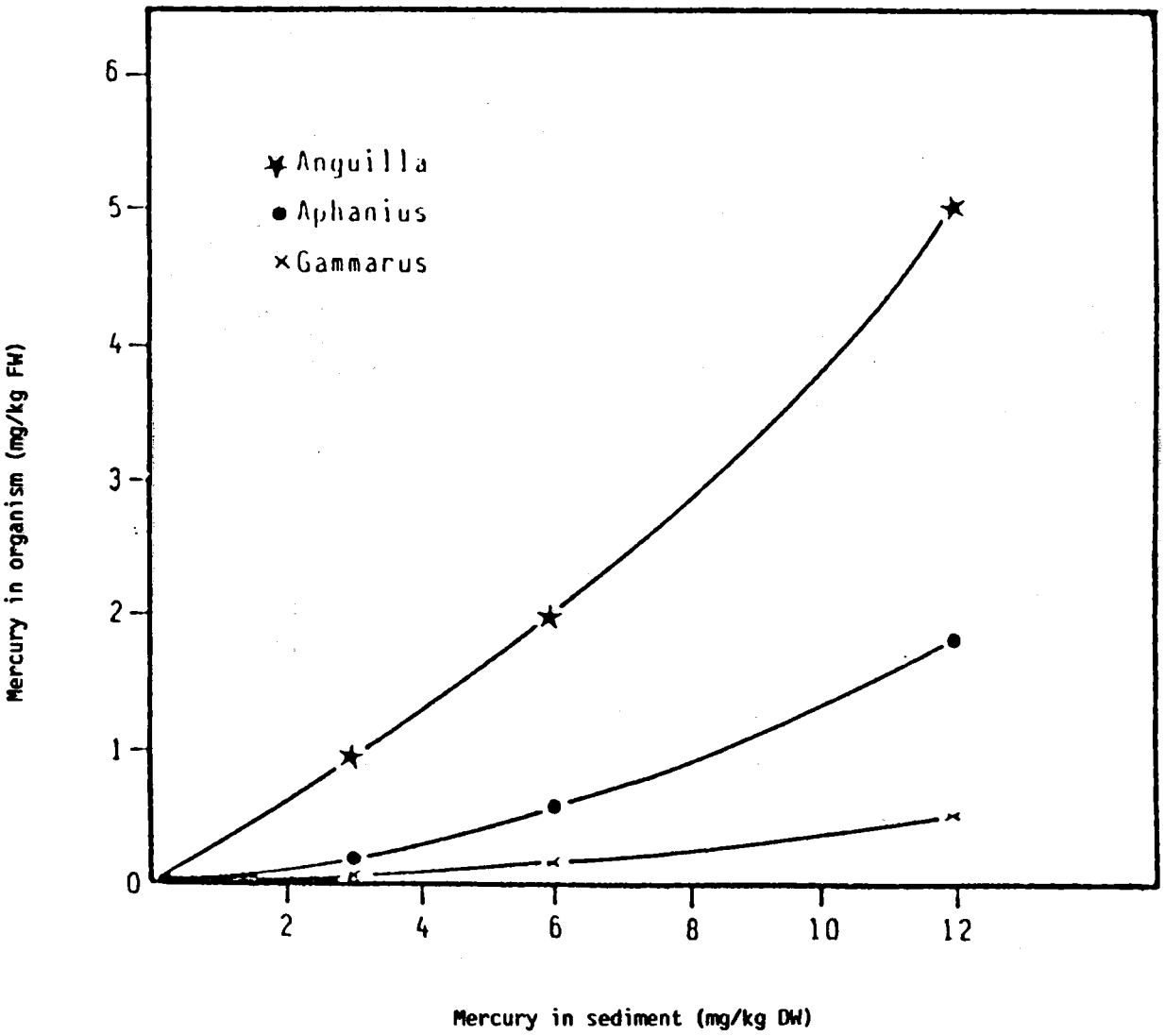



Figure 37. Relationship between mercury concentrations in sediments and biota obtained from tank experiments (Cottiglia et al. 1984).

Also the sediments near the PVC and chlor-alkali plant situated in the Kastela Bay (Split) showed high Hg levels: 8.5 mg Hg/kg DW maximum concentration at the nearest point determined (Stegnar et al. 1981, Vukadin et al. 1986). The plant has been in operation since 1950. It has been estimated that for the period from 1950 to 1985 about 2 MT of Hg/year were released into the marine environment with an effluent concentration of about 0.1 mg Hg/L. Also about 2 Mt/year were released into air. Beginning in 1985 on the mercury discharged with the liquid effluent (circa 0.01 mg Hg/L) into the marine environment has markedly reduced to about 50 kg Hg/year. In the surface layer of the sediments the contamination from the plant is easily detectable (Figure 38). In the subsurface layer of the sediment the Hg levels are about that of background. Mussels collected near the plant also showed much higher levels than mussels from a remote control location (Table 31). Returning to the same site in 1982 and 1983, Tuser-Znidaric et al. (1983) again 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, interestingly, the MeHg concentration in the mussels from the contaminated site was only 1.75 times that of the remote site (Table 34). Recently Mikac et al. (1985) have published data on total mercury, methyl mercury and selenium in sediments, mussels and fish from the same site. High Hg-T concentrations were again found near the outfall in surface sediments (highest concentration: 6.13 mg/kg wet weight). The MeHg levels, however, were low ranging from <0.002 to 0.02 mg Hg/kg wet weight of sediment. The MeHg concentrations in the sediments were not correlated to the Hg-T concentrations in the sediments nor to the amount of organic matter in the sediments. About 0.15 to 1.4% of the Hg-T was MeHg with a median of 0.56%. In mussels (M. galloprovincialis) the highest Hg-T levels (13.3 mg Hg/kg FW) were observed near the chlor-alkali plant but the mussel samples with the highest Hg-T did not have highest MeHg concentrations (0.015 mg/kg FW). Mussels with Hg-T concentrations of 0.4 to 0.7 mg/kg FW had higher MeHg concentrations (about 0.110 mg/kg FW). The correlation between Hg-T and MeHg was not significant, but a negative correlation between Hg-T and the percentage of MeHg exists (Figure 39). These data indicate that the large release of inorganic Hg from the chlor-alkali plants has not significantly increased the MeHg concentrations neither in the sediments nor in the mussels. This is in accordance with the experiments made by Inoko and Matsuno (1984) that MeHg is not formed in chlor-alkali plants. The results also suggest that only a small amount, if any, of inorganic Hg is transformed into MeHg in sediments or biota near chlor-alkali plants.

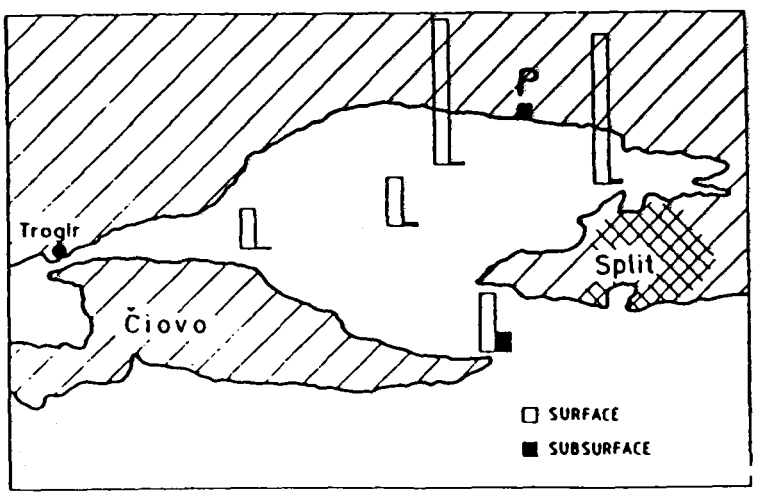



Figure 38. Mercury concentrations in surface and subsurface layers of sediments from the Kastela Bay (Stegnar et al. 1981). P: Chlor-alkali plant.

Table 31. Mercury and selenium concentrations (µg/kg FW) in mussels (soft parts) from the Kastela Bay (Stegnar et al. 1981)

| metal | mean | range | location |
|---|---|---|---|
| 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) |

Table 32. Average mercury amounts (g/day) 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: circa 3720 g Hg-T/day | |

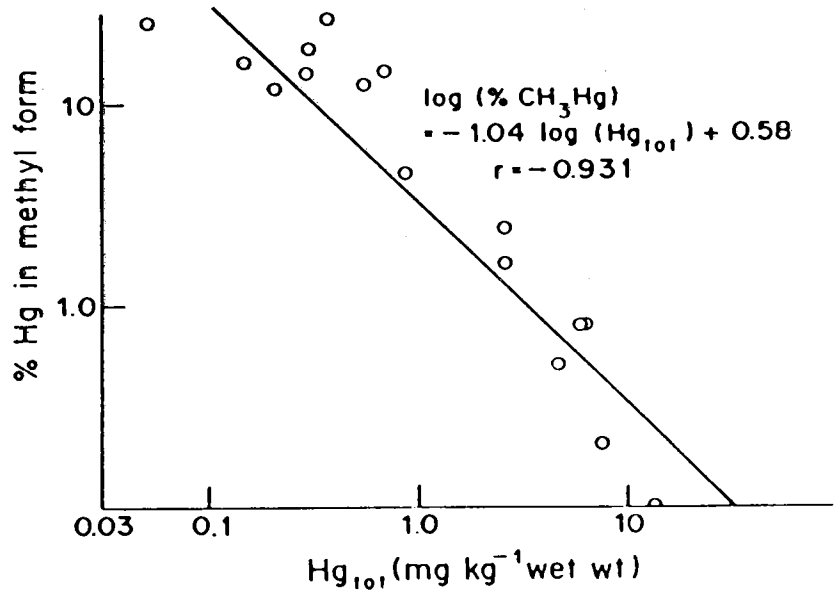



Figure 39. Relationship between total mercury and methyl mercury in the soft parts of mussels from the Kastela Bay (Mikac et al. 1985).

In Israel Hornung and collaborators (Hornung et al. 1984; Hornung, 1986) investigated the release of Hg from a chlor-alkali plant and its influence on the Hg levels in sediments and biota. Sediment concentrations were highest near the plant's outfall and decreased with distance from it. At 20 km from the source, background levels were again reached. Likewise, the Hg concentration decreased in benthic organisms with distance from the source. Figure 40 shows the correlation of Hg levels in three invertebrates (a crab, a bivalve and a gastropod) with that of

the sediments collected in the same sites as the organisms. Note that the carnivorous gastropod showed higher Hg levels in the same locations than the filter-feeding bivalve. Similar correlations were observed for several other species.

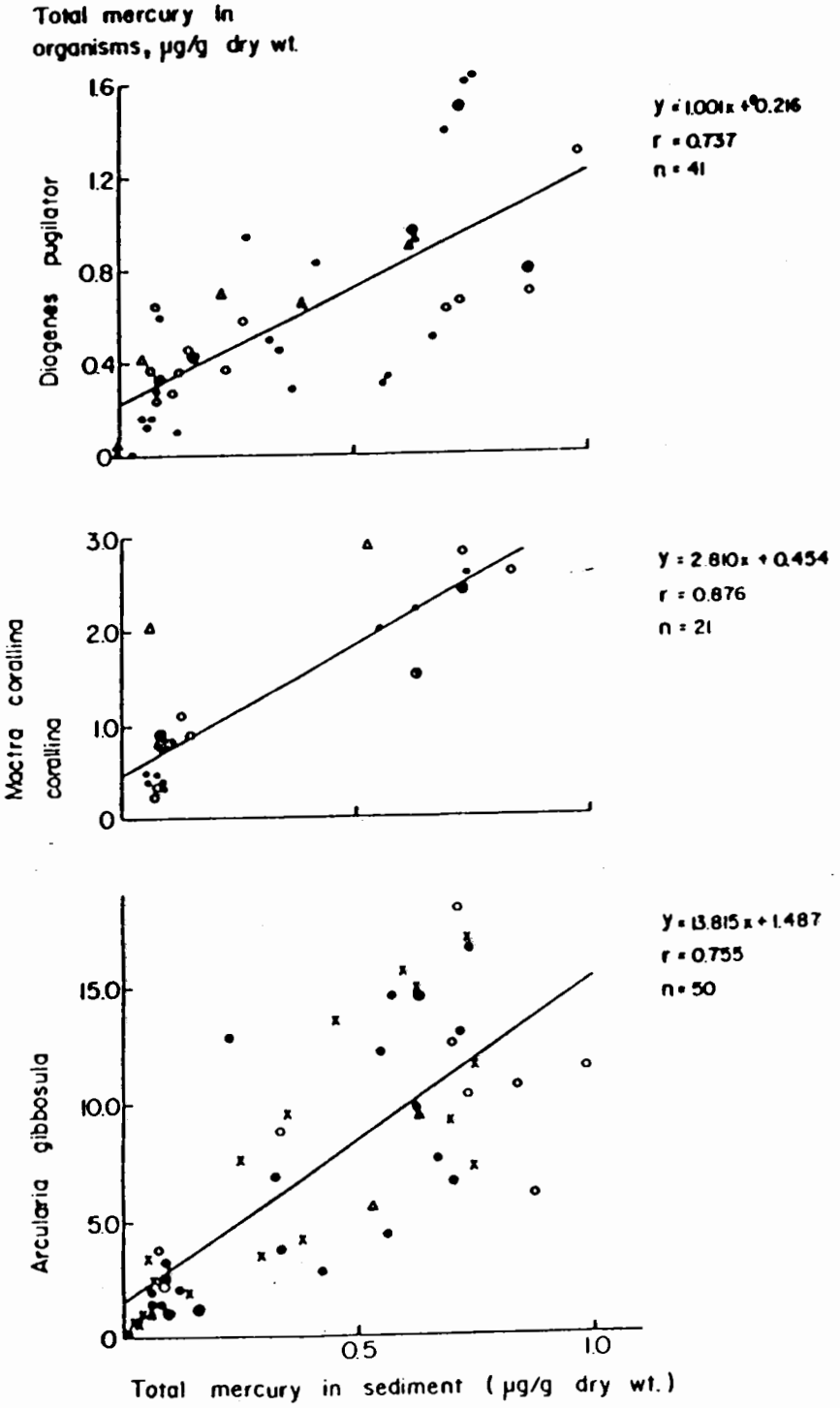



Figure 40. Relationship between mercury concentrations in three benthic organisms and surficial sediments from the coast of Israel (Hornung, 1986).

Note: each point represents Hg levels in organisms and sediment sampled on the same date.

Symbols: Δ = July 1980, 0 = July 1981, ● = Sept. 1981, • = May 1982, x = Nov/Dec 1982.

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 were released into El-Mex Bay from these two land-based sources. In the agricultural drain, the main source, most of the Hg is in particulate form while the chlor-alkali plant discharged predominantely dissolved Hg. This is different from what has been observed in discharges from the Solvay plant and from the sources in the S. Gilla Lagoon. At the stations (2a and 3a in Figure 41) near the two discharges the salinity (as expected) is lowest in the surface layers, at some kilometres offshore normal sea water concentrations were reached. Dissolved and particulate Hg increased near stations 2a and 3a 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 Hg of the Umum agricultural drain. In both stations the particulate Hg in the sea water samples is higher than the dissolved Hg. On the outer stations (2b and 3b) both particulate and dissolved Hg 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 DW (El-Sayed and Halim, 1979). The stations 2a and 3a in the bay had the highest levels (Table 33). 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 Hg levels in several fish species were higher in El-Mex Bay than in other areas along the Alexandria coast (El-Sokkary, 1981).

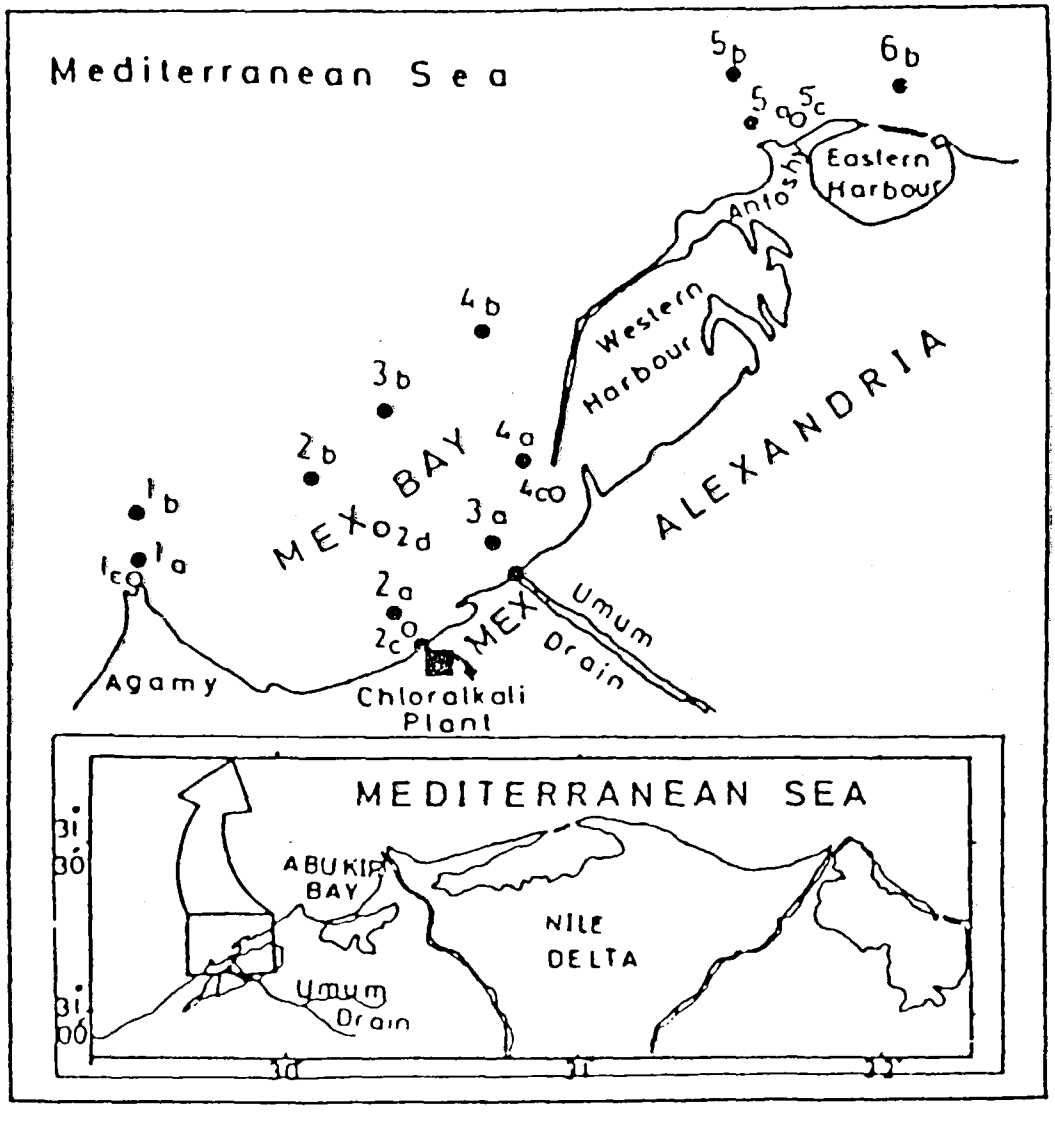



Figure 41. Sampling stations in the coastal area of Alexandria. (El-Rayis et al. 1986).

Table 33. Mercury in sediment and plankton samples from El-Mex Bay (El-Rayis et al. 1986)

| stations | sediment (mg Hg-T/kg DW) | mixed plankton (µg Hg-T/kg 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 |

Table 34. Mercury and selenium concentrations (µg/kg FW) in marine organisms from the Mediterranean

| | | Hg | | Se | | Hg/Se | |
|---|---|---|---|---|---|---|---|
| | n(*) | mean | range | mean | range | ratio | reference |
| Plankton | | | | | | | |
| Adriatic S. | H22 | 130 | 50 - 680 | 3700 | 1900 - 6400 | 0.01 | Kosta |
| N. norvegicus | | | | | | | |
| Adriatic S. | 5 | 1650 | 1100 - 2600 | 1430 | 390 - 2700 | 0.47 | Kosta |
| Murex sp. | | | | | | | |
| Adriatic S. | H2 | 30 | 15 - 45 | 48 | 390 - 2700 | 0.25 | Kosta |
| M. galloprov. | | | | | | | |
| Monaco | H1 | 330 | | 890 | | 0.15 | Fowler |
| Kastella B. | | | | | | | Tusek |
| polluted | 5H10 | 10000M | 7850 -20400 | 980M | 820 - 2100 | 4 | |
| MeHg | | 28M | 14 - 43 | same sample | | | |
| Ciove, unpoll. | 5H10 | 400M | 300 - 750 | 530M | 480 - 1210 | 0.3 | Tusek |
| MeHg | | 16M | 9 - 30 | same sample | | | |
| Strunjan, unpolluted | 4H10 | 50M | 30 - 90 | 900M | 500 - 1270 | 0.02 | Tusek |
| Elefsis Bay | H10 | 150 | 63 - 215 | 405 | 310 - 550 | 0.15 | Grim |
| Ostrea edulis | | | | | | | |
| Adriatic S. | H1 | 40 | | 610 | | 0.03 | Kosta |
| Octopus vulgaris | | | | | | | |
| Adriatic S. | 1 | 70 | | 370 | | 0.07 | Kosta |
| Mustelus vulgar. | | | | | | | |
| Adriatic | 3 | 1850 | 890 - 3550 | 460 | 410 - 550 | 1.6 | Kosta |
| Raja clavata | | | | | | | |
| Adriatic | 1 | 670 | | 450 | | 0.6 | Kosta |
| Torpedo marmorata, adult | | | | | | | Kosta |
| Adriatic S. | | | | | | | |
| liver | 1 | 1150 | | 1980 | | 0.2 | |
| kidney | 1 | 400 | | 670 | | 0.2 | |
| tail muscle | 1 | 650 | | 260 | | 1 | |

Table 34 (cont'd).

| | n(*) | Hg mean | Hg range | Se mean | Se range | Hg/Se ratio | reference |
|---|---|---|---|---|---|---|---|
| Torpedo marmorata, young | | | | | | | Kosta |
| liver | 2 | 165 | 150 - 180 | 225 | 220 - 230 | 0.3 | |
| tail muscle | 2 | 200 | 180 - 220 | 350 | 280 - 420 | 0.2 | |
| M. barbatus | | | | | | | Grim |
| Kissamos Gulf | H2 | 62 | | 185 | | 0.13 | |
| Gera Gulf | H4 | 69 | | 350 | | 0.08 | |
| Saronikos G. | H288 | 290 | | 470 | | 0.24 | |
| M. surmeletus | | | | | | | Grim |
| Kissamos G. | H5 | 80 | | 180 | | 0.17 | |
| P. acarne | | | | | | | Grim |
| Kissamos G. | H6 | 30 | | 450 | | 0.03 | |
| Gera Gulf | H11 | 137 | | 340 | | 0.16 | |
| Antikyra G. | H2 | 180 | | 770 | | 0.1 | |
| Boops boops | | | | | | | Grim, |
| Kissamos Gulf | H10 | 20 | | 430 | | 0.02 | |
| Antikyra Gulf | 1H | 110 | | 1030 | | 0.04 | |
| Seranus scriba | | | | | | | Grim |
| Gera Gulf | 1 | 230 | | 170 | | 0.5 | |
| S. cabrilla | | | | | | | Grim |
| Antikyra Gulf | H10 | 130 | | 550 | | 0.1 | |
| S. scorfa | | | | | | | Grim |
| Antikyra | 1 | 360 | | 750 | | 0.2 | |
| E. guaza | | | | | | | Grim |
| Kissamos Gulf | 1 | 270 | | 620 | | 0.2 | |
| D. annularis | | | | | | | Grim |
| Gera Gulf | H3 | 120 | | 530 | | 0.1 | |
| P. erythrinus | | | | | | | |
| Adriatic coast | 2 | 660 | 470 - 860 | 560 | 480 - 640 | 0.45 | Steg |
| Gera Gulf | H2 | 48 | | 470 | | 3.8 | Grim |
| Mugil labeo | | | | | | | Grim |
| Gera Gulf | H2 | 490 | | 120 | | 1.6 | |
| Maena smaris | | | | | | | Grim |
| Gera Gulf | H3 | 140 | | 570 | | 0.1 | |
| C. conger | | | | | | | Grim |
| Antikyra Gulf | H6 | 250 | | 880 | | 0.1 | |
| T. mediterraneus | | | | | | | Grim |
| Kissamos Gulf | H2 | 70 | | 370 | | 0.1 | |

n(*): H followed by a number n stands for composite sample of n specimens.
The Hg/Se ratio is calculated from the respective means.
Fowler = Fowler et al. (1976a); Fowler and Benayoun (1977)
Grim = Grimanis et al. (1981, 1979)
Kosta = Kosta et al. (1978)
Steg = Stegnar et al. (1979)
Tusek = Tusek-Znidaric et al. (1983)

## 3.7 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 organic Hg: range 13 to 42 ug Hg-T/kg FW (section 3.4.1). Capone et al. (1986) determined that in the green algae Cladophora from a contaminated site, 40% of the Hg-T was MeHg. Salihoglu and Yemenicioglu (1986) determined Hg-T and MeHg in the macro-algae Caulerpa prolifera. They found a mean (n = 17) of 67 ug Hg-T/kg DW (FW/DW circa 10) with a standard deviation of about 17. MeHg made up about 10% of Hg-T.

Mikac et al. (1985) and Tuser-Znidaric et al. (1983) observed that the percentage of Hg-T as MeHg was lower in mussels from a contaminated site then in mussels from an uncontamatined site (section 3.6; Table 34). Unusual results were obtained by Najder and Bazulic (1986). These authors

found that the MeHg concentration decreased with increasing size of the mussels (see section 3.4.4).

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

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

Thibaud (1986) has more extensive data: about 100 muscle samples of the bluefin tuna from the Mediterranean. These data show that MeHg (and Hg-T) increased with body weight of the tuna to about 75% of Hg-T while selenium levels remained almost constant.

Interesting are the results of Halim et al. (1986). In the flesh of six fish species (M. barbatus, S. vulgaris, B. boops, S. pilchardus, E. alleteratus, R. halavi) the organic Hg concentrations in flesh range from about 70 to 85% of the Hg-T and the concentration of organic Hg in these organisms increased with body weight (Aboul-Dahab et al. 1986), but in the liver of these fishes the percentage of organic Hg is only about 7 to 23%. Also Eganhouse and Young (1978) found only an average of 9.6% MeHg in the liver of the Dover sole (Microstomus pacificus). Similar low MeHg percentage were found in the marine mammals (section 3.4.7).

These data are in accordance with the observations that the MeHg percentage increases with the trophic level of the organism and that MeHg increases during life time. The exceptions (mussels) observed need further study. In other oceans the majority of mercury in fish occurs as methyl mercury (Westoeoe and Ohlin, 1975). Virtually all the mercury in large predatory fish such as tuna and swordfish is also present as methyl mercury, although marlin is an exception with only 10% of the Hg-T as MeHg in muscle tissue (Shultz et al. 1976).

## 3.8 Mercury/selenium relationship

The findings that selenium might act antagonistically to Hg (Piotrowski and Inskip, 1981) and that in some organs of man and marine organisms high Hg levels are associated with high selenium concentrations has stimulated the simultaneous collection of Hg and Se concentrations in marine organisms and their environment. Kosta et al. (1975) and Koeman et al. (1973) 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 34 and 35). Only in some bird tissues (liver and brain), molar ratios near to one have been observed (Figure 42). Loenzio et al. (1982) have recently found that in the fish Mullus barbatus the sum of Hg plus Se expressed in moles are linear-related to length (age) of the fish (Figures 43 and 44): even relatively low Hg 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.

Martoja and Viale (1977) and Martoja and Berry (1980) have presented evidence that mercuric selenide particles of a few micron in diameter occur in the connective tissue of the liver from marine mammals. Few particles were found in Atlantic dolphins, but numerous agglomerations in adult Mediterranean specimens. The particles have been identified as pure tiemennite and according to the authors the particles may explain the presence of high Hg and Se levels in the liver of marine organisms since they have been shown to be inert

Table 35. Mercury and selenium concentrations (ug/kg FW) and Hg/Se molar ratio in marine birds (Cottiglia et al. 1984) and their eggs (Renzoni et al. 1982)

| | n | Hg-T mean | Hg-T SD | Se-T mean | Se-T SD | molar Hg/Se of mean |
|---|---|---|---|---|---|---|
| Eggs: | | | | | | |
| L. argentatus m. | 4 | (545 ± | 185) | (515 ± | 215) | 0.4 |
| E. garsetta | 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 |
| 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 DW = 5 x FW.

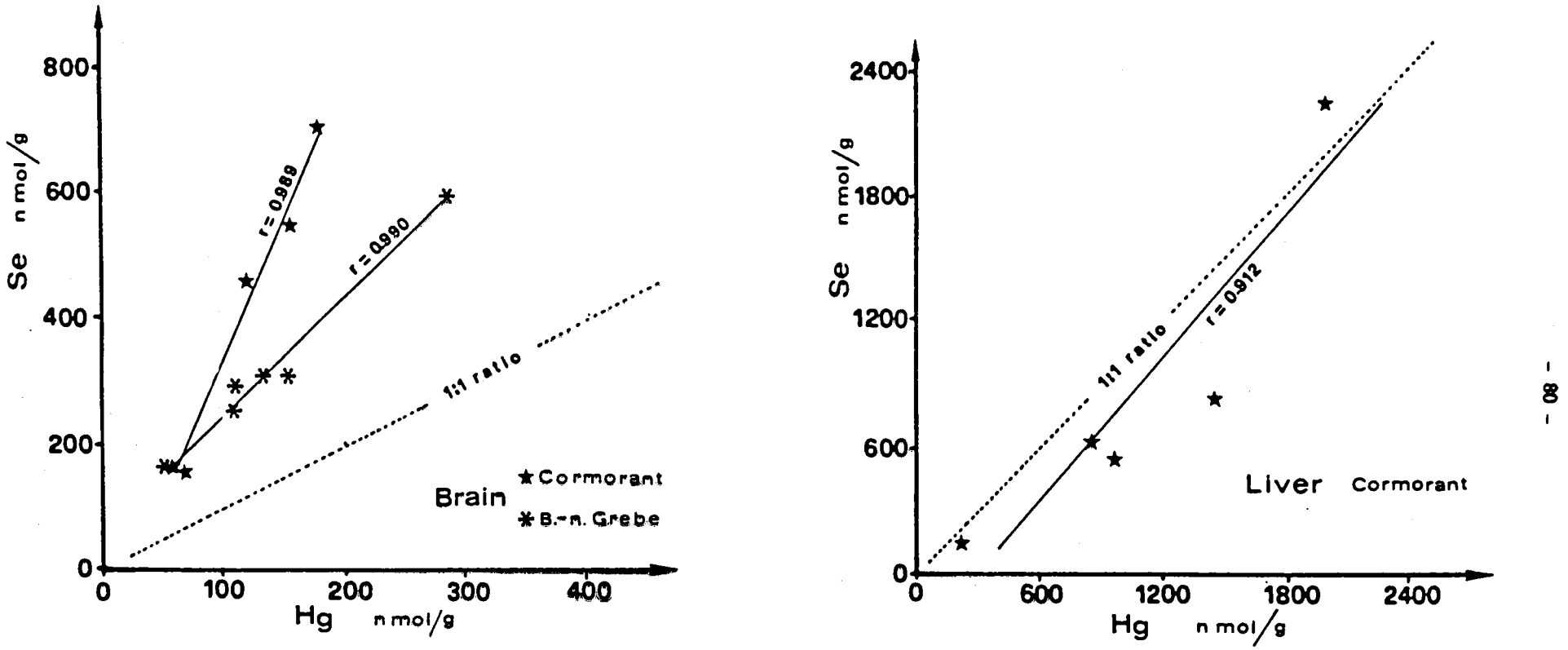



Figure 42. Relationship between selenium and mercury molar concentrations in brain and liver of marine birds. (Cottiglia et al. 1984).

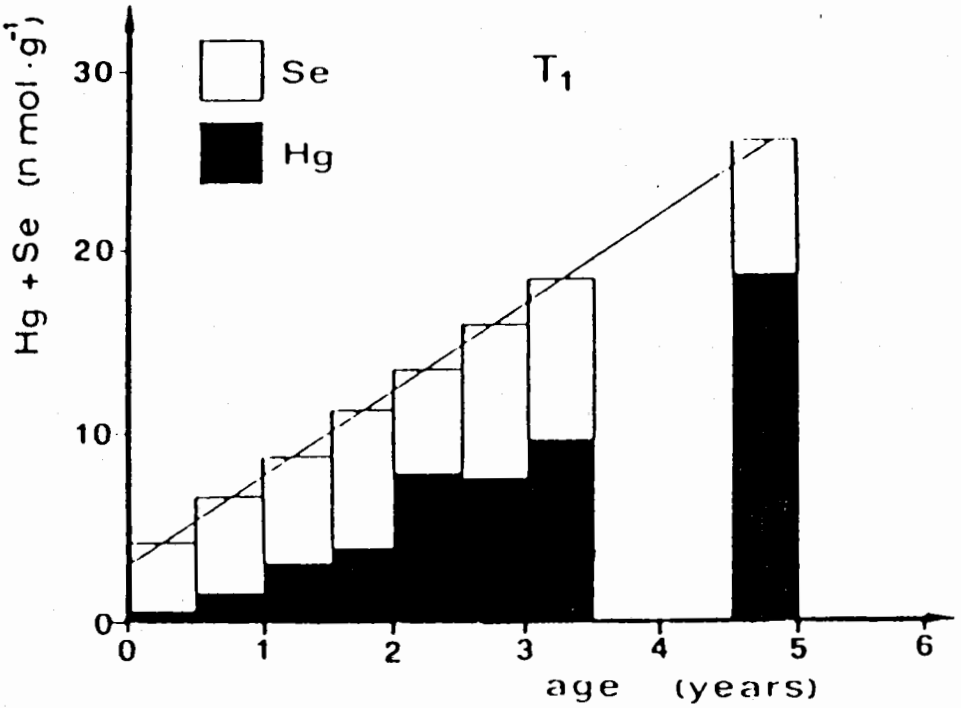



Figure 43. Mercury and selenium in Mullus barbatus from an area high in mercury (Leonzio et al. 1982).

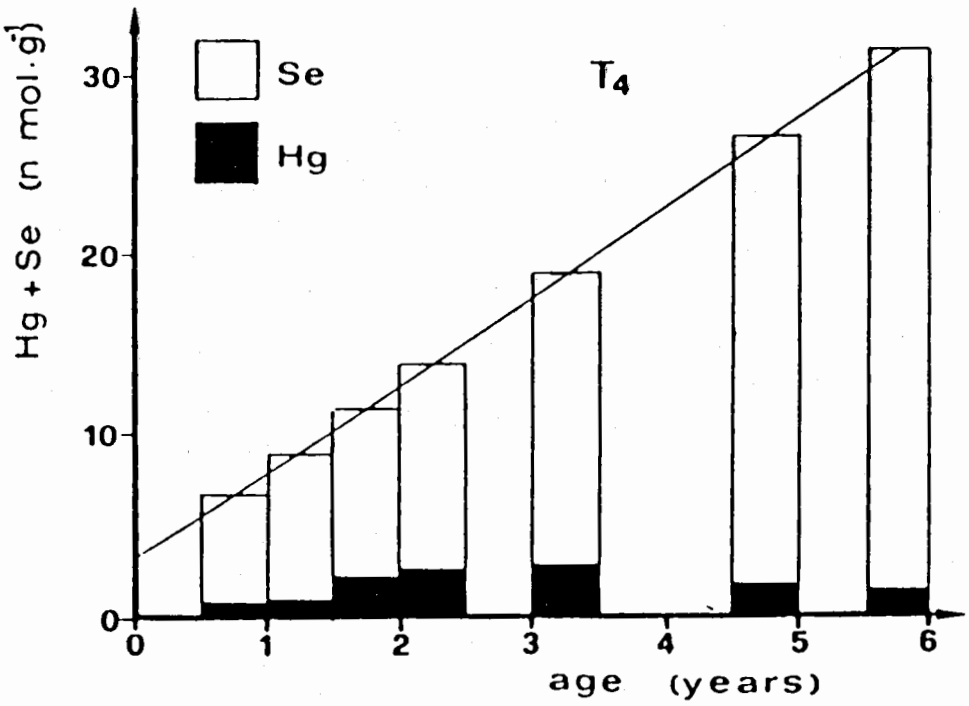



Figure 44. Mercury and selenium in Mullus barbatus from an area low in mercury (Leonzio et al. 1982).

## 3.9 Pollution indicators

Measurements of mercury concentrations in air, sea water, sediments and biota can all serve as pollution indicators. Since sea water and sediment concentrations will influence the Hg levels in biota, their determination is important for a prediction of the levels to be expected in biota. Because sea water masses are subject to horizontal and vertical movements while sediments are quite stationary, sediments will be much more useful in locating pollution sources than water. Furthermore, the Hg concentrations in sediments and biota are at least 1000 times higher than the sea water levels and, therefore, the analytical requirements are much less demanding. On the other hand Hg concentrations in sea water are at present better suitable for a prediction of the Hg levels in biota and its toxicity on biota. So far, the bioavailability of the various mercury species associated with sediments has not been studied sufficiently to allow the prediction of biota levels from sediment concentrations. Also applying a standard reference extraction procedure of sediments would be very useful for the comparison of the results obtained by different authors. This reference procedure should be used always together with other procedures if the investigator prefers other methods. At present only a qualitative relationship between sediment and biota concentrations has been established both for natural and anthropogenic sources. Therefore, sediment levels are very useful to identify sources of contaminations but they must be integrated with Hg concentrations in the biota to assess possible risks, both to marine organisms and humans exposed to Hg intake from seafoods. The accumulation rate, the internal distribution and the release is different for various inorganic and organic Hg species (see section 4.3). Also the levels observed in biota in areas under the influence of natural and anthropogenic sources have clearly shown that the physico-chemical form (species) of Hg play an important role in the bioavailability of Hg. Therefore, key Hg species must be monitored together with total Hg. Total Hg determinations can only serve as a preliminary orientation. The accumulative nature of the Hg species in biota requires that specimens of the same size be compared. However, instead of prescribing a standard size for monitoring (which may not be available to the investigator) regression curves of Hg concentration versus size of a wide range should be examined, since it has been shown that this is much more effective in distinguishing contamination levels in biota than standard sizes. Selecting sessile marine organisms and organisms which migrate over restricted and over wide areas allows the monitoring of areas of different sizes. Selecting organisms belonging to different trophic levels and having different feeding habits allows a differentiation of the paths and routes the different Hg species will take in the environment.

## 3.10 Conclusion on mercury levels

The analytical uncertainty of the measurements, especially in air and sea water, but also in sediments, make the evaluation of and the comparison between the data of different authors extremely difficult, if not impossible. Reference materials and reference standards at the levels at which Hg occurs in the marine environment are only available for biota and sediments. However, these standards are valid only for the standardization of total Hg concentrations, no standards exist for the comparision of key Hg 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 reservations. 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 they are still scarce and sporadic. Nevertheless, the data indicate that the Hg levels of open sea areas are lower than over land. As expected, urban air has higher Hg levels than rural air. Hg levels in air over rural areas in the Mt. Amiata Hg anomaly are considerably higher than over rural areas not influenced by natural Hg sources. The chemical species of Hg in air are at present only operationally defined and a true identification is necessary to understand the role different Hg species play in the atmosphere and in the transport from air to ocean and vice versa.

Due to the uneven distribution of land and oceans in the two hemispheres, over open ocean sites in the northern hemisphere the mean level of "gaseous Hg-T" is estimated to be about 1.5 ng Hg-T/$m^3$ and over open ocean sites in the southern hemisphere about 1 ng Hg-T/$m^3$.

**Seawater:** The lack of proper quality control of the sea water measurements 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" sea water samples, the means of "total dissolved Hg" concentrations range between 7 and 25 ng Hg-T/L. For comparison the range of means of recent equivalent data from non-Mediterranean areas extends from 2 to 14 ng Hg-T/L. Data on some coastal zones seem "very high" 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 simultaneously the same samples. A great handicap in the understanding of the biogeochemical cycle of mercury present the lack of analytical data on chemical species of Hg in sea water.

**Sediments:** High Hg 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 DW range.

**Biota:** The large number of Hg levels in edible marine organisms investigated during the MED POL Phase I project has greatly contributed to a better understanding of the distribution of Hg concentrations in seafoods. Total mercury concentrations increase with size in marine organisms; only bivalve mussels seem to be an exception. In more evolved molluscs (sepia) the Hg concentrations increase with size as in other marine organisms. This increase with size is more evident in organisms which have long lifetimes and high Hg concentrations. More relationships between Hg concentration and size are needed for an accurate comparison of the Hg levels in individual species from different locations and for a prediction of the possible Hg levels to be expected in various seafoods. 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, which are not polluted by anthropogenic sources, generally have higher levels than marine organisms from unpolluted areas of other regions. In particular, data on the Hg concentration versus size for a mollusc and several pelagic fishes illustrate that these species have higher Hg concentrations in the Mediterranean than in the Atlantic. Hg concentrations have been determined in mixed unrepresentative plankton samples of unknown species composition vary widely and therefore no difference between the Mediterranean and other oceans can be established. The usefulness of these data is limited to the establishing of an sea water/plankton concentration factor of 1000 to 5000. Very limited data show that in Mediterranean plankton organisms, as in many other marine organisms, the mercury concentration increases with size. Similar data from the Atlantic are needed to establish if significant differences exist also for plankton organisms from the two regions. Mean Hg concentrations of 1000 µg/kg FW and maximum concentrations above 2000 µg Hg-T/kg FW are not rare in Mediterranean seafoods. The highest concentrations in Mediterranean seafoods were observed in large predatory fishes situated in the highest trophic levels such as tuna (maximum: 6300 µg Hg-T/kg FW), but also in Mugil auratus (maximum: 5600 µg Hg-T/kg FW), Mullus barbatus (maximum: 7050 µg Hg-T/kg FW), Nephrops norvegicus (maximum: 3000 µg Hg/kg FW) and Mytilus galloprovincialis (maximum: 7000 µg/kg FW). High Hg levels in seafoods have been observed in areas II, IV, V and VIII of the Mediterranean. Typical Hg concentrations are difficult to identify. However, it is indicative that rarely mean concentrations are below 100 µg Hg-T/kg FW. Nearly all results have been obtained under quality control measures, so that the majority of the data can be considered reliable. Birds have high Hg concentrations and also they seem to have higher Hg-T levels in the Mediterranean than in the Atlantic. The highest Hg levels of all biota were found in marine mammals. Again higher Hg-T concentrations seem to occur in the Mediterranean species.

**Natural sources:** The data show clearly that Hg sources of natural origin influence the Hg levels observed in sediments and biota. A mussel transplant experiment, in particular, was very illustrative in this respect. However, determining the total amount of Hg in water and sediment is not sufficient for a prediction of the level in biota. The very high concentrations in the sediments in the Gulf of Trieste (up to about 50 mg Hg-T/kg DW), confirmed by two authors, result in only a relatively small increase in the Hg levels in mussels. Much lower concentrations in

sediments (up to 5 mg Hg-T/kg DW) off the coast of the Mt. Amiata anomaly increased the Hg level in M. barbatus to much higher levels. Unfortunately the Hg concentrations of 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 Hg anomalies. The leaching experiments carried out on the sediments from the Mt. Amiata anomaly showed that investigating the chemical species of the Hg present is very important for an understanding of the distribution pattern of Hg in the environment. Similar experiments, taking into consideration the processes involved in the Hg 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 chlor-alkali 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 Hg levels are reached background levels again, even in areas with massive Hg inputs. The chemical species (physico-chemical form) of the Hg released seems to play a very important role in the bioavailability of the Hg released and in its distribution pattern. Hence, the determination of total Hg concentrations is not sufficient to understand and predict the distribution pattern of the Hg release in the various components of the marine ecosystem. Sewage outfalls can increase the Hg concentrations in the adjacent environment.

**Organic mercury:** The few data so far available show that the relative amounts of organic mercury increase with age of the organism and increasing position in the food-chain. Plants and plankton have much lower relative amounts of organic Hg than crustaceans and fish. Bivalve molluscs seem to be an exception as their content of organic (and total) Hg decreases with size. In fishes 60 to 95% of the Hg-T (depending on age and trophic level) is methyl mercury. In the liver of fishes and in marine mammals low percentage of organic Hg has been found.

**Mercury/selenium relationships:** Considerable attention has been given to the simultaneous increase of Hg and Se in marine organisms because Se is an antidote to mercury poisoning. In most cases the Se levels seem to be independent of the Hg levels. But in some special tissues, such as the liver and brain, molar ratios near to one have been observed. In some fishes the sum of the molar concentrations of Hg and Se has shown to be related with length. More data are necessary to see if this is a general phenomena.

**Pollution indicators:** Since Hg is an accumulative element, i.e. the Hg concentration increases with size of the marine organism (bivalves seem the only exception), various marine organisms may serve as indicators of areas of different extension. Sessile organisms may serve as indicator of very small areas, while organisms migrating over medium to large areas can serve as indicators over more or less wide areas. According to the size of the area to be monitored sessile or species with a migrations pattern corresponding to the area to be monitored can be selected.

## 4. BIOGEOCHEMICAL CYCLE OF MERCURY IN THE MARINE ENVIRONMENT

### 4.1 Natural and anthropogenic sources

Mercury is introduced into the marine environment both from natural and from anthropogenic sources. Following the Minamata incident, the great concern about anthropogenic mercury releases has distracted the attention from the potential hazards of natural occurring mercury sources. Relatively high mercury concentrations are found in the geochemical mercury anomalies.

#### 4.1.1. The Mediterranean as a natural geochemical anomaly

Mercury occurs naturally in the environment and is concentrated in geologic belts. Mercury deposits belong to one of the two Tertiary or Quaternary orogenic and volcanic belts: the circumpacific and the Mediterranean-Himalayan belts (Figure 45). A more detailed figure of the

past and present mines of the Mediterranean shows the wide distribution of Hg in the Mediterranean basin (Figure 46). Published detailed surveys are rare (Figure 23) but no doubt the mining companies possess extensive data from the prospecting for possible Hg mining sites. The Hg concentrations higher than background, but too low for mining, may occur in many parts of the Mediterranean. Although a systematic survey of Hg levels in the Mediterranean has not been carried out, it is indicative that 65% of the world's mercury resources are supposedly located in the Mediterranean basin which occupies only 1% of the earth surface (Table 36). In 1970 Italy exported 35% of its production, Spain 95% and Yugoslavia 90% (Nriagu, 1979) showing that themercury is not necessarily dispersed in the country of production. Where the anomalies have been studied their influence on the nearby coastal zones is evident from the above background concentrations in sediments and biota (section 3.5). A transport route may be presented by suspended matter as has been shown by Baldi (Baldi, 1986). This author found that the Hg concentrations of particulate matter in sea water were much higher than the Hg concentrations in the sediments of the same station. Similar results were observed to occur in the Tagus estuary (Figueres et al. 1986) and in the Gulf of Cagliari (section 3.6). In the Tagus estuary the Hg levels in the sediments decrease rapidly with distance from the Hg source, but the Hg concentration in the suspended matter remains high (Figure 47). In the sea the influence of Hg contained in small suspended particles may extend the influence of Hg anomalies over a much wider area than observable in Hg concentrations in sediments.

Anthropogenic sources of importance for the marine environment are mainly metallic Hg released in wastes from chlor-alkali plants where the $Hg^0$ has been used in electrodes and wastes from plants involved in the PVC production that use $HgCl_2$ and $HgSO_4$ as catalysts (Nriagu, 1979). Sewage outfalls can create "Hg hot spots" in sediments (section 3.3).

4.1.2 River inputs and land run-offs

A rough comparison of the watershed of the Mediterranean basin (Figure 48) and the locations of the mining area (as representative for the Hg anomalies) shows that only the Almaden does not drain into the Mediterranean and the Konya only partially. The great influence of the Hg levels in sediment and biota for two areas (Mt. Amiata and Idrija) has been discussed previously (section 3.5). For the other areas no data are as yet available, but an influence on the Hg concentrations in the adjacent marine environment can be foreseen.

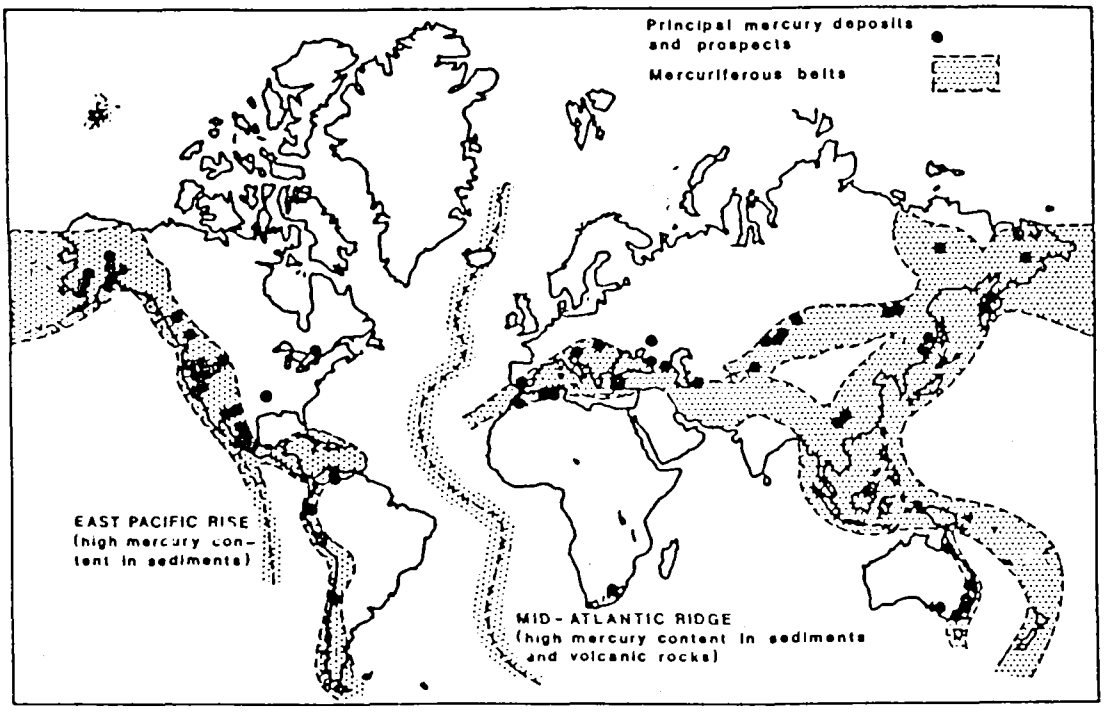



Figure 45. The mercuriferous belts on the earth (Australian Working Group, 1980).

In the framework of the Mediterranean Action Plan an assessment of the total pollution inputs from land-based sources was attempted through the project MED POL X of UNEP (1984) which included also very approximate estimates on the mercury input from various sources (Table 37). It must be pointed out however, that in many cases it was necessary, because of lack of data, to make extrapolations from 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 3.6), future data should be presented on local basis rather than for the whole Mediterranean or for large areas.

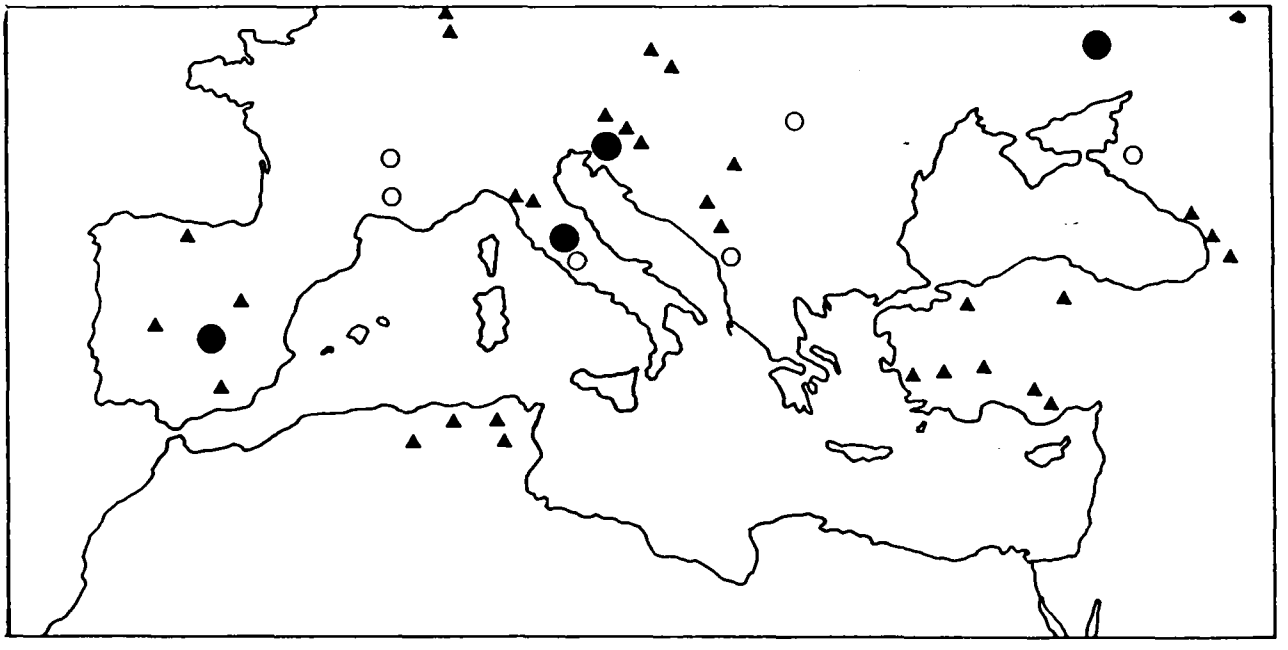


Figure 46. Locations of active and inactive mercury mines in the Mediterranean (courtesy of Mt. Amiata Mining Company)
● = very productive mines; O = presence of mercury; Δ = previously productive mines.

Table 36. Reasonably assured mercury resources and yearly production of mercury in 1975 (Bernhard and Renzoni, 1977)

| | Production (metric ton) | Reserves | ore grades (%) |
|---|---|---|---|
| Mediterranean: | | | |
| Spain | 1622 | 87000 | 1 - 2 |
| Italy | 1048 (*) | 21000 | 0.5 - 0.8 |
| Yugoslavia | 584 | 20000 | 0.2 - 0.9 |
| Algeria | 458 | ? | ? |
| Turkey | 300 | ? | ? |
| Tunisia | ? | ? | ? |
| | > 4015 | > 140000 | |
| Total world | 8585 | > 215000 | |
| Mediterranean in % of world | 47 | 65 | |

(*) the Italian production was discontinued in 1978 because mining was not longer profitable.

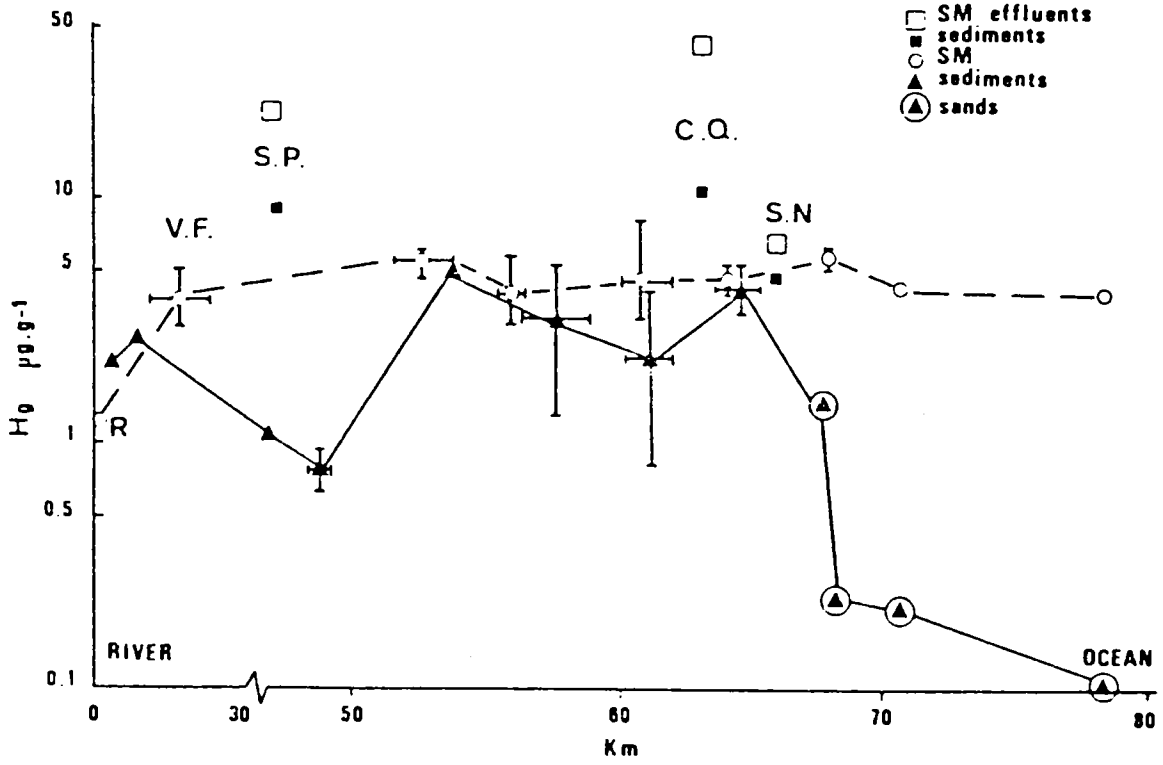



Figure 47. Longitudinal evolution of particulate mercury in the Tagus estuary ■ = sediment; ⓐ = sediment including sand; O = suspended matter. Sources: Sp = Soda Povoa; CQ = Complexo Quimigal; SN = Siderugia Nacional; VF = Villa Franca. (Figueres et al. 1986).

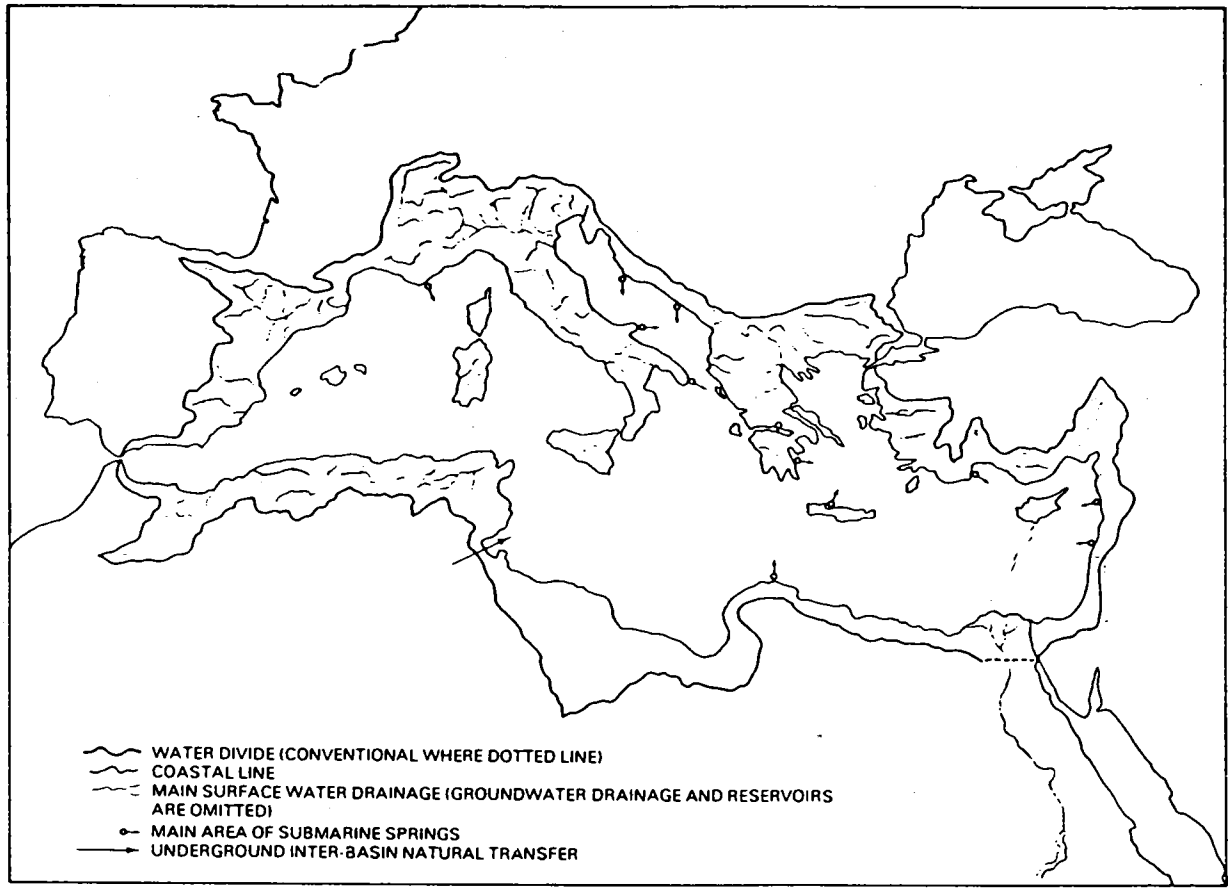



Figure 48. Conventional watershed of the Mediterranean (Ambroggi, 1977). The freshwater drainage area is about 1.8 million $km^2$ including only 30000 $km^2$ of the Nile delta out of the 2.7 $km^2$ of the entire Nile River basin.

Table 37. Estimates on inputs of mercury in the Mediterranean (UNEP, 1985)*

| Region | Originating in coastal zones | | | | carried by rivers | | total |
|---|---|---|---|---|---|---|---|
| | domestic | | industrial | | | | |
| | (t/year) | (% total) | (t/year) | (% total) | (t/year) | (% total) | (t/year) |
| I | 0.04 | 2 | 0.6 | 24 | 1.8 | 74 | 2.5 |
| II | 0.3 | 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 | 0.76 | 0.6 | 6.9 | 5.4 | 122**) | 94 | 130 |

* ) Data are very approximated (see text)

### 4.1.3 Atmospheric inputs

The high volatility of many Hg species suggests that the atmospheric pathway is important in the biogeochemical cycle of Hg. 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 are considered.

Although a precise quantification is difficult, the following global values have been suggested by Matheson (1979): land degassing 17800 t/year, open ocean degassing 7600 t/year, coastal water degassing 1400 t/year and volcanic activity 20 t/year. This estimate of emissions totals 26800 t/year, which is higher than the 18500 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.

Atmospheric emissions from anthropogenic sources are less than those from natural sources; estimates on 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. For degassing McCarthy et al. (1969) considered that Hg levels in soil concentrations were less important than in the underlying mineral deposits. He found degassing rates ranging from 0.64 $\mu$g Hg $m^{-2}day^{-1}$ in areas without underlying mineral deposits to about 42 $\mu$g Hg $m^{-2}day^{-1}$ over cinnabar veins. The author determined the Hg 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 $\mu$g Hg $m^{-2}day^{-1}$. Considering that this soil contained about 5 times more Hg than the average soil, the degassing rate for the US continent was estimated at 0.8 $\mu$g Hg $m^{-2}day^{-1}$. Later this estimate was lowered to 0.3 $\mu$g Hg/$m^{-2}$ day (EPA, 1975).

The natural mantle degassing processes emit elemental Hg vapour for the greater part. The MeHg is thought to have mainly biological origins (section 4.2).

The Hg emitted from volcanoes is a special source. Investigating with INAA (instrumental nuclear activitation analysis) the emission of atmospheric particulate matter collected on Whatmen 41 filter paper from the Etna, Buat-Menard and Arnold (1978) found a geometric mean of 0.25 $\mu$g Hg-T/$m^3$ from three samples in the main plum (about 5°C) and a geometric mean of 0.5 $\mu$g Hg-T/$m^3$ in three samples taken from hot vents (greater than 300°C).

Natural Hg is present in the atmosphere as free vapour (associated with particulate matter as adsorbed elemental or organic Hg), as mercuric chloride vapour, or as monomethyl- and dimethyl Hg. Dimethyl mercury is unstable in the air and is quickly degraded by UV into elemental Hg. The elemental Hg is also in an unstable oxidation state and converts slowly to soluble forms which are readily transferred into atmospheric water droplets. Water and particulate Hg usually accounts for less than 1% of the Hg-T (Fitzgerald et al. 1983). However, these species are mainly responsible for the transport of Hg from the atmosphere to the earth surface, because they are easily washed out by rain or (to a lesser extent) scavenged by dry deposition. To these natural mercury species, Hg from industrial sources has to be added. Johnson and Braman (1974) analysed the Hg species in air which had been moving over the highly polluted Hillsborough Bay of Tampa (Florida). This air had 5 times the Hg-T level of air that had moved mainly over land. The authors found the following species:

| | |
|---|---|
| mercury vapour | 50% |
| mercuric halide vapour | 25% |
| monomethyl mercury | 21% |
| dimethyl mercury | 1% |
| particulate mercury | 4% |

Lindqvist et al. (1984) estimated that total global deposition of mercury lies between 4 and 30 μg Hg-T $km^{-2}year^{-1}$. Buat-Menard and Arnold (1978) and Arnold et al. (1983) made estimates for the western Mediterranean: 50 μg Hg-T$m^{-2}year^{-1}$ (flux of particle deposition: 1 cm/sec). According to these authors the higher values from the Mediterranean are mainly due to higher introduction in the atmosphere from the industrial sources of the 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.

The data on Hg levels in air over land and sea (section 3.1) are consistent with the hypothesis that the major source of atmospheric Hg is continental (Fitzgerald et al. 1983). The Hg is principally emitted into the air in the gas phase and probably mainly as elemental Hg and organo-Hg 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 Hg which most probably is mainly $Hg^0$. The particulate fraction is about 100 to 1000 times smaller than the gaseous Hg 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 Hg concentrations in air and rainwater that the Mt. Amiata Hg anomaly has only a very limited influence on the biogeochemical cycle of Hg in the Mediterranean (section 3.1). Clearly more data are needed to enable us to estimate the contribution of natural degassing fluxes and industrial inputs.

## 4.2 Transformation of mercury species

The transformation processes of Hg has received considerable attention because in the abiotic environment (ore, air, soil and sediment etc.) Hg is predominantly present in its inorganic species while in seafoods most of the Hg occurs as MeHg. Also the Minamata incident poses the problem of the origin of MeHg. One hypothesis suggested that the inorganic Hg release by the chemical factory into the Minamata Bay was transformed into toxic MeHg by micro-organisms resident in the marine sediments. It seems, however, more likely that organic Hg was released from the factory.

The various Hg species have different pathways and routes in the environment. Many of these routes can be taken both by biological mediated processes and by abiological processes. 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 much less emphasis has been placed on non-biological processes than on biological mediated ones and among the biological ones the microbiological have obtained the greatest attention.

Natural foci of Hg dissemination are usually considered to be mercury ore (HgS) and non-mercury ore deposits such as Pb, As, Sn, etc.. The latter are of igneous origin and contain traces of Hg. Natural weathering and man's exploitation of these deposits and use of mercury in chloride and caustic soda production, in paper production, in Hg containing fertilizer, etc., have introduced and still introduce many different forms of Hg into the environment. According to Figure 49 the major pathways of the Hg cycle are mediated by micro-organisms. However, a closer examination of the experimental set-ups used to study the transformation of Hg species show that also abiotic pathways could also play a role. The most important limitations in the transformation experiments are the extremely high inorganic mercury concentrations used. For example, additions of 5 to 100 mg of inorganic Hg salts per kg sediment are usual in these investigations. For comparison background concentrations of Hg in sediments range from 0.02 to 0.05 mg Hg-T/kg DW of sediment (section 3.3). The very high Hg concentrations used in the experiments are selective for Hg-resistant bacteria. Presently, it is not clear if these organisms also carry out the Hg methylation under low environmental mercury concentrations since Hg-resistance can be induced by high Hg concentrations used in the model experiments (Robinson and Tuovinen, 1984).

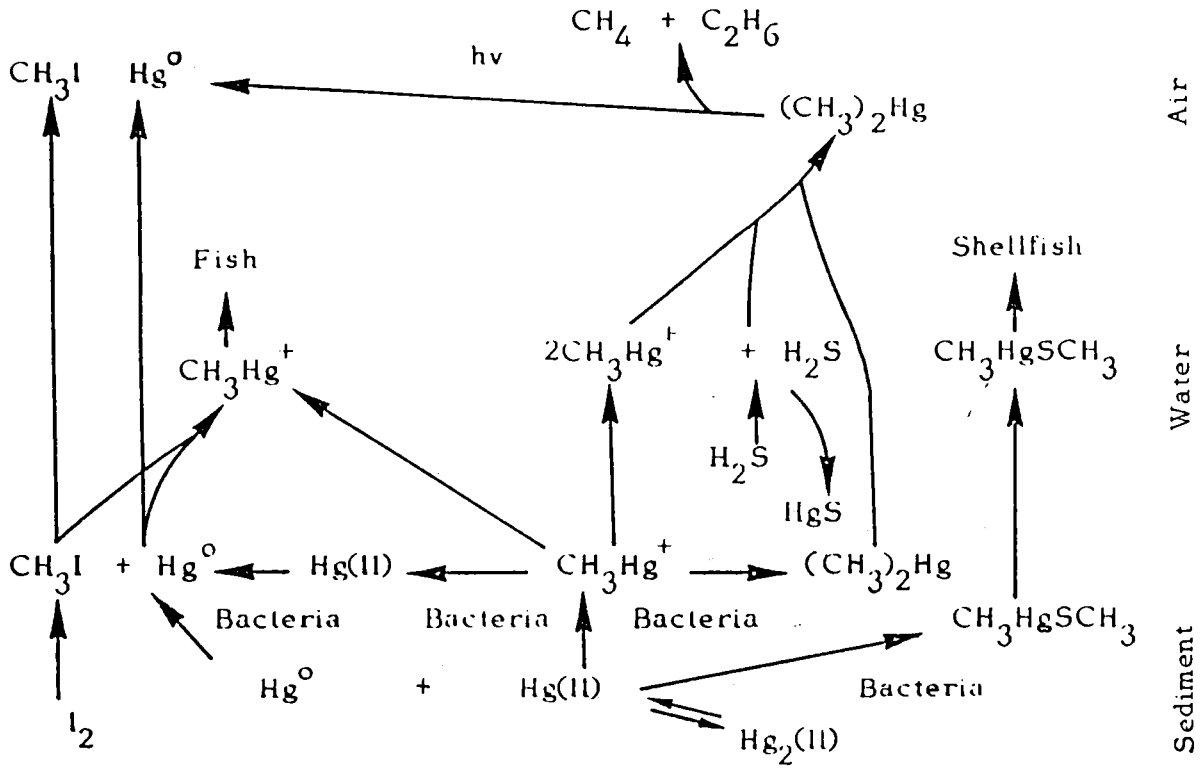



Figure 49. The mercury cycle (Wood and Wang, 1983)

4.2.1 Mercury transformation by bacteria and the origin of methyl mercury

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

$$Hg^{++} \xrightarrow{CH_3\text{-}B_{12}} (CH_3)Hg^+ \xrightarrow{CH_3\text{-}B_{12}} (CH_3)_2Hg$$

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

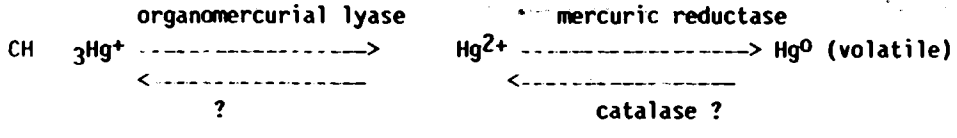
Since it seems that Hg methylation is related to Hg-resistance (and to the resistance to other toxicants) it is interesting to investigate the frequency of Hg-resistant strains among the total number of bacteria isolated from the environment. Colwell et al. (1976) isolated bacteria strains from Chesapeake Bay. The great majority of these bacteria belonged only to seven generic groups (Figure 50). Of these seven groups Vibrio, Pseudomonas, Achromobacter/Alcaligenes/ Acinetobacter and Cytophaga/Flavobacterium species accounted for about 70% of the total number of bacteria strains isolated, but when tested for Hg-resistance about 70% of the Hg-resistant species belonged to Pseudomonas spp.. Also the frequency of resistance to various Hg species was different for strains isolated from water and from sediments (Figure 51).

Hg-resistance seems to be related to Hg methylation but it is not a sufficient characteristic. Various Hg-resistant bacteria strains also carried out different Hg transformations. Vonk and Sijpesteijn (1973) showed that pure cultures of Hg-resistant freshwater 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 Hg 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, six were gram-positive cocci (3 Staphylococcus sp. and 3 Streptococcus sp.). No difference between the aerobic and the anaerobic production rate of MeHg could be established because of the great variability of the results obtained. Blair et al. (1974) isolated seven Hg-tolerant bacteria from Chesapeake Bay. Although most of them anaerobically produced only $Hg^0$, one obligate anaerobe strain generated both $Hg^0$ and $CH_3Hg^+$. One of the facultative anaerobes produced both $Hg^0$ and $CH_3Hg^+$ under anaerobic conditions but $Hg^0$ under aerobic conditions only during the first 24-48 hours. Another facultative anaerobe produced anaerobically only $Hg^0$ and one of the species transformed Hg species aerobically. In another set of eight Hg-resistant strains isolated from the Chesapeake Bay and one from the Cayman Trench only two strains, one of P. fluorescence under aerobic and one of an enteric bacterium under anaerobic conditions could methylize Hg (Olson et al. 1979). With the exception of one strain, where the volatilization under anaerobic conditions was five orders of magnitude higher, total volatilization of Hg of the other 8 strains under aerobic conditions was about the same as under anaerobic conditions. About 30 to 60% of the initial amount present were volatilized within 24 hours. In the following 24 hours the volatilization was one or two orders of magnitude lower. All other strains tested could transform $Hg^{2+}$ to $Hg^0$. Mercuric reductase genetically encoded in plasmids mediated the volatilization. Volatilization was shown to be a phenomenon different from methylization. A strain of C. cochlearium which could decompose DiMeHg 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 inorganic Hg salts.

Sprangler et al. (1973) found that 30 bacterial cultures isolated from freshwater could aerobically degrade MeHg and 21 cultures could anaerobically degrade MeHg. Billen et al. (1974) showed that MeHg was decomposed, anaerobically and aerobically, in the presence of bacterial cultures obtained from river sediments. Furakawa et al. (1969) demonstrated that a bacteria strain (Pseudomonas sp.) from soil could decompose MeHgCl to methane and $Hg^0$. From these data it seems that more bacteria species are capable of reducing Hg salts to metallic Hg than to MeHg and many bacteria are also able to decompose MeHg.

At present it is believed that any amount of MeHg produced is released from the microbial system into the surrounding water, and it enters the aquatic food-chain either as dissolved MeHg associated with organic matter or with particles.

The reduction of MeHg to $Hg^{2+}$ and to $Hg^0$ are both catalysed by enzymes coded in the DNA of bacterial plastids 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). Little is known about the enzymes which transform $Hg^0$ to $Hg^{2+}$ and then methylate $Hg^{2+}$ to MeHg, but it is very likely that the ubiquitous catalase (present in bacteria and animal tissues) may be involved in the transformation of $Hg^0$ to $Hg^{2+}$ (Robinson and Tuovinen, 1984):



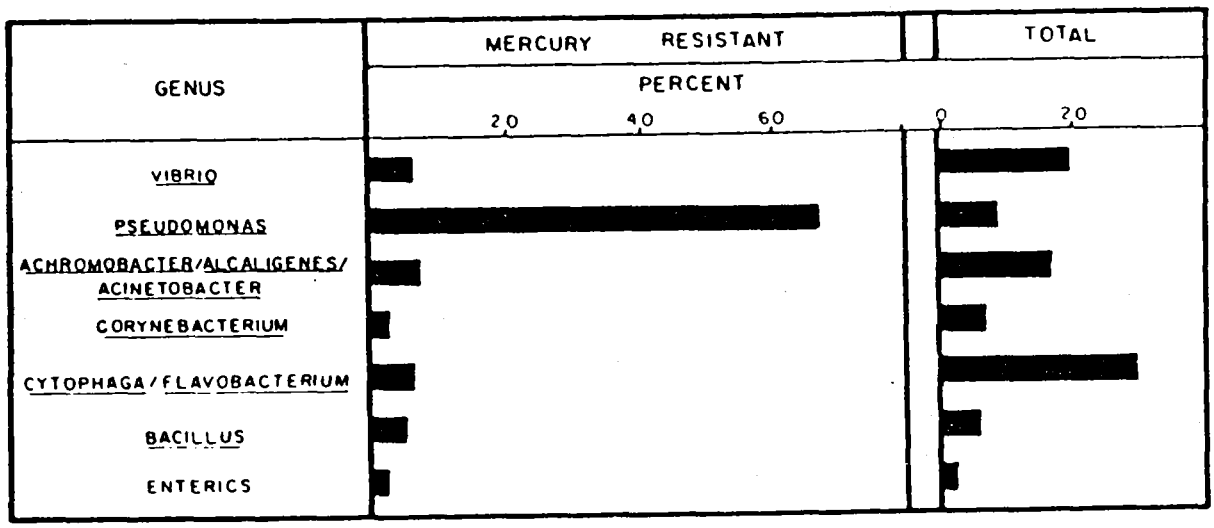



Figure 50. Average distribution of genera in total and $HgCl_2$—resistant populations (Colwell et al. 1976)

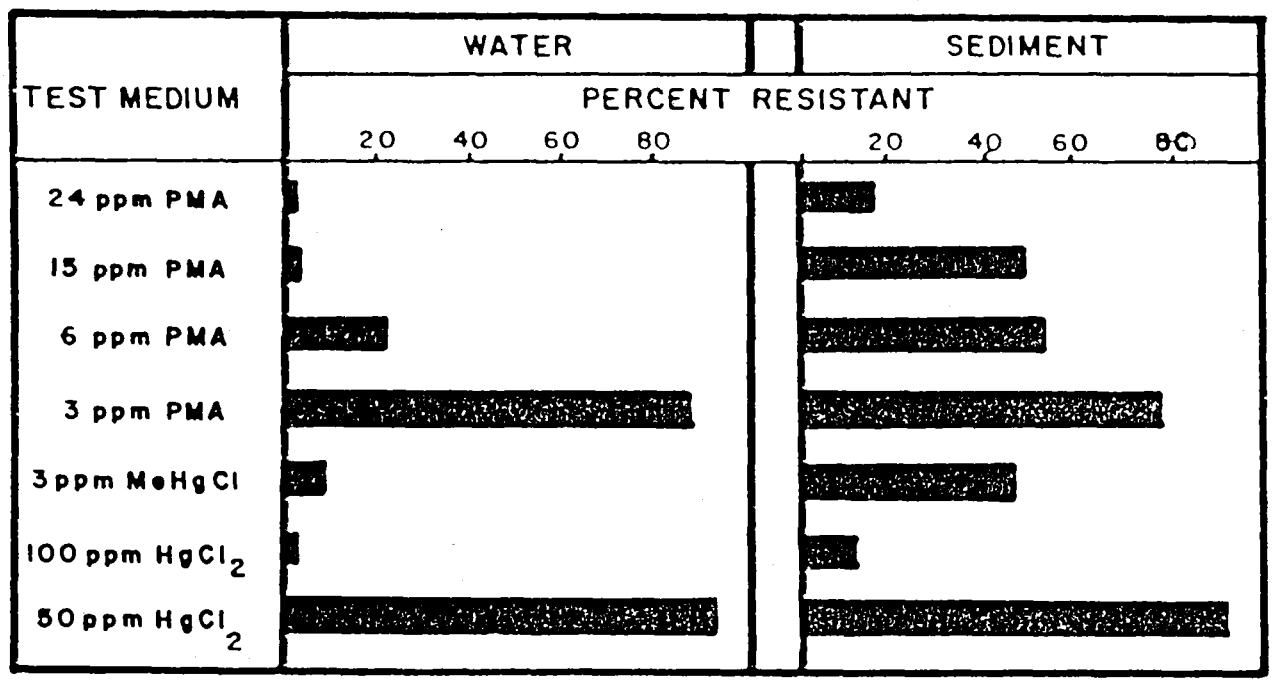



Figure 51. Comparative percentage of mercury-resistant isolates from sediments and water (Colwell et al. 1976)

Hydrogen sulfide is extremely effective in volatilization and precipitation of Hg 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 sulfate reducing bacteria have access to sulfate under anaerobic conditions. In the estuarine environment, the reduction of sulfate by Desulfovibus species to produce hydrogen sulfide is important in reducing $CH_3Hg^+$ concentrations by $S^+$-catalysed disproportionation to volatile $(CH_3)_2Hg$ and insoluble HgS:

$$2\ CH_3Hg^+ + H_2S \longrightarrow (CH_3)_2Hg + HgS$$

The formation of MeHg 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 $Hg^{2+}$ to HgS. Under aerobic or partially aerobic conditions HgS may be oxidized to the sulfate form which can then be transformed into MeHg. The HgS is not convertible to $CH_3Hg^+$ without prior conversion to a soluble salt or to $Hg^0$ (Ehrlich 1981).

### 4.2.2 Mercury transformation by phytoplankton and seaweeds

The great attention given to the transformation of Hg 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 Hg transported by bubbling air into a saturated iodine in KI solution. They observed that during a 9-day experiment the culture solution containing 10 $\mu$M $HgCl_2$ without algae lost 22% of the Hg present at the beginning of the experiment while about 75% of the same Hg was lost when the medium was inoculated with Chlorella populations ranging from 300 million to one thousand million cells/L. Later, Betz (1977) also observed that in a culture of the marine Dunaliella tertiolecta an increase of volatile Hg adsorbed on charcoal coincided with the maximum concentration of chlorophyll a. The experimental design was not optimal and in neither experience was the nature of the volatile Hg investigated, but, nevertheless, the experiences show that micro-organisms other than bacteria and fungi can also transform Hg species.

Seaweeds such as kelp produce iodine and it has been shown that methyl iodide can be synthesised by 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 methylation of $Hg^0$. It is possible that this plays an important part in the formation of MeHg in open ocean waters remote and isolated from sediments by the thermocline.

### 4.2.3 Batch and in situ experiments

Many authors have added Hg salts to freshwater and marine sediments and determined the net MeHg production (review: Bisogni 1979). In these experiments high amounts of inorganic Hg were added. Usually the experiments lasted 10 to 50 days but some were extended to several months. Because of the high Hg concentrations (selective for Hg-resistant bacteria) and long incubation time the results of these experiments cannot easily be extrapolated to natural conditions. Furthermore, under natural conditions other Hg species will be present then the Hg salts added. Still another point needs consideration. In none of these experiments a destinction was possible between methylation and demethylation processes, therefore, all MeHg levels observed are the results of net result of methylation and demethylation.

Olson and Cooper (1976) experimenting with San Francisco Bay sediments found that under anaerobic conditions the MeHg concentration in the sediments was higher than under aerobic conditions (Table 38). Higher MeHg concentrations were also observed in sediments with higher organic content. After 30 days under anaerobic conditions only about 0.1% of the 100 mg $HgCl_2$/kg added to the sediment and 0.8% of the 10 mg $HgCl_2$/kg sediment were transformed into MeHg. In sediments with the lowest organic content, to which 10 mg $HgCl_2$/kg was added, no additional MeHg could be detected. Autoclaved and non-autoclaved sediment samples without Hg additions served as control. Of special interest is that, with the exception of sediment A, none of the controls produced any MeHg neither under aerobic nor under anaerobic conditions and also sediment type A produced MeHg only under anaerobic conditions. The non-autoclaved sample of this sediment produced about four times more MeHg than the autoclaved sample. This raises the question why was no MeHg produced in the controls except under anaerobic conditions. It may also be possible that the amount produced, was below detection limits.

Table 38. 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 DW) | net production in ng/g 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 | ND | 0.6 |
| | 100 | 0.5 | 0.8 |

ND = not detected

Similar experiments were carried out on autoclaved and untreated sediments from an anthropogenically contaminated area in the Haifa Bay. Large amounts of mercury (100 µg Hg-T/L) added with the bacteria medium to the flasks containing the sediments did associate with the sediment and with the surface of the glass flasks. MeHg was observed both under aerobic and anaerobic conditions in the medium above the sediment (Table 39). The MeHg in the sediment was not determined and hence these results are not directly comparable with the experiments discussed previously.

Table 39. Levels of methyl mercury found in the medium above the sediments in percentage of the original added Hg amounts (Berdicevsky et al. 1979).

| | Hg in medium µg/L | MeHg in medium in % of total added after 2-nd | 5-th | 12-th 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 MeHg formed in the medium decreased with increasing Hg concentration and with time of exposure. Unfortunately the MeHg in the sediments was not determined. The same authors also observed that under anaerobic conditions the addition of 1 mg $HgCl_2$/L 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. In order to show that bacteria were necessary to produce the MeHg the authors added Hg-resistant bacteria strains to autoclaved sea water-sediment media. As control autoclaved medium without bacteria was used. Only in the media with bacteria very small amounts of MeHg, i.e. 0.01 to 0.04% of the Hg added at the beginning of the experiment, could be detected. Obviously these results can only serve as a rough indication of what might happen in the environment, since the system also contained, besides sediments, considerable amounts of organic substances of the culture medium. The reduction of MeHg production with duration of the experiment also seems to indicate that the bacteria fauna changed considerably. In fact toxic effects were observed at 1 ug Hg/L under anaerobic conditions and at 10 ug Hg/L under aerobic conditions.

Recently Compeau and Bartha (1984) investigated the influence of redox, pH and salinity on the Hg transformation of Hg species in estuarine sediments using reactors to control and continuously monitor several parameters. They observed that both salinity and Eh(mV) influenced Hg methylation. In sediments spiked with 100 mg $HgCl_2$/kg sediment after 16 days, the concentration of MeHg reached a steady state between methylation and demethylation (Table 40).

Table 40. Influence of salinity and redox potential on the net formation of methyl mercury (Compeau and Bartha, 1984).

| Eh (mV) | salinity | mg MeHg/Kg 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 |

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 sediment slury produced a doubling of the steady-state MeHg concentration. Duringthe experiment volatilization was minimal. Adding 1 mg of MeHg/kg of sediment under anaerobic conditions (- 220 mV) showed that demethylations was higher (double) at a salinity of S = 25 than at a salinity of S = 4. Under aerobic conditions (+ 110 mV) the demethylation was practically the same at both salinities tested and lower than under anaerobic conditions. Again the high additions of $HgCl_2$ has most probably produced artifacts so that these experiments supply only limited amounts of useful information.

Recently several authors (Callister and Winfrey 1986, Korthals and Rudd 1987, Furutani and Rudd 1980, Ramlal et al. 1985, Xun et al. 1987) have used inorganic radio-Hg additions to freshwater model systems. In this way at least the sediment concentrations in inorganic Hg were only slightly increased. In these model experiments freshwater concentrations, however, are still two orders of magnitude higher than natural ones. Of course, the species distribution and abundance is different markedly from the natural one. Therefore, the authors refer to "potential methylation". With this experimental set-up it could be shown that potential net methylation occur also in the freshwater column. Adding radio-MeHg to water and sediment samples also potential demethylation could be demonstrated. However, in nearly all experiments the potential demethylation exceeded potential methylation. To the reviewer's knowledge, similar experiments have not been carried out on marine samples.

Of great interest are the in situ experiments of Bothner et al. (1980). 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 (Puget Sound, Washington, USA). 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 Hg concentration in the sediment and the interstitial water of the station 3A were much higher than those of the uncontaminated station 3. In the experiments Hg-free air was passed through the bell jars. The different (operational defined) forms of volatile Hg in the passing air stream and dissolved Hg in the water above the sediment were determined. In order to obtain a blank and to block the mercury evolving from the sediment, a glass plate was placed under the bell jar which isolated the water contained in the bell jar from the sediment. In both stations no volatile Hg deriving from the sediment could be detected since "blank" and "sample" gave statistically equal results. In both conditions, about 1 ng Hg/h was carried with the air stream into the Hg traps, so it is clear that the Hg was stripped from the water and did not originate in the sediments. However, determination of dissolved Hg 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 Hg in the interstitial water (0.03 µg/L) and in the overlying water (0.01 µg/L). It is interesting to note that in the blank condition and when the jar was placed directly on the sediment 50 to 75% of the volatile Hg was $Hg^0$ and that the increase in the dissolved Hg in the bell jar at station 3A strangely had no measurable effect on the amount of volatile Hg produced, although the concentration of soluble Hg had increased from 30 to 120 ng Hg/L. 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 sediment then the sediment should contain about 70 µg $Hg/cm^3$ (FW = 0.7 DW; specific gravity 2.5). That means that during a year 0.8% of the Hg in the first cm of the sediment was lost to the water as soluble Hg. A second experiment, in which unfortunately the flux of volatile Hg was not determined but one bell jar was kept under limited oxygen, showed that the concentration of dissolved Hg in sea water above the sediment increased more in the oxygen-limited conditons than in the previous oxygenated arrangement.

### 4.2.4 Mercury transformation by higher marine organisms

The data on methylation in higher organisms are still conflicting. The indigeneous microflora of isolated intestines of six fresh water fishes could methylate Hg 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 Hg 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 Hg (Pan-Hou and Imura, 1981) but some of these pure cultures, which had a higher Hg resistance, could demethylate MeHg. The intestinal flora of rats can methylate $HgCl_2$, but no methylation occur through cow rumen microflora. Most of the mercuric compounds passed through unchanged, only a small amount was reduced to $Hg^0$ (Thayer and Brinckman, 1982). It seems that only micro-organisms (including those in the intestine) can methylate Hg.

The liver of marine mammals has been indicated as a site for demethylation because MeHg is present at low percentage of the total high concentrations, but experimental evidence is still missing. Also in some marine fish low MeHg percentages have been observed (section 3.7).

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

4.2.5 Abiotic Hg transformations

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

Photomethylation using methanol, ethanol, acetic and propionic acids produced MeHg from mercuric chloride (Akagi et al. 1977). About 0.1% of the total $HgCl_2$ present was transformed into MeHg in 20 hours. Hayashi et al. (1979) also observed photomethylation of inorganic Hg when aliphatic amino acids were irradiated with UV light for 4 hours. The formation of MeHg 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 MeHg 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 Hg (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 (1982) investigated several factors which influence the Hg 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 and 1 mg HA, one would obtain the following in 3 days at pH 7. Starting from the influence of temperature (because, as can easily be 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 at a concentration of 750 mg Hg/L;
6 mg HA methylate 0.000003% of the inorganic Hg present in 3 days;
1 mg HA/L methylate 0.0000001% of the inorganic Hg per day; and
1 mg HA/L methylates 0.000035% of the inorganic Hg/year

This is a very small amount of MeHg indeed. Model experiments under conditions which are near those found in the natural environment, especially at much lower Hg concentrations, are needed to confirm this extrapolation. However, only a very small amount of MeHg per unit volume is present in aquatic biota (see section 4.2.6).

4.2.6 Methyl mercury "requirements" of marine biota

The data discussed above show that small amounts of MeHg can be produced by bacteria and abiotically. Unfortunately in all experiments high concentrations of Hg-salts have been used which allows an extrapolation only to highly contaminated environments. In the in situ experiment of Bothner et al. (1980) no MeHg could be detected but $Hg^0$ was produced. Could it be possible that the amount of MeHg produced in uncontaminated marine environment is too small to be detected under the experimental conditions employed by the authors?

Following a model calculation carried out by Topping and Windom (1981) on the amount of total mercury incorporated by phytoplankon, a similar calculation may give an idea on the amount of methyl mercury to be removed from sea water to allow phytoplankton an accumulation of 2% MeHg of Hg-T.

(a) Assuming a phytoplankton primary production of 50 g $C/m^{-2}$ $year^{-1}$ which is about equal to a production of 100 g DW $m^{-2}$ $year^{-1}$ (Topping and Windom, 1981), in an euphotic zone of 100-m depth 100 g DW of phytoplankton are produced in 100 $m^3$ of sea water. This equals a phytoplankton production of 1 mg DW $L^{-1}$ $year^{-1}$.

(b) Plankton caught with small pore size plankton nets (mainly phytoplankton) contains about 100 ng Hg-T/g DW (Table 10). Hence 1 mg DW plankton biomass accumulates about 0.1 ng Hg-T from one litre of sea water a year.

(c) Assuming that 20% of the Hg-T is MeHg then phytoplankton should accumulate 0.05 ng of MeHg $L^{-1}$ $year^{-1}$ or 0.0001 ng MeHg $L^{-1}$ $year^{-1}$.

For comparison the means of the Hg-T concentration in sea water in the Mediterranean areas range from 7 to 25 ng Hg-T/L. In coastal areas the primary production will be higher, but nevertheless, it will still remain a very small amount of MeHg/L. Certainly too small to be detectable in a field experiment with conventional techniques. Since the annual production of higher trophic levels is much smaller than that of phytoplankton the uptake of MeHg by these organisms, although they reach higher Hg concentrations than the phytoplankton, should not accumulate higher amounts than the phytoplankton from sea water on a per litre basis.

## 4.3 Uptake and release of different mercury species by biota

Few experiments have been carried out on Mediterranean organisms, therefore, in order to gain an understanding of the dynamics of uptake and release of mercury results obtained on marine organisms from other areas have also been considered.

Fisher et al. (1984) compared heat-treated cells (45°C) of unicellular algae with live cells after exposing the cells to radioactive inorganic Hg diluted in different concentrations of stable inorganic Hg (to obtain different specific activities) and then confronted the concentration factors obtained. 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 Hg association with the cells was directly proportional to the external Hg concentration, as would be expected if the internal Hg concentration were not regulated. As the cells divided to produce new cells the total particulate Hg content increased but the Hg concentration per cell remained constant. Heat-killed cells accumulated comparable amounts to living cells. The authors interpreted this to mean that the Hg 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 earlier that formalin-killed diatoms accumulated more Hg than live cells, most probably because the surface of the cells had been changed by the formalin treatment. Also Davies (1976) concluded that Hg is taken up by passive diffusion.

Results with freshwater planktonic organisms indicate a very rapid elimination of MeHg, with a biological half-time ($BT_{1/2}$) of about 3 days (Huckabee et al. 1979). This is most probably due to fast growth during elimination and hence the fast loss is mainly due to "biological dilution".

The uptake of Hg by molluscs has been studied by Cunningham and Tripp (1975), Fowler et al. 1978, Miettinen et al. (1972), Unlu et al; (1970) and Wrench (1978). Working on the Mediterranean species Fowler et al. investigated the uptake and release (loss) of radioactive-labelled $HgCl_2$ and MeHg from food and water by mussels (M. galloprovincialis) and shrimps (Lysmata seticaudata). When the mussels were exposed to $HgCl_2$ and to MeHg only in sea water, the uptake of MeHg 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 MeHg from water is not an important route into the mussels. When both radioactive-labelled water and labelled food (phytoplankton for mussels and mussels for shrimps) were offered, after 35 days the mussels had accumulated about twice as much radioactive MeHg as $HgCl_2$ and the shrimps had 10 times more MeHg than $HgCl_2$. This shows that MeHg is accumulated easier than inorganic Hg. The relative amounts accumulated depend, 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 Hg and MeHg faster under in situ conditions than in the laboratory. Probably more food was available under in situ conditions and hence the "biological dilution" was greater. But strangely, the MeHg was lost by mussels under in situ conditions faster (smaller half-time) than

the $HgCl_2$. Unfortunately the authors did not report whether the in situ mussels had grown more than the mussels kept in the laboratory. In shrimps no difference was noted.

| | biological half-times in days | |
|---|---|---|
| | MeHg | $HgCl_2$ |
| mussels in situ | 63 | 82 |
| in laboratory | 380 | 140 |
| shrimps in situ and in laboratory | 530 | 110 |

The validity of the results on mussels and shrimps depends on the assumption that the Hg 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 Hg. Summarizing also the laboratory results from other authors, in molluscs the biological half-time ($BT_{1/2}$) for inorganic Hg range from 20 to 40 days and for MeHg from 150 to 1000 days (Miettinen et al. 1972; Jaervenpaeae et al. 1975; Seymour and Nelson, 1971; Cunningham and Tripp, 1975). The variation in the biological half-time are due to the metabolic activity and growth rate during loss experiments, and without information on these parameters the data are difficult to compare. Experiences from transplanting mussels from contaminated sites to clean sites showed that the mussels transplanted in the Gulf of Trieste from a site exposed mainly to Hg originated from mining wastes and natural run-off from a Hg geochemical anomaly to a clean site had a BT1/2 of approximately 60 days (Figure 31). In similar transplantations Riisgard et al. (1985) observed very different $BT_{1/2}$ for mussels (M. edulis) collected near contaminated sites. One site (Chiminova) was contaminated by a factory producing Hg-containing fungicides and another site (Gryne no. 42) through leakage from a waste deposit of the Chiminova factory. The BT1/2 of the mussels from the Chiminova site had a very long $BT_{1/2}$ of more then 300 days while the mussels from the Gryne site had a $BT_{1/2}$ of only about 50 days. The authors determined also the Hg species in these mussels before the elimination experiments and they found that only about 25% of Hg-T was organic in the mussels from the two sites of which about 1% was phenyl-Hg. However, in the mussel from the Gryne site only 15% of total organic Hg was MeHg (about 4% of the Hg-T) while in the mussels from the Chiminova site 87% of the total organic Hg was MeHg (about 22% of the Hg-T). The authors explained the difference in $BT_{1/2}$ with the difference in chemical species and relative amounts of these Hg species taken up in the different sites. But some questions still remain: in what form were the organic Hg which was not identified as MeHg or phenyl-Hg? Also another mussel (Macoma balthica) exposed to the wastes from the Cheminova site released so little Hg that no $BT_{1/2}$ could be estimated. But in this mussel only about 6% of the Hg-T were MeHg and phenyl-Hg. These experiences with mussels exposed in natural situations illustrate that laboratory results cannot be easily used for an interpretation of field observations and also in field observations it is very important to determine the chemical Hg species involved.

Experimental studies of uptake, accumulation and loss of MeHg and inorganic Hg in two species of flatfish (plaice and thronback ray) both from water and from food have been carried out by Pentreath (1976a). Uptake of inorganic Hg by plaice from water was only directly proportional to the water concentration up to 3 ug Hg/L. The loss occurred with a $BT_{1/2}$ of 190 days. A similar $BT_{1/2}$ was observed in the thronback ray. However, when exposed to MeHg in sea water no measureable loss in the ray could be detected. When Hg was fed to plaice in the form of radioactive labelled worms (Nereis), the uptake efficiency for inorganic Hg was low (3 to 14%), while the efficiency for MeHg was very high (80 to 100%). The loss of inorganic Hg was quite rapid ($BT_{1/2}$ from 30 to 60 days) and the loss of MeHg was very slow ($BT_{1/2}$ from 275 to 325 days). Also the tissue distribution of the two Hg forms was very different. When the fish were exposed to MeHg, the MeHg was partitioned strongly into the muscle, similarly to the distribution observed in fish sampled from natural environments. On the other hand when the fish were exposed to inorganic Hg, the inorganic Hg was largely found in the body organs. These results are consistent with the diet being the major source of MeHg, almost complete uptake of MeHg from the food, and little or no demethylation and subsequently little or no elimination from the organism. Inorganic Hg, on the other hand is taken up with a low efficiency, which may be due to low absorption and fairly rapid metabolism in the liver and a fairly rapid excretion.

Since HgS is a source of Hg to the environment it is interesting that the uptake of HgS from sediments by freshwater fish has been studied (Gillespie and Scott, 1971). Although uptake from control sediments (0.024 µg Hg/kg DW) was appreciable, fish exposed to sediments containing 50 mg Hg/kg DW as HgS accumulated considerable higher amounts of Hg than the controls.

## 4.4 Transport through the food-chain

Experiments on the uptake from one trophic level to the next have been discussed in section 4.3.

Buffoni et al. (1982) and Bernhard (1985) used another approach to study the uptake and release dynamics of Hg in a marine food-chain. These authors developed a relatively simple model of a pelagic food-chain (sea water, plankton, sardine, tuna). The Hg concentration in the muscle tissue of tuna is of special interest, because the bluefin tuna caught in the western Mediterranean can be divided into two distinct populations according to their mercury concentrations: one "low-mercury population" and the other "high-mercury population" (section 3.4.5). Tuna migrates over wide areas such as the western Mediterranean and the eastern Atlantic. Therefore, their Hg levels should be indicative for the Hg concentration in their food-chain and in the marine environment through which the tuna migrate.

As data base for the model served general data available on Hg metabolism (section 4.3) and specific Hg-T concentration in muscle tissue versus the weight of specimens of tuna and sardines from the Italian waters and the Strait of Gibraltar. The model considered the uptake of inorganic and MeHg from sea water and from the food of tuna and of sardines and the release (loss) of both Hg species from these two species according to published biological half-time for fishes. Sardines were taken to represent the prey of tuna because Hg-T versus weight data on sardines were available for the two regions considered. Also other pelagic organisms showed the same differences in Hg-T concentrations between the western Mediterranean and the Atlantic (section 3.4).

The growth of sardines was modeled with Bertalanffy's growth equation and for the growth of tuna a new fomula was developed. The uptake of inorganic and MeHg could not be modeled for phyto- and zooplankton because no data are available on the relationship of Hg concentration versus size for single plankton species. Therefore, the authors had to use a common concentration factor to present the first trophic levels (plankton). It may be worthwhile pointing out that in this way the first part of the model is static, and only the part of the model which deals with uptake by the sardines and by the tuna is dynamic.

The curves generated by the model fit well the Hg-T concentration observed in both populations and predict that little inorganic Hg will be present in the muscle of the tuna (Figure 52). Also the Hg-T data from sardine from the Strait of Gibraltar and the Italian coast are well presented by the curves shown in Figure 53. The model predicts that in sardines proportionally more inorganic Hg is present in the muscle tissue than in the muscle tissue of tunas, because the sardines belong to a low trophic level than the tuna. In detail it is predicted that the inorganic Hg will increase until an equilibrium condition between uptake and release of the inorganic Hg is established, while the MeHg concentration continuously increase with size. The prediction of this general distribution pattern of Hg-T and MeHg has been confirmed in sardines and in bonitos (see below).

On the basis of their model simulations the authors could explain the differences in the Hg concentrations observed in the two bluefin populations; how the Hg-T can increase with size of the organisms, and how at the same time the percentage of MeHg 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 transform inorganic mercury into MeHg, because the difference in the uptake and loss kinetics between MeHg and inorganic Hg are sufficient to explain the high MeHg enrichment observed in older specimens and in species located in the higher trophic levels. Different growth rates of tuna could be the cause of the Hg-T differences, but simulating various growth rates in the "low-mercury-tuna" showed that only a reduction of eight to ten times in the

growth rate could produce Hg-T levels which were similar to those obtained in the "high-mercury-tuna" (Bernhard and Buffoni, 1982). In addition, the data on growth of tuna from the Mediterranean and the Atlantic differ insignificantly from each other (Sella, 1929; Rodriguez-Roda, 1957; Tiews, 1960; Scaccini, 1965; Sara, 1973; Mather, 1974). These observations show that the growth rates cannot be the cause of the Hg differences observed.

Due to lack of suitable data on the Hg concentrations versus weight or age in representative plankton organisms (the food source of the sardines) the Hg concentrations of sardines from the two areas were used to predict the Hg levels in plankton, and assuming the same concentration factor for sea water/plankton (CF = 5000) also for a hypothetical sea water concentration. The calculations indicated that plankton from the western Mediterranean should have about five times the Hg concentration of Atlantic plankton. The same concentration differences should occur in the sea water of the two regions.

Buffoni et al. (1982) and Bernhard (1985) examined the data on Hg concentrations published, and they concluded that differences in Hg-T predicted by the model will not become evident because of the great variability of the sea water and plankton data published (section 3.2 and 3.4.1).

This prediction has recently been criticized by Aston and Fowler (1985) and Aston et al. (1986). Despite the fact that these authors acknowledge the uncertainty and variability of the sea water data they still maintain that the present available data are sufficiently precise to demonstrate that Hg levels in the Mediterranean are the same as those of the Atlantic. Likewise these authors maintain that general data on mixed plankton samples and euphausids without any indication of the Hg concentration versus size relationship are sufficient to demonstrate that no difference exists between Mediterranean and Atlantic plankton.

The Strait of Gibraltar may be an ideal site for testing this prediction because lighter Atlantic water is flowing into the Mediterranean in the surface layers and heavy Mediterranean water is flowing out to the Atlantic in the bottom layers. The discussion in section 3.2 on the available data and especially the conflicting results obtained in the Strait of Gibraltar show, however, that the uncertainty of the data is still too great to reveal a possible difference.

The same authors voice another criticism, namely that the sardines are not a representative food item of the tuna, because they observed once that during a fishing contest near Monaco all small tuna caught had exclusively euphausids in their stomachs. Scaccini (1965) summarizing the biology of Thunnus thynnus writes that very small to immature tuna feed on micro- and macro-plankton (including euphausids), larger tuna feed on many different pelagic species such as sardines, anchovy, Scomber spp, but also molluscs such as sepia and squid and crustaceans. In the model sardines were taken as a typical food item for tuna because extensive Hg data existed for sardines both from the Mediterranean and Atlantic.

Like all models, the tuna food-chain models need verification. Some predictions have already been confirmed. Capelli et al. 1986 (Figure 18) found that the distribution of inorganic and organic Hg in Sarda sarda occurs as predicted with inorganic Hg reaching a steady state and MeHg continues to increase with the weight of the specimens. A similar distribution has recently been observed for sardines (Cerrati, 1987).

The weakest part of the model is its static part. The model's first trophic levels need dynamic modelling since at present it is based only on concentrations factors and estimated on the possible Hg concentrations in plankton. Unfortunately, data on the distribution of Hg species in natural phytoplankton and zooplankton organisms of different size are missing for the Atlantic and Mediterranean. The importance of these data for an understanding of the dynamics of Hg species in the first trophic levels is shown by the increase of Hg level with size in euphausids (section 3.4.1). Once similar data becomes available also for other plankton organisms, the Hg dynamics in the organisms belonging to the first trophic levels can be modeled, and the model may be able to differentiate the fluxes of organic and inorganic Hg in the Mediterranean and the Atlantic.

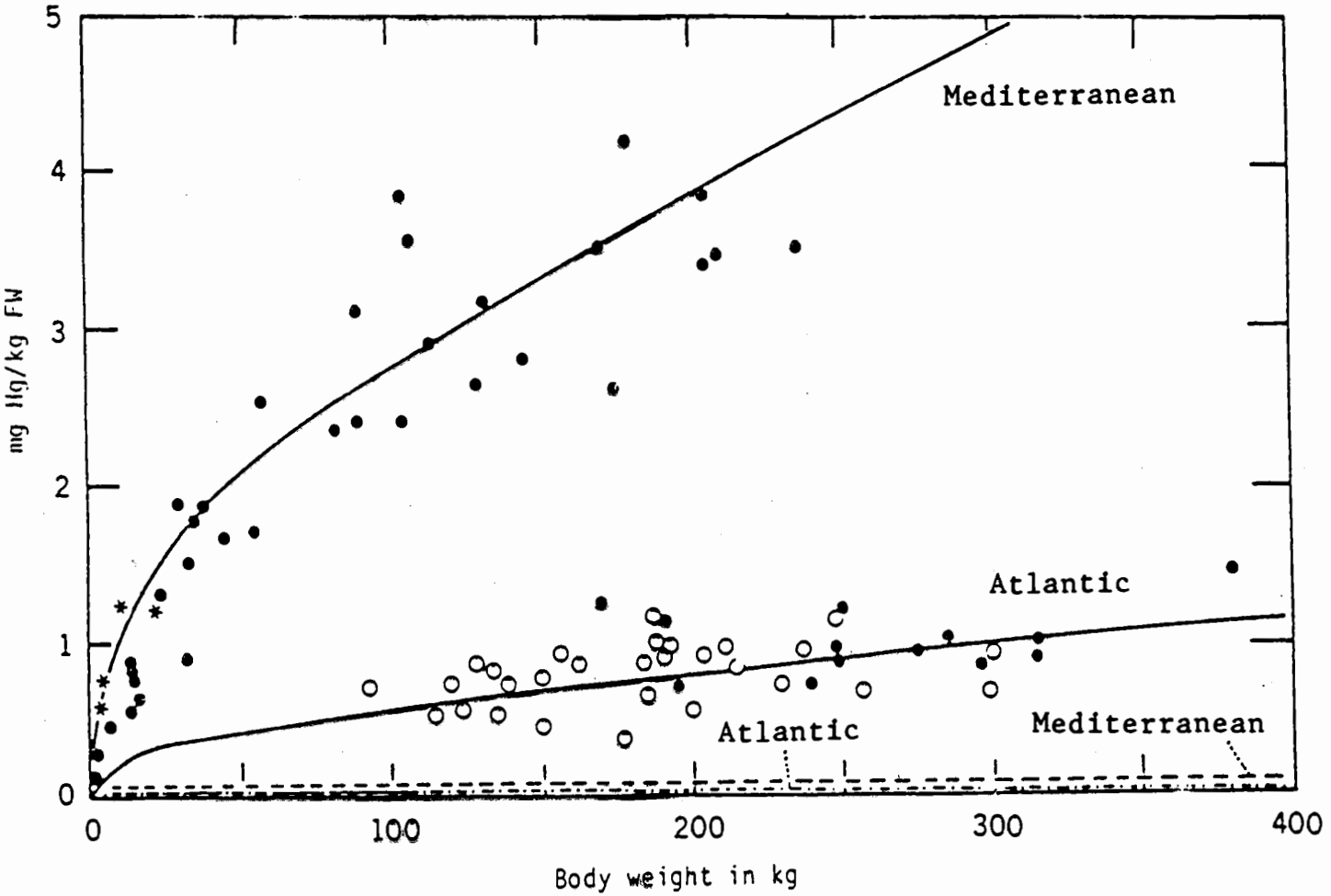



Figure 52. Total mercury concentrations in Thunnus thynnus from the Strait of Gibraltar (O), Tyrrhenian Sea (●) and Spanish coast (✱). The continuous lines show total Hg concentrations calculated by a model; intermittent lines show inorganic Hg concentration calculated by a model (Bernhard, 1985).

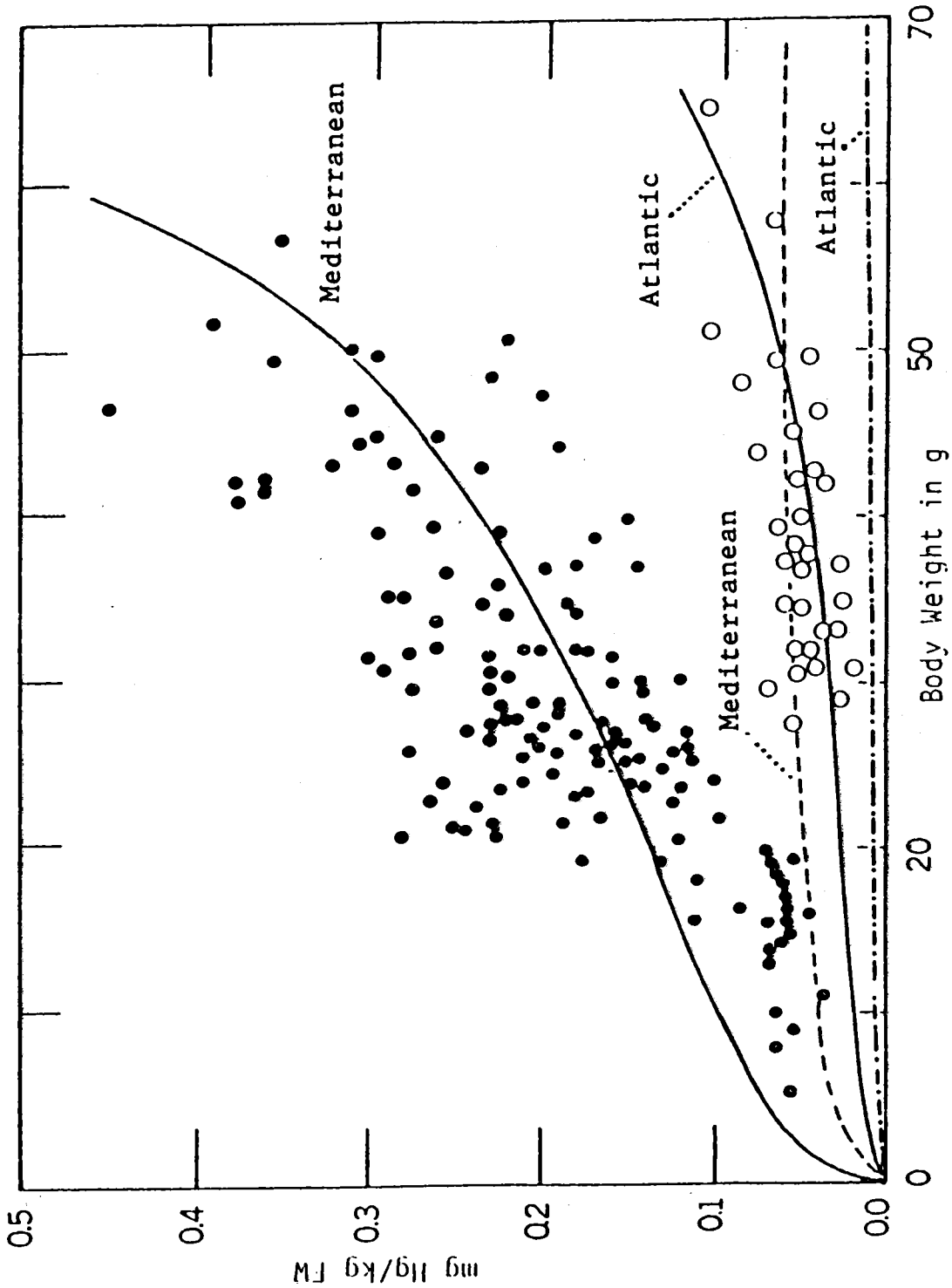



Figure 53. Total mercury concentrations in Sardina pilchardus from the Strait of Gibraltar (O) and Tyrrhenian Sea (●). The continuous lines show total Hg concentrations calculated by a model; intermittent lines show inorganic Hg concentration calculated by a model (Bernhard, 1985).

## 4.5 Biogeochemical cycles

The uncertainties in many Hg concentrations and the general lack of data on fluxes allow only an approximate description of possible pathways and sinks in a general biogeochemical cycle of mercury in the Mediterranean. Zafiropoulos (1986) has listed the main pathways and sinks proposing also some indicative values. However, due to the heterogeneous distribution of Hg in the geological formations of the land surrounding the Mediterranean Sea it does not seem opportune to attempt a general description of the entire Mediterranean. It seems more appropriate to describe the biogeochemical cycle in general terms and illustrate the possible pathways and compartments in an example of the Mediterranean area.

The most important mercury sources for the marine environment are rivers and atmosphere. The mercury in the atmosphere originates from degassing of the land and of the sea, and from emissions of volcanoes (section 3.1). The degassing over mineral deposits (Hg geochemical anomalies) should be considerably higher than over the land with a Hg background concentration, and the degassing over the land should be higher than over the ocean. The predominant Hg species in the atmosphere is $Hg^0$. Soluble and particular Hg constitute about 1% of the Hg-T, but these fractions are involved in the most important fluxes from the atmosphere to the sea and to the land through wet and dry deposition. To these natural sources, anthropogenic Hg species also will contribute, which according to their origin may contain organic Hg also.

The natural Hg 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. In river water practically all inorganic and organic Hg will be bound to organic dissolved matter or associated with particles (either to suspended matter or to the bedload sediments). The high sediment concentrations in the rivers draining natural Hg geochemical anomalies and the higher than background Hg concentrations in sediments of the adjacent coastal areas illustrate this transport route. In the estuaries the larger Hg-containing particles are deposited near the river mouth while the lighter particles are transported further into the sea. At the same time inorganic Hg and the organic Hg produced biotically and abiotically in the river system will be released into the sea water, and together with the MeHg produced in the marine environment, it will be taken up by marine organisms, mainly autotrophs. These autotrophs will then introduce both inorganic and organic Hg into the food-chain. During the path through the food-chain the different uptake efficiencies and release half-time of inorganic and organic Hg enrich the organic Hg (methyl mercury) with respect to inorganic Hg, resulting both in higher total and organic Hg concentrations in older specimens and in species occupying higher trophic levels (section 3.4 and 4.3). The inorganic Hg will increase during the growth of an organisms to a certain relative amount until the uptake and release will reach a dynamic equilibrium at which the concentration of the inorganic Hg will remain about constant and the increase in Hg-T will be entirely due to the increase in methyl mercury (Figures 17 and 53, section 4.3). The Hg associated with particles, faecal materials and dead organisms will sink in the water column and after partially cycling through various detritus feeders and bacteria they will reach the bottom sediments. There Hg associated with inorganic and organic particles and contained in organisms will cycle through the benthic fauna and finally will be deposited and adsorbed in the sediment.

In the sediment, complicate processes abiotically or mediated by micro-organisms will transform the different Hg species. During these processes the methyl mercury is produced which is the predominant Hg species in many seafoods (section 3.7). At present it is not known if also abiotic process in the sediments or biotic and abiotic processes in the water column can produce organic Hg species.

Baldi (1986) has proposed a scheme of such a biogeochemical cycle for the Tyrrhenian Sea with indications on typical concentrations of Hg in the various compartments (Figure 54).

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

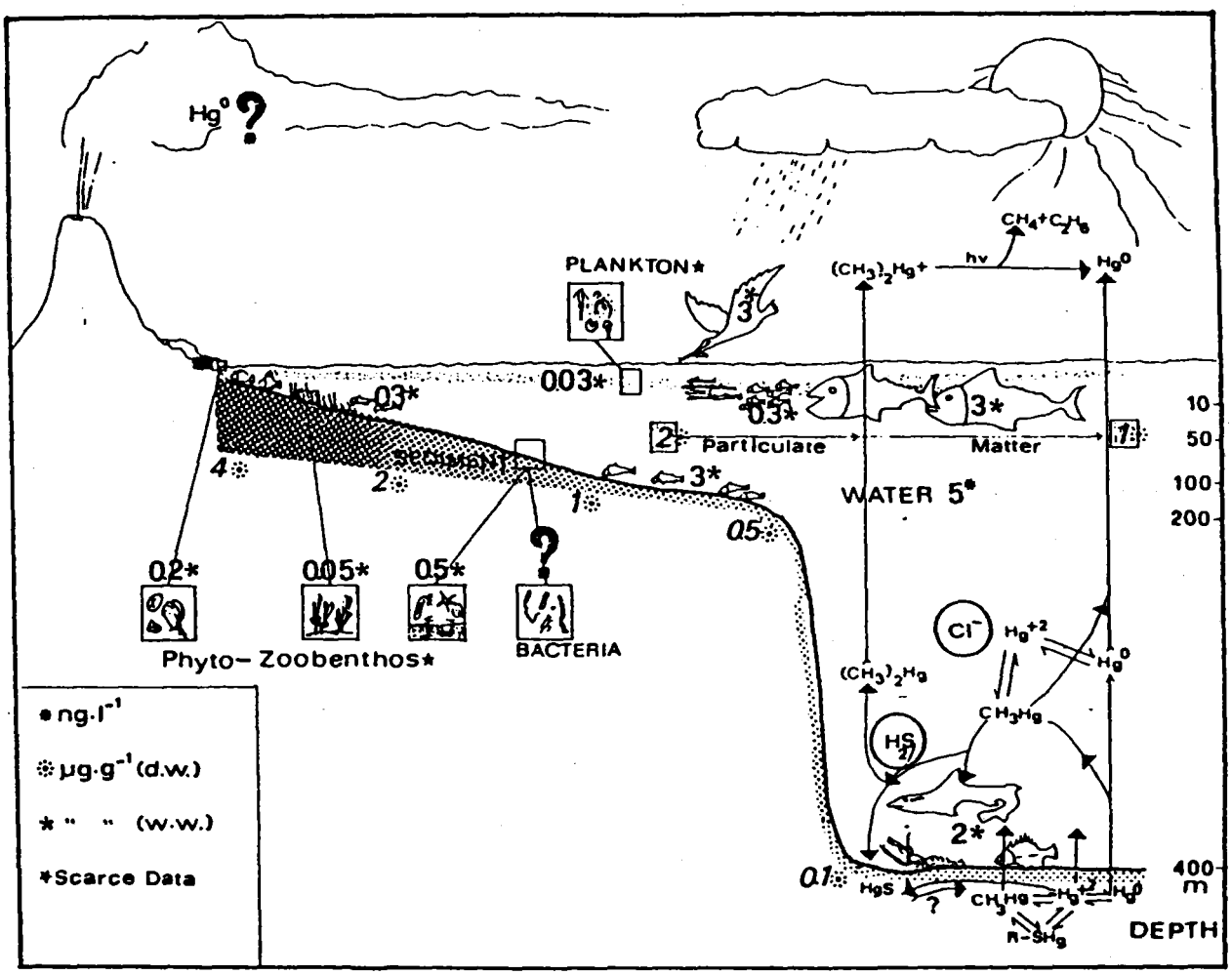



Figure 54. A biochemical cycle of mercury in the Tyrrhenian Sea suggesting typical mercury concentrations for several compartments (Baldi, 1986)

## 4.6 Conclusion on mercury biogeochemical cycle

The Mediterranean belongs to the Mediterranean-Himalayan mercury belt. Mercury anomalies are frequent in the Mediterranean and seem only to be absent from its south-eastern basin. These anomalies contribute to the mercury input into the marine environment over large areas.

Several mercury species occur in the marine environment. From the point of view of health protection methyl mercury is the most important Hg species. Model experiments have shown that MeHg can be produced by bacteria resident in sediments and also by abiotic process, but the ecological importance of the processes leading to the production of MeHg is not yet clear. Present evidence seems to indicate that the production of MeHg by bacteria is more an exception than the rule since more bacteria species investigated can transform Hg(II) species into metallic Hg than into MeHg. It has been shown also that other microorganisms (algae) can transform Hg species, but so far no algae has been found that can produce MeHg. It has been suggested that methyl iodine produced by algae in surface waters may be a methylation agent, but this has still to be demonstrated.

The data on methylation by higher aquatic organisms are still conflicting. Some authors have reported methylation by the intestinal flora of fishes, but others could not confirm these results. The liver of marine mammals has been indicated as a demethylation site but so far no evidence has been published showing that marine organisms other than bacteria and algae can transform Hg species.

Uptake and elimination experiments with marine shellfish and fish have shown that inorganic Hg is taken up with low efficiency and released with a relative short biological half-time while MeHg is taken with a very high efficiency and released with a half-time of years. These very different kinetics of the two Hg species result in an increase of MeHg during the lifetime of organisms which is more evident in long-living organisms. Except for organisms of the first trophic level, the distribution pattern of both inorganic and organic Hg after experimental exposure showed that the uptake through food is the dominant route of entry. A model of the pelagic food-chain of tuna shows how the Hg concentration in marine organisms increases with age and that predators with long life spans have higher Hg concentrations than their prey, i.e. organisms from lower trophic levels. It also predicts correctly that methyl mercury increases faster than inorganic Hg during the specimen's lifetime and it reaches higher concentrations in organisms belonging to higher trophic levels.

Estimations on the amount of methyl mercury taken up by autotrophs (phytoplankton) on a per litre basis result in very low fluxes of about 0.0001 ng $MeHg/L^{-1}$ $day^{-1}$. This shows that a very small amount of methyl mercury in the sea water is sufficient to allow the MeHg in the phytoplankton to reach about 20%. The MeHg in the phytoplankton will also allow the much less frequent organisms in higher trophic levels to reach the levels observed. These estimations have still to be confirmed by measurements in nature, but show that one is dealing with a very small amount of MeHg per unit volume.

## 5. EFFECTS OF MERCURY 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 adult survival but also on reproduction, development and growth rates are needed. Many biological effects of pollution will not show up in the short-term bioassay test for acute toxicity, because some effects are slow to develop or slow to produce a general debility that interferes with some of the normal life functions of the organism. The fact that organisms that have survived the short-term exposure die later after being transferred into clean non-toxic water also indicates 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 patterns, 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) for an estimation of long-term effects from applying 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.

Evidence presented in section 4.3 shows that the uptake of Hg in marine organisms depends both on the chemical species of Hg 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 Hg directly from the surrounding sea water. For all other organisms in higher trophic levels the uptake through the food-chain is important.

However, even if appropriate data are available on single species' reactions to pollutants during a life cycle, their effects on ecosystems can not 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 can changes on natural ecosystems be linked to specific pollutants. 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 no adequate data available to assess the general risk of Hg on marine biota and ecosystems.

Data on chronic and sublethal effects of Hg from the Mediterranean are limited, therefore data on the effects of Hg on marine organisms in general are reviewed. In reviewing the data available it is unfortunate that, with one exception, no data seem to have been published on the effect inorganic Hg and MeHg cause when supplied to marine organisms via the food chain. Therefore, only the data on algae and bacteria consider dominant routes of exposure. Another serious limitation, encountered in most bioassays, consists in the fact that the effective exposure concentrations during the experiments have not been determined by chemical analysis.

## 5.1 Phyto- and zooplankton

Davies (1978) reviewed the effects of 'heavy metals' on phyto- and zooplankton organisms. Unfortunately, in the majority of bioassays neither the concentration in the sea water has been determined after addition of mercury nor the effect of chelating substances (commonly used in the culture medium) has been taken into consideration; consequently the effective concentrations are unknown. For example, Smith (1983) showed that if the phytoplankton organisms were tested in batch culture the effective concentration of Hg in the sea water is reduced markedly during the first day and most of the Hg is associated with the algae. Later during growth, the cell number of the algal population increases, and consequently the Hg 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 µg Hg/L. However, also without chelators some algae can withstand much higher Hg concentrations: 1 to 10 µg Hg/L. The greater tolerance is due to a reduced uptake of Hg (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). Determining the effects of $HgCl_2$ and MeHg showed that an inhibition of C-14 uptake of natural phytoplankton populations began at less than 0.1 g Hg/L for MeHg and at 1 µg Hg/L for $HgCl_2$ (Knauer and Martin, 1972). For comparison, Holderness et al. (1975) observed that growth of the freshwater green alga Coelastrum microporum was not inhibited at concentrations of 0.8 µg MeHg/L. Inhibition started only at 3 ug MeHg/L. In zooplankton organisms 2 µg Hg/L decreased the faecal pellet production during the initial 2 days, but not in successive days (Reeve et al. 1977), probably because the effective Hg concentration had decreased in the meantime.

## 5.2 Macrophytes

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

## 5.3 Bacteria

Very few data exist on toxicity of Hg compounds on marine bacteria. Jonas et al. (1984) observed that natural populations from Chesapeake Bay showed 40 to 60% growth inhibition at 1 µg inorganic Hg/L. A similar inhibition was also observed for 1 µg MeHg/L. Toxic effects of MeHg were observed already at 0.1 µg Hg/L. Unfortunately, the authors did not test low concentrations of inorganic Hg so that the onset of the inhibition of inorganic Hg was not determined. Their data seemed to indicate that inorganic and organic Hg 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 tuna. Of the 14 strains tested 9 showed effects at lower concentrations: 800 to 1600 µg $CH_3HgCl$/L and 4000 to 8000 µg $HgCl_2$/L. Five strains were more resistent and showed effects only at 6.4 to 12000 µg $CH_3HgCl$/L and 16000 to 32000 µg $HgCl_2$/L. It is not clear why the strains examined by Pan-Hou and Imura (1981) were more resistent than the natural populations studied by Jonas et al. (1984). Probably the strains of Pan-Hou and Imura were obtained from another author who had isolated them on a medium which was selective for Hg-resistant strains.

## 5.4 Crustaceans

The LC-50 at 48 hours for newly hatched zoeae of Palaemonetes vulgaris (shrimp) was 10 µg $HgCl_2$/L for unfed and 15 µg $HgCl_2$ for larvae fed with Artemia salina. It was estimated that no effects would occur during a 48-hour exposure at 5 µg $HgCl_2$/L for fed larvae and at 3 µg $HgCl_2$/L for unfed larvae. Transferring larvae into clean sea water after a 48 hour exposure to study delayed effects showed that none of the larvae exposed to 32 µg $HgCl_2$/L survived for more than one day demonstrating the severe limitation of short-term bioassays. Exposures of 45 hours to 10 and 18 µg $HgCl_2$/L markedly delayed the first molting and caused deformations. The growth of young Penaeus indicus was not significantly reduced at 6 µg Hg/L (McClurg, 1984).

Vernberg and Vernberg (1972) and De Courney and Vernberg (1972) showed that U. pugilator adults (fiddler crab) could survive for months in sea water containing 180 µg $HgCl_2$ while all stage I zoeae exposed to the same concentration died after only 48 h. In three species of fiddler crabs 100 µg MeHg/L had no effects on regeneration of limbs and molding (Weis 1977). However, this concentration caused a complete inhibition of melanogensis in the growth of U. thayeri, partial inhibition of U. pugilator but no inhibition in U. rapax. At 500 µg MeHg/L the growth inhibition was observed for the most U. thayeri and the least for U. rapax. Inorganic Hg inhibited limb generation at 1000 µg Hg/L but had no effect at 100 µg Hg/L. Pre-exposing U. pugilator to 60 to 100 µg MeHg/L did not reduce the inhibitory effects of 500 µg MeHg/L, 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 (Callahan and Weis, 1983). This may indicate that Hg does not induce metallothionin (MT) but that MT 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 µg Hg/L 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 µg Hg/L did not affect respiration rate, growth, or molting frequency. Higher concentrations were not tested.

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

## 5.5 Molluscs

Very few data exist on molluscs. The 7-day LC-50 for mussels (M. edulis) is 150 µg Hg/L (Martin et al 1975). Growth of the shell is reduced to 50% after exposure to only 0.3 µg Hg/L (Stromgren, 1982). At concentrations above 1.6 µg Hg/L 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 Hg and MeHg. Sharp and Neff (1985) exposed embryos of F. heteroclitus at different times after hatching at various concentrations (0 to 100 µg Hg/L) of $HgCl_2$ and MeHg. Comparison of 4-day 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 MeHg was more toxic but its relative toxicity to $HgCl_2$ varied widely from about half as toxic to several times more toxic than inorganic Hg. When embryos of the killifish from a polluted and unpolluted sites were exposed for one week to 30 µg MeHg/L it was observed that the embryos from the polluted site had virtually no anomalies while those from the other site showed a range malformation from unaffected to rather severely affected (Weis et al. 1981). Also when exposed to 50 µg MeHg/L, 55% of the embryos from the polluted site exhibited no malformations while the embryos from the unpolluted sites showed marked malformations. At the

same time the embryos had taken up about between about 5.5 to 7 mg MeHg/kg. For comparison, the inorganic Hg short-term 96-h LC-50 of adult F. heteroclitus ranges from 230 and 2010 µg Hg/L which is about 8 to 70 times greater than the teratogenic dose for this species (Jackim et al. 1970, Klaunig et al. 1975). The 96-h LT-50 of F. heteroclitus larvae is 5320 µg MeHg/L (Weis et al. 1985). However, when Fundulus heteroclitus adults were maintained in only 5 µg MeHg/L they failed to produce additional clutches of eggs (Weis et al. 1985).

In order to investigate if the pretreatment with MeHg could also increase the tolerance to later exposure of MeHg Weis et al. (1982) investigated pretreatment of embryos and adults of F. heteroclitus. They observed that embryos of F. heteroclitus from an unpolluted site showed more malformations after exposure to MeHg than to $HgCl_2$. In a polluted site, however, the tolerance to $HgCl_2$ was lower than to MeHg. The MT 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 µg MeHg and later to 10 to 50 µg MeHg/L, caudal fins were regenerated more slowly than the controls. This failure to develop a protective mechanism by a pretreatment is supported by the observation that exposing embryos to MeHg did not increase the MT level over controls (Weis, 1984). Therefore, it seems that the acquired greater tolerance of embryos from polluted sites must have been induced by trace metals other than Hg. Interestingly, Weis (1984) observed that eggs had very little 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 inorganic Hg or MeHg did 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 MeHg in freshwater only (food was not contaminated) showed that MeHg concentrations of 0.3 ug Hg/L and lower had no effect on all three generations. Maximal acceptable toxicant concentrations were between 0.3 and 0.93 ug Hg (as MeHg)/L (hardness 45 mg/L: pH 7.5). On the other hand the mean 96-h LC-50 for 20-week-old (12 g) and yearlings was 75 µg MeHg/L. 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 Hg levels, followed by liver gill, brain, gonad and muscle. Between 90 to 95% of the total MeHg body burden was located in muscle. The mean muscle concentration in first generation trouts dying after exposure to 2930 ng (as MeHg)/L was 23.5 mg Hg/kg FW. In the second generation that died after exposure to 930 ng Hg/L the mean muscle level was 9.5 mg Hg/kg FW. Relating toxicity to Hg concentrations in the body tissues showed that body levels of 2.7 mg Hg/kg FW had no effect but at body levels of 5-7 mg Hg/kg FW effects could be detected. No appreciable elimination of Hg was observed after 12-16 weeks.

## 5.7 Marine mammals

Two seals exposed to daily oral dosage of 250 µg MeHg/kg body weight did not show any abnormal blood values but a reduction in activity and body weight. Two seals dosed with 25 mg MeHg/kg body weight died after 20 and 26 days of exposure and after showing previously severe symptoms of poisoning (Ronald et al. 1977)

## 5.8 Enclosed pelagic ecosystems

Pulse additions of 5 µg Hg/L to large plastic containers (1.5 $m^3$ and 15 $m^3$) with and without nutrient additions showed that the Hg concentration decreases rapidly in the bulk of sea water and inhibited the relative carbon assimilation rate in the bag without nutrient addition during the whole 15-day experiment (Kniper et al. 1983). In nutrient-enriched enclosures the phytoplankton growth was inhibited by concentrations above 2 to 2.5 µg Hg/L in the bulk. Similar observations were made by other authors (Grice and Menzel, 1978). Pulse additions of 5 µg Hg/L 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 Hg in the enclosure had droped below 2 µg Hg/L. Pulse additions of 1 µg Hg/L on the other hand had no

observable effects. Studying the biochemistry and toxicity of mercury in controlled experimental ecosystem Wallace et al. (1983) found that the high affinity of Hg to the organic matter present in the system was the most important parameter governing the distribution of the chemical species of Hg. About 90% of the Hg was present in particulate, colloidal and high molecular weight dissolved forms and thus it was not bioavailable. In fact, if these fractions of organic matter were removed by ultrafiltrations from the sea water, bioassays showed that 1 µg Hg/L were toxic to natural phytoplankton populations.

### 5.9 Conclusion on effects

The available data on the toxicity of Hg on marine organisms show 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/L of inorganic Hg. However, since the actual concentration in sea water was not determined by chemical analysis but deduced from the amount of Hg added to the medium, the actual effective concentrations may well be lower. The results obtained in large plastic containers indicate that the inorganic Hg added is rapidly transformed into other Hg species and which are apparently less bioavailable. Organisms higher in the food-chain can apparently withstand considerable concentrations of both inorganic and organic Hg. This is most probably due to the fact that the dominant exposure routes of Hg is through the food chain. This pathway, however, has not to be investigated. Therefore, the data so far available are not sufficient to assess the risk of Hg pollution. Future studies on the effective toxic concentrations should be accompanied by data on the actual Hg concentrations of different Hg species determined by chemical analysis in the water, the food and in the body tissues of the organisms. Also the concentrations of relevant Hg species in the edible muscle tissue and the target organs or tissues (critical organs) should be determined because this information may be used to compare data obtained in the laboratory with field data.

## 6. POTENTIAL HEALTH HAZARD FROM MERCURY INTAKE WITH SEAFOODS

### 6.1 Food consumption pattern of Mediterranean populations

Food preference, prices and availability greatly influence the seafood consumption pattern. In general, in the coastal areas seafood is more available than in the hinterland, especially in the less developed countries. Certain parts of the population such as fishermen, fish vendors and their families have greater access to seafood than other persons. Also persons on diet may consume preferentially fish and shellfish. No general seafood consumption studies have been carried out in the Mediterranean countries. Based on seafood supply data (considering landings, export and import) national averages and percentage of seafood of the Mediterranean origin can be estimated (Table 41), but these data are not suitable for an estimation of the risk of Hg intake from seafoods because averages are based on supply (consumption is estimated as 50% of the supply) and because the estimated averages do not give any indication on the consumption pattern of individuals and different population groups. How misleading these figures can be is illustrated by the food consumption survey carried out for three different age groups in 9 regions of the US (Rupp et al. 1980). For example, in New England, the average saltwater finfish consumption for adults was 4.55 kg/year, while the 50% percentile was only 3.46 kg/year. This means that 50% of the population consumed only 3.46 kg while the average was higher by about one kg/year. The 90% percentile was 9.85 kg/year and the 99% percentile 20.27 kg/year. 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. The maximum consumption was 29.76 kg/year 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, the 50% and the 90% percentile were both zero, but the 99% percentile was 2.44 kg/year. Or in other words more than 90% of the New Englander consumed no freshwater finfish at all. One percent of the population consumed at least 22 times the average and the highest consumption (8.2 kg/year) was 74.5 times higher than the average. Unfortunately

similar data are not available for the Mediterranean. Since no data exist some general observations may be considered. In the Mediterranean countries with predominant 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 seafoods than in the habitual residence in the hinterland. This seafood is more likely of the Mediterranean origin and, therefore, it contains more Hg than the frozen fish available in the hinterland which, in many countries, is imported from the non-Mediterranean fishing ground (Table 41) and thus contains less Hg than the local seaside food (section 3.4). This qualitative scenario indicates that a large section of the general population consumes at least one seafood meal a week with a higher frequency during summer. However, with the exception of extreme consumers, large parts of the Mediterranean populations will not exceed two meals a week on a long-term basis.

This means that the attention must be directed towards the consumption of critical groups with high seafood consumption. But here problems arise also. The individual with the highest consumption of seafood is not necessarily the person most exposed since the Hg intake depends also on the Hg concentration in fish and shellfish species consumed. This has been illustrated by Nauen et al. (1980b). Estimating the Hg intake in Italy, the authors found that a higher consumer of seafoods had only about 40% of the Hg intake per kg body than a lower consumer (Table 42).

Table 41. Estimated average national consumption of fish and fishery product for the years 1979-1981 in the Mediterranean and other selected countries

| Country | weekly consumption: total (FAO, 1983) [g(live wt)/person] | weekly consumption: Mediterranean origin (UNEP, 1983) (%) | non-food uses (1000 MT live weight) (FAO, 1983) |
|---|---|---|---|
| Algeria | 20 | 100 | - |
| Cyprus | 80 | 30 | - |
| Egypt | 45 | 10 | - |
| France | 230 | 4 | 2.4 |
| Greece | 155 | 60 | - |
| Israel | 160 | 8 | - |
| Italy | 120 | 55 | 3.4 |
| Lebanon | 55 | 25 | - |
| Libya | 75 | 30 | - |
| Malta | 200 | 20 | - |
| Morocco | 55 | 10 | 103 |
| Spain | 300 | 10 | 175 |
| Syria | 15 | 10 | - |
| Tunisia | 75 | 100 | 1.1 |
| Turkey | 60 | 10 | 101 |
| Yugoslavia | 30 | 45 | 0.1 |
| World | 115 | - | 19100 |
| Faeroe Island | 950 | - | 100 |
| Iceland | 855 | - | 810 |
| Japan | 800 | - | 1810 |
| USA | 155 | - | 1230 |
| USSR | 245 | - | 2240 |

Consumption is estimated to be 50% of the supply taking into consideration export and import (Crispoldi 1976).
About 90% of the "non-food uses" is fishmeal.
Note: in UNEP (1983) consumption has been erroneously estimated as 100% of the supply.

## 6.2 Marine food consumption by critical groups

Very few seafood consumption data of critical groups exist for the Mediterranean.

Paccagnella et al. (1973) selected the population of Carloforte (Sardinia) for an epidemiological study, because its average consumption of seafoods 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 (section 6.4). About 65% of these persons eat seafood more than 3 times a week. Some 11.7% consumed 7 and more meals of seafoods and 1.5% as many as 13 to 14 meals equal to about 1400 g seafood a week. Nauen et al. (1980b, 1983) reported that fishermen from three Italian locations had consumed 5 to 11 kg FW of 71 different species in 3 weeks (1.8 to 3.8 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 and person (Table 42). Nauen et al. (1983) ranked also the seafoods species according to consumption frequency. Sardine and cuttlefish (Sepia) were the most frequent species consumed in the locations studied, followed by squid (Loligo), hake (Merluccius), octopus, whiting (Merlangius), deep-water shrimp (Parapenaeus), mantis shrimp (Squilla), mussel (Mytilus), picarel (Maena), pilchard (Engraulis) and the horse mackerel (Trachurus). This ranking is an average of the observations made in the three locations and considerable difference existed between species consumption pattern. Therefore, this ranking can only be considered as an example and in other areas of the Mediterranean complete different species rankings in the seafood consumption are to be expected.

Estimates and data from the Mediterranean and other European regions range from 2100 to 5600 kg $week^{-1}$ $person^{-1}$ (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 for Japan high seafood consumption rates have been reported (Doi and Ui, 1975). Of 34 tuna fish retailers 22 ate 100 to 200 g tuna meat daily besides 70 to 300 g shellfish and other fish meat. One person consumed daily 200 g FW of tuna meat in addition to 1000 g of other seafoods. The daily tuna consumption of tuna fishermen aboard the ship ranged from 50 to 400 g during seasonal periods of 130 to 180 days.

It can, therefore, be assumed that there may exist extreme consumers of seafoods which are able to consume 800 to 1000 kg of seafood/day (5.6 to 7 kg $week^{-1}$ $person^{-1}$) over long time periods.

## 6.3 Direct and indirect intake of mercury through seafoods

Only few studies in the Mediterranean area investigated direct Hg intake. Others have determined Hg in blood and hair. At Carloforte (Sardinia) Paccagnella et al. (1973) analysed typical diets containing edible part of tuna and other seafoods:

| | |
|---|---|
| Tuna | 1230 (50–2800) µg Hg-T/kg FW |
| other fish and shellfish | 330 (10– 490) µg Hg-T/kg FW |

Since only during summer (July/August) tuna is available from the local tuna trap the authors estimated that the average intake of mercury of the Carloforte populations was 150 µg $week^{-1}$ $person^{-1}$ in summer and 100 µg/week/person in winter. The group with the highest consumption (14 seafood meals a week) had an estimated mercury intake of 700 µg Hg $week^{-1}$ $person^{-1}$ in the summer when tuna was available and 460 µg Hg $week^{-1}$ $person^{-1}$ in the winter without the supply of fresh tuna.

Table 42. Seafood consumption and estimated mercury intake by five fishermen from three Italian towns (Marina di Ravenna, Fiumicino and Bagnara Calabra) recorded during a period of 20 days. (Nauen et al. 1980b)

| | | Marina Ravenna | | Fiumicino | Bagnara Calabra | |
|---|---|---|---|---|---|---|
| Age (years) | | 52 | 55 | 54 | 36 | 28 |
| Weight (kg) | | 65 | 86 | 82 | 68 | 60 |
| Species | Classif. | seafood consumed (g in 20 days) | | | | |
| Anguilka 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 sp. | F | | | | 250 | |
| Loligo vulgaris | M | 400 | 900 | | 640 | 330 |
| Maena sp. | F | | | | 570 | 150 |
| Merlangius merlangus | F | | | | 970 | 860 |
| Merluccius merluccius | F | | | 1675 | | |
| Mola * | | | | | 200 | 370 |
| Mugil cephalus | F | 500 | 700 | | | |
| Mytilus gallovincialis | M | | 600 | | 450 | 400 |
| Octopus vulgaris | M | | | 1250 | | |
| Parapenaeus longirostris | C | | | 350 | 350 | 270 |
| 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 | M | | 1600 | 580 | | |
| Squilla mantis | C | 1500 | 1500 | | | |
| Tapes decussatus | M | 2670 | | | | |
| Thunnus alalunga | F | | | | 335 | |
| Thunnus thynnus | F | | 110 | | 935 | 340 |
| Torpedo sp. | F | | | 100 | | |
| Xiphias gladius | F | | | | 1590 | 1390 |
| Total consumption in 20 days (g) | | 10900 | 9010 | 7945 | 8560 | 5260 |
| Total Hg intake (µg/20 days) | | 2000 | 1670 | 1755 | 4720 | 3260 |
| Weekly consumption (g) | | 3815 | 3155 | 2780 | 2995 | 1840 |
| Weekly Hg intake (µg Hg) | | 700 | 585 | 615 | 1650 | 1140 |
| µg Hg/kg body weight/week | | 10.5 | 7.0 | 7.7 | 24.5 | 19.0 |

* unidentified species

** assumed Hg concentration

C = crustacean; M = mollusc; F = fish

Nauen et al. (1980b, 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 Hg levels in the fish and shellfish consumed. Special attention was given to fishermen and their families (section 6.2). 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 for an individual was estimated for a 3-year old child which reached 8.6 times the weekly tolerable allowance (section 6.5) or about 30 µg Hg/kg body weight/week.

For Japanese tuna fishermen Doi and Ui (1977) assumed an average concentration of 500 ug Hg/kg FW in tuna and the average daily consumption rate, and they arrived at a weekly intake from tuna for these fishermen of about 500 µg Hg. The retailers ingested an additional Hg intake of about 140 µg Hg per week from other seafoods which contained on the average 0.1 mg Hg/kg. This high Hg intake, in particular from tuna, was reflected in high Hg concentrations in hair and blood, supplying indirect evidence for high Hg intakes from seafoods (section 6.4).

Another (indirect) route of Hg to human populations comes from the use of fishmeals and other foodstuffs in raising chicken, pigs, etc. The Hg-T and the MeHg concentrations in fishmeals were higher than in meat and bone meals (Szprengler, 1975). For example, feeding chickens with herring meals containing 0.014 and 0.018 mg Hg-T/kg DW instead of meat or bone meals raised the chicken's body Hg levels (March et al. 1974). The species used for the production of fishmeals vary with regions. About 90% of the non-food uses of landings (Table 41) are estimated to be fishery products converted into fishmeal (Crispoldi 1987). In northern Europe fishmeals are produced mainly from capelin and herring, in the Mediterranean mainly from the large catches of sardines and anchovies (Table 43). Turkey, Spain and Morocco are the largest producers of fishmeals in the Mediterranean. Also wastes from tuna, herring, mackerel, lobster, crab, shrimp and various other species are used for fishmeals production. Of course, not all fishmeal produced is also used in the country of origin. For example, Peru exports 96%, Chile 91% and Norway 81%, while large amounts are imported by many European countries.

The Hg content of these fishmeals can be estimated from the Hg concentration in fresh species (section 4.4.5) and a DW/FW ratio of 5. Direct determination for the Mediterranean fishmeal are not available. For comparison Hg-T of herring meals from Canada (British Colombia) and Newfoundland), Denmark and Norway range from 0.09 to 0.29 mg Hg-T/kg DW (Anonymous, 1971). White fishmeals from Britain, Canada, Denmark, Iceland and S. Africa also had similar ranges (0.04 to 0.29 mg Hg-T/kg DW). Beasley (1971) found a mean concentration of 0.44 mg Hg-T/kg DW in Engraulis mordax from the Californian coast, 0.6 mg Hg-T/kg DW in Clupea herengus from the Massachusetts coast, 0.5 mg Hg-T/kg DW menhaden (Brevoortia patrona) from the coast of the state of Mississippi and 0.34 mg Hg-T/kg DW in the menhaden (B. tyrannus) from the Chesapeake Bay. Taking into consideration that these are dry weight levels and applying a FW/DW ratio of 0.2 will reduce these levels by a one-fifth on a fresh weight basis. Since the Hg-T concentrations in the Mediterranean white fishes are higher than those mentioned above, fishmeal produced from the Mediterranean species also should have higher Hg levels.

In general non-marine foods contain little Hg and most of the data on mercury in foodstuffs only report the total mercury content and do not distinguish between methyl mercury and other mercury compounds (WHO, 1976). The older data on total mercury intake via food in some countries has been reported at 20 µg/day or lower (WHO, 1976). Cigna-Rossi et al, (1967) estimated an intake of 7 to 12 µg Hg-T/day for the average Italian. Schelenz and Diehl (1973) reported 70 µg/day for the Federal Republic of Germany, and Cohen (1974) reported 5 to 10 µg Hg/day for England. For Sweden, it was estimated that about 5 µg Hg/day came from sources other than fish and marine food, (i.e. drinking water and terrestrial food) (Swedish Expert Group, 1971) . Bread and cereals contribute more than 50% to the mercury intake from terrestrial food. Because mercury pesticides are no longer used for treating seeds the mercury intake from terrestrial sources may have decreased since the 1960s. Most studies of mercury content in food suggest that the contribution of MeHg from terrestrial food is negligible (Swedish Expert Group, 1971).

Table 43. Nominal catches and net imports of fish (in metric tons) in the Mediterranean for 1980 (UNEP, 1983)

| Country | Total production | Net imports | Mediterranean catch | Clupeidae (Sardines) | Engraulis encrasicolus (anchovy) | Carangidae (Trachurus) | Bonito and tuna | Gadiformes | Sparidae | Mullidae | Cephalopoda |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 | 8 436 |
| 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). Year book of Fishery Statistics
(i) Catches and landings, Vol. 52
(ii) Fishery commodities, Vol. 53
(b) FAO/GFCM, Statistical Bulletin No.4

## 6.4 Mercury in hair and blood of humans

The high Hg intake with seafoods by persons eating large amounts of seafood was also reflected in the concentration of Hg in hair and blood. 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 Hg levels in their hair [mean (n=5) of 7.6 ± 3.4 ppm] than persons consuming less seafood [mean (n=6) of 1.1 ± 0.6 ppm]. In the above mentioned site of Carloforte (Sardinia) (section 6.3) the average hair mercury level in the high consumers (estimated summer intake: 700 ug Hg/person, winter intake: 460 ug Hg/person) was 11 mg Hg/kg (range: "not detected" to 60 mg/kg) (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 a hair level of about 45 mg Hg/kg and six others reached hair concentrations between 16 and 20 mg Hg/kg. Also in the inland town relatively high hair concentrations were observed. One woman had about 30 mg Hg/kg and three had levels between 16 and 25 mg Hg/kg, despite the fact that none of the persons examined in the inland town had consumed more than 2 fishmeals a week.

Bacci et al. (1976) studied the total and methyl mercury concentration in blood, urine, hair and nails of 16 persons from the town of Vada, who consumed from 0 to more than 6 meals of seafood a week. The fish came from the banks of the Vada about 10 km west of the Solvay chlor-alkaline plant (section 3.6). 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. Also this high hair concentration is within the range of possible effects, but no symptoms had been observed.

High Hg levels were also observed in the hair of high seafood consumers from other regions. The tuna fishermen mentioned by Doi and Ui (1977) (section 6.3) had hair concentrations ranging from 25 to 46 mg Hg/kg. The mean mercury concentration in the hair of the retailers was 26 mg Hg/kg (range 6.4 - 44 mg Hg/kg) while blood levels averaged 100 ug Hg/L (range 45 - 175 ug Hg/L). One individual had at one time 65 mg Hg/kg hair. Again no symptoms of Hg poisoning were reported.

## 6.5 Evaluation of potential health effects and tolerable intakes

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.

From data collected during the epidemics of methyl mercury poisoning of 1953-1960 in Japan and of 1971-72 in Iraq, 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 200 to 500 µg Hg (as MeHg) for a 70-kg person. This long-term intake is associated with a blood level approximately in the range of 200 to 500 µg Hg/L and a hair concentration of between 50 to 125 mg Hg/kg. With increasing blood or hair Hg levels the manifestation of neurological symptoms and the severity of toxic effects rise rapidly. Applying a safety factor of 10 to the long-term ingestion of 200 to 500 µg Hg would result in a "safe intake" of 20 to 50 µg Hg/day for a 70 kg person or on a weekly basis 140 to 350 µg Hg/week (GESAMP, 1987). FAO/WHO (1972) suggested a Provisional Tolerable Weekly Intake (PTWI) of 200 µg Hg (as MeHg) or 300 µg Hg (as Hg-T) for a 70 kg person. For persons having different weights (e.g. children) the weekly intake can be estimated for the PTWI expressed in µg Hg/kg body weight: 3.3 µg MeHg per kg body weight a week and 5 µg total mercury per kg body weight a week. These PTWI for mercury have been reconfirmed (WHO, 1980), but with the additional restriction to lower (unspecified) levels for pregnant and lactating women because the reevaluation of the WHO Environmental Health Criteria for Mercury emphasized the sensitivity to methyl mercury on the growing brain.

Several authors have shown in animal experiments that selenium can reduce the toxic effects of inorganic and organic mercury. Reviewing available evidence on the health effects of methyl mercury, Piotrowski and Inskip (1981) concluded that the knowledge about the protective effect of selenium is limited to experiences with animal models and no direct evidence of a protective effects in humans has been presented. Therefore, in estimating the tolerable intake limits for humans the high selenium content in marine fish cannot be taken into consideration.

Legal limits, i.e. maximum concentrations in seafood of 0.5 or 0.7 mg Hg/kg FW, in force in some Mediterranean countries present a special problem. Table 44 shows the weekly intakes of methyl mercury that could be reached by different combinations of seafood consumption (meals) and methyl mercury concentration in seafoods. From this table one can see that a person weighing 70 kg who eats seafoods twice a week can safely consume fish and shellfish containing on the average 750 ug Hg/kg FW. From similar calculations were derived the legal limit of 0.7 ppm FW (0.7 mg Hg as MeHg/kg FW) or the even more severe limit of 0.5 ppm FW in force in some Mediterranean countries. The 0.5 ppm FW takes into consideration persons of lower body weights. 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 intakes is exceeded for periods of ingestions lasting over months and years. Higher levels are allowed for certain types of fish on the basis that these fish can not be contaminated by anthropogenic sources since the habitats are in general remote from these sources.

However, the application of legal limits present two problems: one is related to health protection and one regards the economics of marine fishery. The legal limits are supposed to protect the human population from methyl mercury poisoning but this is not the case as can be seen from some simple calculations. A 70-kg person who eats seafood containing 500 ug Hg/kg FW 14 times a week will have an intake of 1050 µg Hg (as MeHg)/week. This is 5 times the PTWI. Consuming the same amounts of seafoods at 750 µg Hg/kg would exceed the PTWI by about 8 times. On the other hand, a 70-kg person who eats only one meal a week can eat seafood containing about 1300 µg Hg/kg FW or about twice the legal limit. Hence persons eating one meal a week or less are not in need of legal limits while the persons consuming many meals of seafoods containing legal concentrations are at risk but are not protected by the enforcement of legal limits. In addition, most high consumers are fishermen and their families who consume seafood which does not reach the fish market and hence is not subject to control.

From the economic point of view a real enforcement of the legal limits would have severe consequences on the Mediterranean fisheries since most of the large and economically more valuable specimens would be banned from sale.

Therefore, the evidence speaks against legal limits and in favour of intake limitations. These intake limitations can only be achieved by advising high consumers of seafoods on the quantity and species to be eaten.

Table 44. Relation between concentration of methyl mercury (µg MeHg/kg FW) in marine foods and seafood consumption in g fresh weight and number of meals of seafood and weekly intake of methyl mercury per 70-kg person

| Mercury | Weekly seafood meals | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| in seafood | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 14 | |
| (µg MeHg/kg FW) | (150 | 300 | 450 | 600 | 750 | 900 | 1050 | 2100 | g/week of seafood) |
| 100 | 15 | 30 | 45 | 60 | 75 | 90 | 105 | 210 | (µg MeHg/person/week) |
| 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 | |

# 7. CONCLUSIONS ON POTENTIAL HARM

## 7.1 Potential harm to living resources

Mercury concentrations which may be hazardous to marine organisms and marine ecosystems are difficult to assess. Three kinds of data are available: laboratory experiments on toxicity and on the uptake and release dynamics of Hg compounds, experiments with confined natural ecosystems and observations in natural ecosystems under influence of natural or anthropogenic mercury sources.

Experiments on the uptake and release dynamics and the distribution of Hg species within the organisms have shown that the uptake of the more toxic organic mercury species (methyl mercury) by organisms located in higher trophic levels occurs principally through the food-chain, but bioassays only assess the uptake of Hg compounds from sea water and not also through the food chain. This explains the low sensitivity of organisms in high trophic levels to both inorganic and methyl mercury in sea water, and shows that bioassays relating Hg concentrations in the sea water to adverse effects to biota can be used only to assess the toxicity of organisms belonging to the first trophic levels (autotrophs, bacteria and herbivours) for which the direct uptake from sea water is the most important uptake route. Unfortunately in most bioassays the toxic concentrations were not determined by chemical analysis but deduced from the Hg additions to the test medium so that only nominal concentrations were considered. The limited data available on autotrophs show that inorganic Hg is toxic to the most sensitive phytoplankton species at about 20 ng/L. Less sensitive species were affected at much higher nominal concentrations: 1000 ng (as $HgC_{12}$)/L and 100 ng (as MeHg)/L. Since during the static bioassay the Hg concentration decreased, the really effective Hg concentration must be lower. In order to arrive, at least, at some estimation of Hg toxicity one could assume that effects to the most sensitive autotrophs should not occur at concentrations five times lower than the nominal effective concentration tested. This would result in "minimal risk" concentrations for inorganic Hg salts of about 4 ng Hg/L. For sensitive phytoplankton species no data exist on the effective concentrations of methyl mercury. Since for less sensitive species MeHg was 10 times more toxic than inorganic Hg, a factor ten may be used for an estimation of the lowest effective concentration. At 0.1 to 0.2 ng Hg (as MeHg)/L could serve as a provisional "minimum risk" concentration for phytoplankton exposed to MeHg. Natural population of bacteria are less sensitive. The MeHg at 100 ng Hg/L inhibited growth. Inorganic Hg was not tested at nominal concentrations lower than 1000 ng Hg/L.

Some strains of phytoplankton species are much less sensitive than others. This tolerance may have been acquired while the strains were kept in stock cultures. The tolerant strains may also have been isolated from polluted environments. In bacteria Hg tolerance can be induced by pretreatment with Hg. On the other hand, experiences with fishes have shown that pretreatment with Hg will not increase tolerance, but Hg tolerance may be induced by pre-exposure to other trace metals. This would mean that some populations can become Hg-resistant in areas under influence of natural or anthropogenic mercury sources and by exposure to other trace elements.

Experiments with confined natural ecosystems showed that additions of inorganic Hg to enclosed environments were effective at about 1000 ng Hg/L. Additions of other Hg species have not been tested. Interestingly, the Hg added became rapidly associated with the particulate matter and the large organic molecules present in the sea water of the enclosure. Under favourable conditions within 24 hours 87% of the inorganic Hg added was found. The Hg was then removed from the water column by sedimentation of the particles. Carrying out bioassays in sea water passed through ultra-filters retaining particles and organic molecules greater than 10000 molecular MW showed that much lower Hg concentrations were toxic in the filtered sea water than in the unfiltered water. This illustrates that the Hg species introduced into natural environments may be rapidly transformed and that the addition of inorganic Hg to natural ecosystems may have smaller effects than those predicted from standard bioassays. It also explains why total Hg concentrations in natural sea water are often higher than the toxic concentrations without causing any adverse effect.

In assessing the impact of Hg in wastes released into the sea it is important to take into consideration that wastes do not contain pure inorganic or organic Hg compounds. Consequently, in effluents the chemical species causing the toxicity may be only a few per cent of the total Hg determined in the effluents. This is in agreement with the observations made in several Mediterranean coastal sites where wastes are discharged from chlor-alkali plants. Organisms living within a range of 10 to 20 km distance from the discharges had Hg levels several times above background levels reaching 5 to 6 mg Hg-T/Kg FW. However, any adverse effects on marine biota observed near the outfalls could not be attributed directly to the Hg in the wastes but seem rather be due to the release of other wastes (mainly carbonates) discharged simultaneously.

Increased body levels, with 60 to 90% of the total Hg as methyl mercury, were observed in marine species living near geochmical Hg anomalies and also in large pelagic fishes (e.g. tuna, swordfish, etc.) that migrate over large distances. The highest concentration was determined in marine mammals. In an old pelagic dolphin the enormous concentration of about 900 mg Hg-T/kg FW was determined in the liver and 40 mg Hg-T/Kg FW in the muscle tissue. It is worth noting that in the liver and muscle tissue of this dolphin the percentage of methyl mercury was very low: muscle 20%; liver 1.5%. The high Hg concentrations in these marine organisms are believed to be caused by the natural mercury sources (Hg anomalies) present in many parts of the Mediterranean. These natural Hg sources belonging to the Mediterranean-Himalayan mercuriferous belt are evidenced by the large number of Hg mining sites, many of which are not anymore active.

Despite the large amount of data available only few conclusions can be drawn. Marine organisms apparently can live with high concentrations in their body tissues without being adversely affected. In most cases these high concentrations are of natural origin. The relative abundance of inorganic and methyl mercury in both anthropogenic and natural sources seemed to be of the greatest importance for the prediction of the fate of the various Hg species in the environment and their toxicity to biota.

## 7.2 Potential hazards to human health

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. Fish and other seafood are the main sources of methyl mercury intake by human beings. Individuals belonging to "critical groups", mainly workers in the fishing industry (harvesting, processing and trading), and their families have been shown to have high daily methyl mercury intakes (up to several hundred ug/week).

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 200 to 500 ug Hg (as MeHg) for a 70-kg person. This long-term intake is associated with a blood level approximately in the range of 200 to 500 µg/L and a hair concentration of between 50 to 125 mg Hg/kg. Applying a safety factor of 10 would result in a "safe intake" of 20 to 50 µg Hg/day for a 70 kg person or on a weekly basis 140 to 350 µg Hg/week. FAO/WHO (1972) suggested a Provisional Tolerable Weekly Intake (PTWI) of 200 µg Hg (as MeHg) or 300 µg (as Hg-T) for a 70 kg person. For persons having different weights (e.g. children) the weekly intake can be estimated, for the PTWI expressed in µg Hg/kg body weight: 3.3 µg MeHg per kg body weight per week and 5 µg total mercury per kg body weight per week. These PTWI for mercury have been reconfirmed (WHO, 1980), but with the additional (not quantified) restriction for pregnant and lactating women, because the reevaluation of the WHO Environmental Health Criteria for Mercury emphasized the sensitivity to methyl mercury of the growing brain.

Weekly intakes of methyl mercury could be reached by different combinations of fish consumption and methyl mercury concentration in different seafood species. Persons (of 70 kg weight) eating one seafood meal or less a week on a long-term basis can consume fish containing 1300 µg Hg (as MeHg)/kg FW and more. On the other hand a fisherman at sea consuming 14 or more meals of seafoods a week can only consume seafoods which contain 100 µg Hg (as MeHg)/kg FW or less without exceeding the Provisionally Weekly Tolerable Intake limit. High hair and blood Hg levels of these persons eating large amounts of seafood indicate the high Hg intake from seafoods.

It should be pointed out that the PTWI incorporate 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 PTWI that relatively small scale studies fail to demonstrate an increased prevalence of health effects at intakes higher than the PTWI. Even at 10 times higher intake than the PTWI, one should expect only one person would be affected among 20 studied.

Many Mediterranean countries have legal limits (500 to 700 µg Hg (as MeHg) in one kg of fresh seafood). These legal limits do not protect the population as intended. In fact, a 70-kg person who eats seafood containing 500 µg Hg/kg FW 14 times a week will have an intake of 1050 µg Hg (as MeHg) a week. This is 5 times the PTWI. Consuming the same amounts of seafoods at 750 µg Hg/kg would exceed the PTWI by about 8 times. On the other hand a 70-kg person who eats only one meal a week can eat seafood containing about 1300 µg Hg/kg FW which is about twice the legal limit. Hence persons eating one meal a week or less are not in need of legal limits while the persons consuming many meals of seafoods containing high amounts of Hg are most at risk, but are not protected by the legal limits.

On the other hand from the economic point of view a real enforcement of the legal limits would have severe consequences on the Mediterranean fisheries since most of the large and economically more valuable specimens would be banned from sale.

Therefore, the scientific evidence speaks against legal limits on maximum concentrations in seafoods and in favour of counselling persons who eat large amounts of seafood on advisable intakes, both regarding quantity and the species to be consumed.

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 Hg concentrations in seafoods from many of its regions many persons especially in coastal zones are exceeding their tolerable intakes. Efforts should be made to identify these critical groups.

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