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ASSESSMENT OF THE STATE OF POLLUTION OF THE MEDITERRANEAN SEA BY ZINC, COPPER AND THEIR COMPOUNDS

FAO WHO

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TABLE OF CONTENTS

Page No.

EXECUTIVE SUMMARY

1. INTRODUCTION 1

2. SOURCES AND INPUTS OF ZINC AND COPPER IN THE MEDITERRANEAN 2

2.1 Natural sources 2

2.2 Anthropogenic sources 4

2.2.1 Modes of inputs and loads 5
2.2.2 River inputs 5
2.2.3 Anthropogenic inputs of zinc and copper and their fate in the Mediterranean 9

2.2.3.1 Mining of zinc and copper 9

2.2.4 Industrial uses 11

2.2.4.1 Zinc 11
2.2.4.2 Copper 14

2.2.5 Sewage and sludges 18
2.2.6 Zinc and copper binding in sludges 18
2.2.7 Fate of zinc and copper after the discharge of sewage and sludge into the sea 19

2.3 Atmospheric inputs of zinc and copper in the Mediterranean 20

2.3.1 Concentrations and flux data 20
2.3.2 Mineral dust transport over the North Western Mediterranean 23
2.3.3 The N.W. Mediterranean coast: a case study 25
2.3.4 Summary and preliminary conclusions for zinc and copper atmospheric inputs 27

2.4 Summary and conclusions 28

3. LEVELS OF ZINC AND COPPER IN THE MEDITERRANEAN 29

3.1 Data quality assurance and intercalibration 29

3.2 Zinc and copper in the air 33

3.3 Zinc and copper in seawater 33

3.3.1 Zinc levels 34
3.3.2 Copper levels 38

3.4 Zinc and copper in sediments 42

Page No.

3.5 Zinc and copper levels in biota 50

3.5.1 Zinc and copper in plankton 50
3.5.2 Seaweeds 55
3.5.3 Crustaceans 59
3.5.4 Molluscs 59
3.5.5 Fish 62
3.5.6 Birds and marine mammals 66

3.6 Levels in ecosystems under the influence of anthropogenic activities 66

3.7 Summary and conclusions 71

4. EFFECTS OF COPPER AND ZINC ON MARINE BIOTA 71

4.1 Biochemical effects 71

4.1.1 Zinc uptake and effects on cell membranes 71
4.1.2 Zinc and copper interactions with cytosolic components and effects on intermediate metabolism 72
4.1.3 The role of zinc and copper in nuclear metabolism 73
4.1.4 The role of Cu-, Zn- and other metallothioneins in marine animals 73
4.1.5 Effects of copper and zinc on lysosomal biochemistry 75
4.1.6 Effects of copper and zinc on the endoplasmic reticulum 77
4.1.7 Effects of copper and zinc on ATP synthesis 78
4.1.8 Summary 79

4.2 Other effects 79

4.2.1 On algae 79
4.2.2 On crustacea 80

4.2.2.1 Zinc 80
4.2.2.2 Copper 81

4.2.3 On polychaetes 83
4.2.4 On echinoderms 83
4.2.5 On molluscs 83

4.2.5.1 Effects on burrowing and crawling 83
4.2.5.2 Effects on shell growth 83
4.2.5.3 Effects on valve closure and heart rate 84
4.2.5.4 Effects on filtration rates 84

4.2.6 On fish 85
4.2.7 Summary 86

5. EFFECTS OF ZINC AND COPPER ON HUMAN HEALTH 86

5.1 Toxicity of zinc and copper to man 86

5.2 Relationship between the uptake of zinc and copper from seafood and the ADI for man 87

6. CONTROL MEASURES AND RECOMMENDATIONS CONCERNING COPPER AND ZINC 89

6.1 The existing provisions within the Barcelona Convention 89

6.2 National regulations 90

6.3 The E.C. and other provisions 92

6.4 Scientific rationale for establishing control and restriction measures for copper and zinc 94

    6.4.1 Environmental protection 94
    6.4.2 Human health protection 95

7. CONCLUDING RECOMMENDATIONS 96

7.1 Marine ecosystems 96

7.2 Human health 97

8. REFERENCES 98

EXECUTIVE SUMMARY

Zinc and copper which appear in Annex II of the LBS protocol are found in nature principally in sulphide deposits and in minerals of basaltic rocks. Zinc also occurs as a silicate complex and as the carbonate. Weathering and erosion of the earth's crust release and transport zinc and copper into the marine environment, mainly by surface runoff, rivers and atmospheric deposition. Anthropogenic activities also contribute to the level of inputs into the marine environment. Such activities are: mining, industrial processing of ores and metals and the disposal of metals and their compounds mainly in sewage and sludges. Other activities such as combustion of fossil fuels and waste incineration and smelting release zinc and copper into the atmosphere which are subsequently transported to the sea via various pathways.

If atmospheric inputs as well as inputs through the straights of Gibraltar and Bosphorus are taken into consideration, the estimated loads into the Mediterranean sea are 92,400 tons per year for zinc and 29,000 tons per year for copper.

The levels of zinc in seawater can be as high as 450 µg l^{-1} especially in polluted harbours. However, in clean offshore areas the values range from 1 to 5 µg l^{-1} and can even go down to 0.02 µg l^{-1}. The reported copper concentrations for the Mediterranean are lower and vary from 0.2 µg l^{-1} to 50 µg l^{-1} in the vicinity of point sources.

The concentration levels of these metals found in sediments vary with the extraction method used. For total extraction and subsurface samples the background levels for zinc and copper are estimated to be 20 and 15 µg g^{-1} DW respectively. In polluted areas, concentrations of up to a few thousand µg g^{-1} have been reported, copper values being lower than the zinc ones.

The concentrations of these metals in marine biota vary with the species. The highest concentrations are found in some molluscs such as oysters where concentrations of Zn may exceed 100 µg g^{-1} FW and those of copper 20 µg g^{-1} FW. From the MED POL data it has been estimated that the average zinc value for the entire Mediterranean in the mussel Mytilus galloprovincialis is 27 µg g^{-1} FW and in the fish Mullus barbatus is about 4 µg g^{-1} FW. The respective values for copper are 1.3 µg g^{-1} for M. galloprovincialis and 0.4 µg g^{-1} for M. barbatus.

Seafood is a major source of zinc and copper for man. Intake of excessive doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and irritation of the central nervous system followed by depression. However, in general, the concentrations found in edible species do not pose a threat to human health. The reported lowest lethal dose known for zinc for a human is 500 µg kg^{-1} bw/day, and zinc has not been implicated in any, human disease derived from the eating of seafood. Also, copper poisoning of dietary origin is rare in man and higher mammals owing to the powerful emetic action of copper (WHO, 1984).

However, both metals have been found to have adverse effects on marine life at concentrations much lower than those occurring in polluted areas. Copper concentrations in seawater as low as 10 µg l^{-1} had a significant inhibitory effect on the shell growth of M. edulis (Manley et al., 1984) and

5 µg l^{-1} on the reproduction of the isopod Idothea baltica. Zinc values of between 10 and 40 µg l^{-1} have shown to have harmful effects on the life of marine organisms.

In order to protect marine organisms, communities and ecosystems, the concentrations of both metals in seawater have to be reduced to levels which are not harmful. For this purpose it is necessary to limit the inputs of copper and zinc in the marine environment both in quantity per unit time discharged and as concentration of the metals in liquid effluents and sludges.

It is recommended that environmental quality objectives are set for the coastal waters of the Mediterranean. In order to achieve these water quality objectives, it is also recommended that limit values are set for all effluent discharges into the Mediterranean sea.

For the protection of human health, it is recommended that the situation is monitored and that legal limits should be imposed only when and where necessary.

1. INTRODUCTION

According to the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based Sources (LBS Protocol) the Contracting Parties shall take all appropriate measures to prevent, abate, combat and control pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources within their territories.

Article 6 of this Protocol stipulates that:

- The Parties shall strictly limit pollution from land-based sources in the Protocol Area by substances or sources listed in Annex II to this Protocol;

- To this end they shall elaborate and implement, jointly or individually, as appropriate, suitable programmes and measures;

- Discharges shall be strictly subject to the issue, by the competent national authorities, of an authorization taking due account of the provisions of annex III to the Protocol.

Item 1 of annex II to the protocol includes 20 elements with their compounds, namely zinc, copper, nickel, chromium, lead, selenium, arsenic, antimony, molybdenum, titanium, tin, barium, beryllium, boron, uranium, vanadium, cobalt, thallium, tellurium and silver. The FAO/UNEP/IAEA Consultation meeting on the assessment of pollution by the elements listed in item 1 of Annex II to the LBS protocol (Athens, 13-15 February 1991) divided the elements into three groups:

Group I: includes those elements for which sufficient information is available for their evaluation and preparation of the relevant assessment document.

Group II: includes those elements of concern and for which additional information should be generated in the near future to allow a proper evaluation and preparation of the relevant assessment document.

Group III: includes those elements for which the limited information available indicates low concern and for which no action is necessary at the present.

Group I includes zinc, copper, nickel, chromium, lead, selenium, arsenic and boron. Immediately after the consultation meeting, work was initiated for the preparation of assessment documents on zinc, copper, nickel, chromium, lead and arsenic.

According to the proposal of the Meeting of Experts for the Technical Implementation of the LBS protocol (December, 1985) which was adopted by the Fifth Ordinary Meeting of the Contracting Parties to the Barcelona Convention (September, 1987), assessment documents should include inter alia chapters on:

- sources, point of entries and amounts of pollution for industrial, municipal and other discharges to the Mediterranean sea;

- levels of pollution;
- effects of pollution;
- present legal, administrative and technical measures at national and international level.

In 1986, a document on the state of pollution by cadmium, copper, zinc and lead was prepared and presented to the Fourth meeting of the Working Group for Scientific and Technical Cooperation for MED POL (Athens, 16-20 June 1986) as document UNEP/WG 144/11.

The present document, for which FAO was entrusted with the overall technical responsibility, has been mainly prepared by Professor M. Scoullos of the University of Athens. The preliminary document was presented to the 1993 Joint Meeting of the Scientific and Technical Committee and the Socio-Economic Committee (3-7 May) requesting delegations to submit comments for its improvement particularly information on sources and on existing legal provisions relevant to pollution control in the countries. Since it had only been distributed at the meeting, the participants agreed that all those delegations, which wished to do so, should send their comments to the Secretariat by the end of September 1993 to allow for the preparation of an updated version (para. 61 and 62 of the report of the meeting, document UNEP(OCA)/MED/WG.66/8).

As no comments or input were received by the deadline date, MED POL national coordinators were reminded of the decision of the Joint Committee's meeting. There were 5 responses to the reminder, 3 of them containing comments which have been taken into consideration in the preparation of the present version.

Assessment documents have already been prepared for all 9 groups of substances included in Annex I to the LBS protocol as well as for the pathogenic micro-organisms which are included in Annex II. This is the first assessment document with proposed measures concerning elements and compounds listed in item 1 of Annex II for which Article 6 of the LBS protocol applies. The measures recommended aim to limit inputs of copper and zinc in the marine environment. They consist of limit values for discharges as well as quality objectives for seawater.

2. SOURCES AND INPUTS OF ZINC AND COPPER IN THE MEDITERRANEAN

2.1 Natural sources

Dissolution and weathering of geological sources are calculated to release some 720000 tonnes/y Zn worldwide (GESAMP, 1976). Sulphide deposits are the principal ores for zinc and copper and they are often associated with sulphides of other metals such as cadmium, lead and iron. Zinc and copper are also found in significant concentrations in minerals of basaltic rocks. Zinc also occurs as a silicate complex and as the carbonate.

Weathering and erosion of the earth's crust release and transport zinc and copper into the marine environment, mainly by surface runoff, rivers and atmospheric deposition. Figure 1 (UNEP/FAO/WHO, 1989) shows the main mineral deposits and mining sites of Zn, Cu and Pb in the Mediterranean.

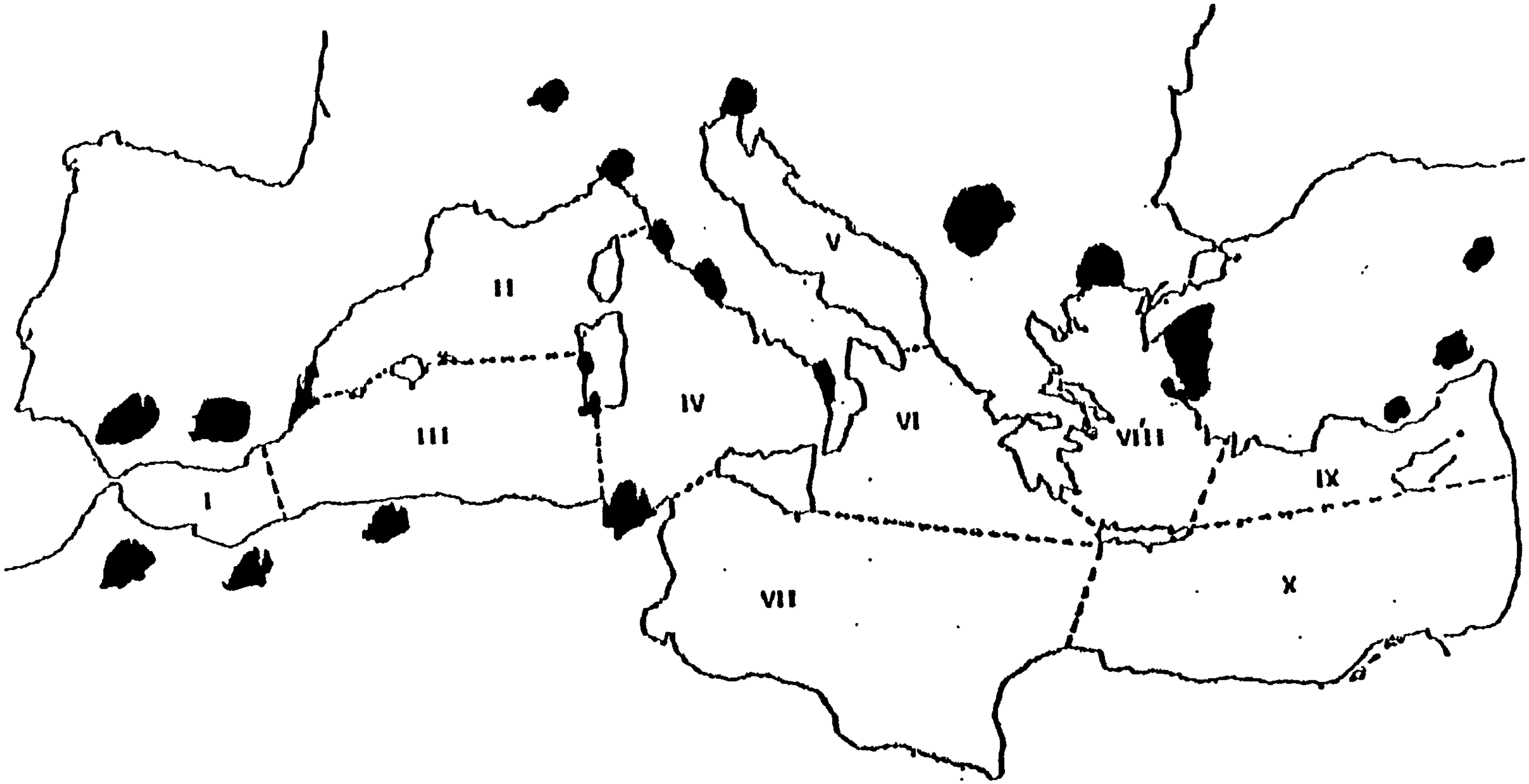


Fig. 1 Areas of zinc, copper and lead mining activity in the MED POL regions

Natural sources are present in these regions where higher than average zinc and copper concentrations occur. Sediments and biota from these areas - and consequently the rivers draining them - are expected to have elevated zinc and copper concentrations. The latter levels are probably reflected in the marine environment. However, since mining has been closely connected with the existence of ores for many centuries, it is extremely difficult to make any attempt to differentiate between natural and anthropogenic inputs in these regions. The coastal Lagoon of Mar Menor (Portman) in Spain and the Lavrion Coast in Greece are examples of such sites influenced by historic lead-zinc mines (Scoullos, 1982; De Leon et al., 1983).

Surface run-off (which combines natural and anthropogenically generated zinc) can be a significant source. In the South California Bight, for example, run-off contributes approximately 100 tonnes of Zn per year, 74% of which is in particulate form (Young et al., 1977). River inputs include both natural and anthropogenic sources (see section 2.2.2).

Other natural sources of zinc and copper include underwater, hydrothermal and volcanic activities which can occur particularly in the Eastern Mediterranean region, but which have been poorly studied.

The marine fluxes of zinc and copper to the Mediterranean can be included in the natural sources. These inputs enter the Mediterranean via the straits of Gibraltar and the straits of Bosphorus and the Dardanelles and, although poorly studied, have been roughly quantified by Dorten et al. (1991) on the basis of data selected from literature. The figures derived are quite substantial and suggest that (a) for zinc some 23500 tonnes/y enter via Gibraltar and a further 80 to 1300 tonnes/y enter via the Bosphorus, and (b) the copper loads are 9200 tonnes/y and 180 to 6350 tonnes/y, respectively.

The calculated loads from the Black Sea reflect the expected input in the outflow water without any subsequent metal enrichment from sources close to the Turkish coast.

These calculated inputs, even though they are very approximate, indicate that the mass balance for these two metals might be considerably different from that assumed for the Mediterranean in the past.

2.2 Anthropogenic sources

Anthropogenic activities such as mining, the industrial processing of ores and metals and the use and disposal of metals and metal compounds have resulted in increased inputs of zinc and copper into the oceans. Other sources including combustion of fossil fuels, waste incineration and smelting, release zinc and copper into the atmosphere which are subsequently transported by various pathways to the sea.

Industrial processes which give rise to zinc in their waste solutions include zinc and brass metal works, zinc and brass plating, basic steel works, steel galvanization, silver and stainless steel tableware manufacture, viscose rayon, yarn and fibre production, battery production, paint and dye manufacturing, anti-corrosion in cooling towers (together with chromium), organic chemical thermoplastic products, fertilizers, petroleum refining, as well as pulp and paper manufacture and production of newspapers and magazines.

Copper is also used in various industrial processes, in alloys, as a chemical catalyst, and in antifouling paints as an algicide and in wood preservatives.

Metallic copper is used in industry and for jewellery and ornamental purposes. Copper bearing solutions arise from metal plating operations in the subsequent rinse water, while jewellery processing also involves plating of or on copper. Copper is also a major component in the electrical wiring industry. Electroplating and etching of printed circuits in the electronic industry produce copper containing wastes. It is also used in agriculture.

2.2.1 Modes of inputs and loads

Zinc and copper inputs into the marine environment include surface runoff, river outflow, domestic and industrial effluents discharged directly to the sea through outfalls, dumping of sewage and industrial sludges and discharges via the atmosphere.

Elevated concentrations of zinc and copper are present in the suspended solids of wastewaters and sewage sludges as a result of industrial waste inputs and corrosion within the urban water supply network, and in urban runoff containing metals derived mainly from the surface of streets and highways (Forstner and Wittmann, 1983; UNEP/FAO, 1986a).

2.2.2 River inputs

Rivers transport zinc and copper arising from natural weathering as well as from inland industries or urban centres, from increased erosion due to mining, and from agriculture.

The atmosphere above urban and industrial centres can be enriched with copper and zinc by as much as four orders of magnitude above normal background (Forstner and Wittmann, 1983). Rainfall or dry deposition can transport such zinc and copper to the marine environment.

The inputs and total load of zinc into the Mediterranean from land-based sources have been assessed by the joint UNEP/ECE/UNIDO/FAO/UNESCO/ WHO/IAEA/ Project (MED POL X) (UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984; UNEP, 1989). (There has been no similar assessment for copper although there have been some assessments made by UNEP from other sources (see Table 7). The project involved the assessment of heavy metal loads derived from domestic sewage, industrial wastewater and river waters.

a. **Domestic sewage**. The assessment was based on data such as resident population density, tourism and industry. Direct measurements of heavy metal concentration and domestic sewage flows were available only in some cases.

b. **Industrial waste water**. For the assessment of zinc, and a few other heavy metal inputs (but not for copper) from industrial waste water, a flexible approach was used. Wherever there were analytical data for heavy metal concentrations in industrial effluents, they were used with wastewater flows to calculate inputs. When no such data were available, indirect information such as production figures, water consumption and number of employees were used. In collecting information on zinc loads in industrial effluents the following problems were encountered:

i) Information on the exact location of industrial plants relative to the coastline was often missing.

ii) Industries were not consistently classified.

iii) Information on trace contaminants in industrial wastewaters was scarce.

iv) Reporting systems from country to country were not comparable.

c. **River discharges**. Rivers were very rarely monitored for heavy metal concentrations. The sample pretreatment and analytical techniques used varied widely from country to country, making comparisons difficult. Average pollutant concentrations and mean water discharges were available for 30 out of a total of 68 major Mediterranean rivers. For the remaining 38 the heavy metal input was estimated by extrapolation.

d. **Atmospheric inputs** were not included in the aforementioned project. An attempt is made in section 2.3 of the present report to summarize the existing data on atmospheric inputs of zinc and copper in the Mediterranean.

The results of the project are summarized in Tables 1 and 2. Rivers carry 18000 tonnes of zinc per year compared to 6900 tonnes contributed by direct discharges from activities in the coastal zone. About 16% of the total zinc load was attributed to natural inputs.

Table 1

Estimated loads of zinc in the Mediterranean from land based sources in tonnes/year (UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984).

Zinc loads originating in the coastal zone	6900
- Domestic	1900
- Industrial	5000
Loads carried by rivers into the Mediterranean	18000 (14000-22000)
- Anthropogenic	14000
- Background	4000
Total Mediterranean loads	25000 (21000-29000)
- Anthropogenic	21000

Table 2

Estimated loads of zinc in tonnes/year entering the Mediterranean regions
(% of total in brackets) (UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984).

Region	Zinc
I	300 (1)
II	5200 (21)
III	700 (3)
IV	3000 (12)
V	8600 (35)
VI	1600 (6)
VII	500 (2)
VIII	2500 (10)
IX	1100 (4)
X	1200 (5)
Total	24700

High inputs enter the Adriatic (region V, 8600 tonnes/y) and the northwestern basin (Liguro - Provencal, region II, 5200 tonnes/y) (see Fig. 1 and Table 2), which are bordered by industrialized countries and receive major river discharges. These two regions receive 56% of the total load. Regions IV and VIII (Tyrrhenian and Aegean Seas) receive moderate amounts (22% of total inputs). The other Mediterranean regions (I, III, VI, VII, IX and X) each receive less than 6% of the total load and together they approximate to 21% of the total.

These river inputs have been considered by Dorten et al. (1991) to be overestimates. These authors used a small set of accurate water analyses for a few rivers (see Table 3) and by making a number of assumptions they calculated the net river fluxes of zinc to be between 6 to 1635 tonnes/y and of copper 360 to 6350 tonnes/y.

Table 3

Dissolved trace metal concentrations in Mediterranean rivers and
in the open Mediterranean Sea (Concentrations are given in nM)
(from Dorten et al., 1991).

River	Cu	Zn
Rhône	30.4(18.6-44.6)	79.5(50.1-103.7)
Po	25.7(17.3-33.8)	57.7(19.1-93.3)
Ebro	15.3(8.7-22.6)	42(16.8-65.7)
Arno	27.5(17.7-39.2)	30.6-306
Nile	14.9(11.6-22.8)	
Krka	1.57-1.78[a]	4.6[a]
Open Med.Sea	1.37[b]-3.93[b]	5-20[c]

[a] Data from Martinèiæet al. (1987)

[b] Data from Morley et al. (1990)

[c] Data from Morley personal communication

These calculations give a range of the "uncorrected" flux values which are higher than those reaching the open Mediterranean, particularly for copper which, in many cases, is reduced in concentration by non-conservative estuarine processes.

Huynh Ngoc et al. (1987) measured the concentrations of zinc in the dissolved, suspended and sedimentary phases of Rhône river water using differential pulse anodic stripping voltametry. For total desorbable zinc (operationally defined as that measured in unfiltered water at pH 1.5 to 2), the concentration in the river water (upstream) was 2.0±0.6 µg l^{-1} and in the delta water lower at 1.05±0.25 µg l^{-1}. This might explain to some extent the differences observed between previous input calculations (frequently based on concentrations from upstream monitoring networks) and the more recent assessments.

Furthermore, these authors found that in non-delta waters only about 35% of the zinc was in true solution, 25% adsorbed on suspended material and 40% was in the suspended matter but not desorbable. The total zinc content in suspended matter (including adsorbed zinc) was around 70 µg g^{-1}, lower than other values found in the literature.

Metal enrichment attributed to the exchange of waters through the Straits of Gibraltar (see section 2.1) has been discussed by Boyle et al. (1985) and Van Geen et al. (1988). According to these authors a significant proportion of the heavy metal enrichment may originate in coastal waters outside the basin and may be at least in part attributable to anthropogenic activities.

There is a considerable literature on the fate of copper in river and estuaries and several types of behaviour have been described (e.g. conservative, mobilization from particles, and removal from solution). In estuaries, copper either behaves conservatively or, as in the Arno and the Rhône, can be removed from solution. Removal from solution is generally ascribed to coprecipitation of copper with organic and oxyhydroxide colloids undergoing coagulation during estuarine-mixing processes.

The relatively few reports available on Zn behaviour in estuaries are conflicting in their conclusions. However, in most Mediterranean rivers zinc either behaves conservatively (Rhône and Po) or is removed (Arno). These variations appeared to be related to river zinc concentrations, which are relatively low in the Rhône and Po and elevated in the Arno (Dorten et al., 1991).

The major part of this load is associated with particulate material. According to Martin and Gordeev (1986) more than 90% of the river sediment discharge settles within the estuaries and the coastal zone so that less than 10% of the river load reaches the open sea. Relatively few studies have been made to determine the fraction of trace metals which is complexed by organic matter and that which occurs as labile fraction.

Elbraz-Ponlichat et al. (1990) and Martin et al. (in press) have determined complexed copper in the Western Mediterranean, using C_{18}SEP-PAK. During July 1989, April 1990 and February 1992, 20% to 35% of SEP-PAK extractable (hydrophobic) fraction of copper was detected in surface waters (0.4 to 0.8 nM) in the Gulf of Lion. At all stations the percentage of hydrophobic fraction in the surface waters was higher than that in bottom waters, linked apparently to primary production. Vertical profiles show that maximum concentrations correspond either to the maximum of primary production (Elbraz-Ponlichat et al., 1990) or the maximum of the degradation products of phytoplankton (Martin et al., in press).

2.2.3 Anthropogenic inputs of zinc and copper and their fate in the Mediterranean

The main anthropogenic sources, apart from combustion, relate to: a) metal mines, b) industrial uses, mainly metallurgical and other metal and chemical processing and c) to the disposal of sewage and sludges.

2.2.3.1 Mining of zinc and copper

Zinc is found in sphalerite and other sulphide ores. Copper is mined mainly in the form of chalcopyrite. Most of the mines are underground. The ore is first broken, crushed, enriched and treated with water and reagents. The concentration process involves flotation, gravity or magnetic processes, and the waste rock forms the "tailings". The concentrated ore is then heated in a furnace to release the crude metal ("smelting").

The concentration process is usually conducted at the mine; smelting tends to take place elsewhere, mainly close to the necessary energy source and/or the market for the metal. Secondary production of zinc and copper (recovery from scrap) plays an increasingly important role since it is less energy intensive than primary production.

Waste waters from the various processes are generally treated by lime precipitation and sedimentation tanks or ponds. All solid mining wastes can leach zinc, copper and other metals into the environment. The leaching rate is related to the acidity of the water in contact with the solid waste. Contamination due to the increased surface area of metal bearing rocks in mining areas can continue at a diminishing rate for hundreds of years.

Oxidation leaching and metal leaching processes from mine tailings are well known (Sodermark, 1983). Such leaching can be reduced significantly (theoretically by 90%), if old deposits are properly covered, sealed and screened off from air and water. In mining areas, surface water zinc concentrations as high as 50 mg l^{-1} have been reported (Durum et al., 1971). The main sites of zinc, copper and lead mines in the Mediterranean area are shown in Fig. 1.

CEC/EOA (1977) has reported that the annual production of zinc from ores is around $5x10^6$ tonnes worldwide. However, the actual world mine production of zinc may be higher because the World Bureau of Metal Statistics, in its March 1991 report, has published a figure of 5.4 million tonnes for zinc mine production for 1990, out of which 5.2 million tonnes represents the smelter/refinery production produced throughout the world but excluding centrally planned economies (CPEs). Similarly the copper in 1990 production was 7.2 million tonnes, 7.1 million tonnes of which represent the smelter/refinery production. The distribution of production and consumption 1990 in the various parts of the world is shown in Table 4.

If the approximate figures given for the centrally planned economies are included, the overall zinc and copper production is raised to approximately 7.2 million tonnes and 9.5 million tonnes per year respectively.

Table 4

Annual production and consumption of zinc and copper in various parts of the world (in million tonnes).

	Zinc		Copper	
	smelter production	consumption	smelter production	consumption
N. America	1.0	1.1	2.5	2.4
Western Europe	2.1	1.8	1.7	3.2
CPEs	2.0	2.0	2.4	2.3
South America	0.5	0.4	1.6	0.4
Oceania	0.3	0.1	0.2	0.1
Asia	1.1	1.5	1.5	2.7
Africa	0.2	0.2	0.8	0.1

In 1971, France produced 218000 tonnes of zinc and Italy 140000 tonnes according to the CEC/EOA (1977); the corresponding consumption was 264000 tonnes and 203000 tonnes (1972) respectively. These figures for zinc production are considerably different from those which appear in UNEP/FAO/WHO, 1989 (see Table 5). This table shows that the total zinc production from ore increased in Mediterranean countries from 355000 tonnes in 1975 to 499000 in 1984, an increase of 44% mainly due to increased production in Spain, France, Turkey and Greece, offset to some extent by some reductions in Italy, Yugoslavia and Morocco.

Table 5

Zinc and copper production from ore in Mediterranean countries (in thousand tonnes) Source: Samin.

Country	Zinc		Copper	
	1975	1984	1975	1984
Albania	-	-	9.8	15.0
Algeria	11.3	14.6	0.4	0.2
Cyprus	-	-	9.9	1.3
France	13.9	36.4	0.1	0.2
Greece	14.4	22.6	2.5	-
Italy	77.8	44.3	0.8	0.9
Morocco	18.8	11.9	-	21.8
Spain	84.2	228.0	51.6	63.5
Tunisia	6.0	6.7	-	-
Turkey	25.6	50.7	27.3	27.1
Yugoslavia	103.4	85.8	114.9	137.6
Total	355.4	499.0	217.3	267.6
Change %	+40.4%		+23.1%	

The production of copper increased in Mediterranean countries by 23.1% between 1975 and 1984.

2.2.4 Industrial uses

2.2.4.1 Zinc

Major industrial uses of zinc are in the production of rolled and wire drawn zinc, sheet products, zinc-copper alloys, manufacture of light alloys, and metal plating, galvanising and thermoplastic products.

(a) Primary and secondary metal production

Primary metal production involves roasting (ca 1200), sintering and smelting. The production mainly relies on thermal processes and therefore the emissions are to a large extent into the atmosphere.

Secondary zinc production is based on recovery from scrap, involving materials such as containers or residuals from plating scrap.

(b) Metal plating industry

Zinc is used in the electroplating process (for zinc plating) in cyanide solutions. It may also be used in metal colouring process plants. Zinc is used in anodizing plants and also zinc plated steel may be treated with phosphoric acid. The industrial plant can vary from small electroplating shops with a few tonnes per week capacity to major metal plating works producing tens of thousand tonnes of finished product per year. Electroplating in small and medium size plants takes place in all the major cities and ports of the Mediterranean.

Wastes

Most zinc bearing wastes originate from electroplating dipping baths. In most cases the bath solution is alkaline and contains zinc-cyanide, NaOH, Na_2CO_3, Na_2SO_4, NaCN, and Rochelle salt.

Zinc in the wastes is mainly in the form of $Zn(CN)_2$ with some present as $Zn_2Fe(CN)$. These wastes are mainly a clear liquid because zinc is soluble in alkaline solutions of pH above 9. Sometimes, however, precipitated zinc compounds form a suspension with a white-grey milky appearance. Most wastes are generally cyanide bearing and may include aluminium, lead and copper, depending on the other processes used. Thus, effluents may include both insoluble zinc and dissolved zinc as well as floating scum and oil.

Plating solution may contain as much as 34000 mg l^{-1} of zinc. Processes which give rise to zinc bearing wastes are pickling baths (>40 mg l^{-1}), brass mill wastes (40-1500 mg l^{-1}), zinc plating (70-350 mg l^{-1}) and silverware (5-220 mg l^{-1}). Zinc concentrations in the effluent vary according to plant management. Average concentrations of zinc in general electroplating wastes are between 5 and 8 mg l^{-1} but may rise from 11 mg l^{-1} in silverware plants, to 110 mg l^{-1} in cyanide bearing wastes from automobile manufacture.

Zinc plating of one tonne of product usually results in a discharge of 0.4 kg of zinc in an effluent flow of approximately 8 m^3/h. Plating bath water, including cleansing and rinsing, produces 60 litres of waste per 1 m^2 of plated surface in a plant designed to reduce water consumption.

Zinc coating and silverware processing are both batch processes leading to semi-continuous discharges of wastes. Most plants operate one or two shifts per day. Weekly cleaning of baths may result in a peak flow on a certain day of the week. There may also be peak discharges due to accidental or intentional spills and dumpings. These peak concentrations may not be recorded by routine monitoring programmes, leading to an underestimate of the loads discharged to the marine environment.

(c) Steel galvanizing plants

Steel galvanizing is usually carried out in large plants, particularly for the production of galvanized pipes where plants exist with a capacity of 5000 to 50000 tonnes per year. Most plants use the Hot Deep Galvanization technique, which is in many respects similar in principle to zinc electroplating, but the industry is often more mechanized and processes are more continuous with the use of automatic controls.

The acidic galvanization wastes originate mainly from the process of fluxing which, in large galvanizing plants, is continuous; the wastes contain zinc sulphate together with other salts.

The effluent is a clear or slightly coloured liquid solution with a pH ranging between 2 and 3, and contains zinc and iron ions as well as sulphate and chloride anions. When pH levels are raised, a milky suspension is formed which finally yields a slurry type of sediment.

Large galvanization plants produce approximately 5 to 15 m^3 of total plant wastes per tonne of galvanized steel capacity. Approximately 5 to 10% of these wastes are galvanization fluxing wastes i.e. approximately 1 m^3 of process wastes per tonne of plant production capacity.

Small zinc plating plants using a batch operation discharge in a semi-continuous mode (depending on number of batches per day). In larger plants, discharges are continuous for at least 12 hours per day. For a plant to become economical, a two-shift operation is required. The mode of discharge is extremely important for the recipient water body and the ecosystem present there.

(d) Viscose rayon production

Zinc is discharged from the viscose rayon production process; the effluent may contain from 250 to 1000 mg l^{-1} zinc.

(e) Wood pulp production and newsprint production

Little information is available on the concentrations of zinc in wastewaters from these processes. It has been noted that a large wood pulp mill used 6 tonnes of zinc per day.

(f) Cooling water

The use of a commercial process called "Cathanodic Treatment" leads to zinc being discharged in the blow down of circulating water systems. Zinc concentrations of 6 mg l^{-1} have been found.

(g) Paint production

Zinc has been found in the wastes from the paint industry in concentrations ranging from 0.3 to 10 mg l^{-1}. Zinc is used together with other metals in pigments used by the plastic industry, glass and ceramic glazers, enamels etc. When producing yellow pigments (cadmium sulphide/zinc sulphide) zinc salt is added to cadmium metal dissolved in a mineral acid, the amount depending on the final colour required. In an alternative process, zinc and cadmium are precipitated from solution as carbonates which are then reacted with sodium sulphide to precipitate the mixed sulphide pigment required (OECD, 1975).

(h) Miscellaneous

With the decreasing use of cadmium stabilizers, zinc is increasingly used as a replacement to prevent the degradation of synthetic materials. Zinc is released by the burning or disposal of these products.

Also, zinc-cadmium alloys are used in particular for the soldering of aluminium, and the petroleum industry produces motor oils which contain zinc.

Waste treatment

Zinc in the rinse solution of plating and metal processing industry is relatively difficult and expensive to separate from the other metals with which it is associated in the waste streams. Its price does not encourage its recovery. "Cleaner" production techniques are under investigation at present. Although there are several technologies available, e.g. based on ion exchange, precipitation-sedimentation, reverse osmosis, adsorption onto particles (such as activated carbon), evaporation etc., which could be used, the favoured method is the destruction of the cyanide complexes and pH adjustment, followed by precipitation and settling or separation by filters (see below).

Ion exchange recovery of zinc is used mainly in order to reduce its concentration in wastes from viscose rayon production and other similar industries. Ion exchange could easily reduce the effluent concentration from 250-1000 mg l^{-1} to 20 mg l^{-1}.

(i) Zinc cyanide destruction and precipitation (for wastes from metal plating industry)

The first stage of zinc cyanide destruction involves oxidation which can be by chlorination, to form $Zn(OH)_2$, which then precipitates after pH adjustment. The following chemical processes take place:

$$Zn(CN)_2 + 2HOCl \dashrightarrow Zn(OH)_2 + 2CNCl$$

$$2CNCl + 3HOCl + H_2O \dashrightarrow 5HCl + 2CO_2 + N_2$$

Following such treatment, the plant effluent contains less than 1 mg l^{-1} of zinc and under optimal operational conditions a zinc concentration of less than 0.2 mg l^{-1} can be achieved. The precipitate can be settled or separated by filtration.

(ii) Precipitation (for wastes from galvanising plants)

Fluxing wastes contain 20 to 60 mg l^{-1} of zinc while total plant wastes contain 1 to 5 mg l^{-1} zinc. Treatment by pH adjustment and settling, preferably of the fluxing wastes before mixing with total plant wastes which can reduce zinc concentrations to 2-4 mg l^{-1}, can lower the concentration in the final effluent to less than 0.5 mg l^{-1}.

Disposal of sludge

Sludge containing zinc should be dried by evaporation or filtration and disposed of in a solid form by land-filling. Sites should be selected and prepared carefully, using an appropriate lining and with monitoring devices in order to prevent ground and surface water being contaminated by zinc-containing leachates. It should be stressed that some of the zinc inevitably forms zinc sulphate which is very soluble and toxic to natural fauna.

There is no inventory of the practices, quantities and sites for such sludge disposal in the Mediterranean. However, it is possible that a major part of such disposal is being carried out with no proper national or local control and therefore zinc leachates from these sources should be also included in the list of permanent inputs from industry to the Mediterranean.

Treatment technologies for zinc containing waste water

The use of activated carbon, following sulphite precipitation for removal of residual zinc from plating waters, has been suggested by Peters and Young (1985). Activated carbon treatment can be used as a polishing step following either hydroxide or sulphite precipitation and removal. It has been shown to be effective for both removal of zinc and excess sulphite from plating wastewaters. In the absence of chelating agents and other interfering substances, removal of zinc exceeded 70% and sulphite removal exceeded 50% over the pH range 7 to 10. In the presence of 100 mg l^{-1} of ammonia or cyanide (acting as an interferent) zinc removal following sulphites removal exceeds 74%. The activated carbon polishing step offers an alternative treatment to minimize the potential for H_2S gas evolution and the concern for sulphite toxicity associated with the precipitation of heavy metals sulphites.

2.2.4.2 Copper

Principal industries

(a) Metal processing and plating

Industrial copper utilisation occurs in large industrial complexes including copper mills and appliance manufacturing. The production of electrical cables and automobile radiators is another major use of copper. Electroplating also gives rise to copper wastes.

Copper is electroplated by using four types of baths, the most common copper salts being alkaline cyanide and acid sulphate, but pyrophosphate and fluoroborate can also be used. The copper is electroplated where a thick coat is required. Plant size varies from small shops processing a few tonnes of copper per year to large industries processing hundreds of tonnes of copper and brass products per year.

Chromates are often coated on to copper. Immersion plating is used to put a copper coat on steel, gold on copper, and tin on copper.

Wastes

Plating process wastes may contain up to 120 mg l^{-1} of copper, and brass mill wastes up to 400 mg l^{-1}, while other processes may lead to waste concentrations generally up to 50 mg l^{-1}. Exceptions are copper wire mills (800 mg l^{-1} average) and 1000 mg l^{-1} in silver plating wastes.

Final plant wastes usually contain 20 to 80 mg l^{-1} copper according to the amount of rinse water used. Continuous rinsing (following dipping) and stationary rinse waters contain between 5 and 20 mg l^{-1} of copper.

The two main types of copper plating processes - the alkaline cyanide and the acid sulphate process - produce different types of wastes.

The alkaline cyanide copper plating involves electroplating in baths containing 15 to 60 g l^{-1} Na_2CO_3, 5 g l^{-1} NaCN or KCN and 20-40 g l^{-1} $Ca(CN)_2$. pH levels are maintained at 11-12.5. Plating baths wastes contain small monocline crystals of $Cu(CN)_2$ and dissolved tetrahedral complex of monovalent copper $CuK_3(CN)_4$ as well as KCN, NaCN and other salts and heavy metals. Wastes are strongly alkaline with pH between 11 and 12.

The alkaline cyanide process produces 30 to 40 m^3 of wastes per tonnes of plant product. The wastes are turbid and dark coloured and they contain suspended matter together with small crystals in suspended and sludge form. They have a typical copper cyanide odour and should be kept in their alkaline form to prevent the emission of HCN. The wastes can contain oils and other metals.

The acid sulphate process involves electroplating in baths containing 50 g l^{-1} sulphuric acid and 200 g l^{-1} copper sulphate. In many cases thiourea-dextrin molasses are added. All the substances used in the baths appear in the bath wastes and from the various rinsing operations. These processes produce 20 to 30 m^3 of wastes per ton of plant product. Acid sulphate wastes are clear with a typical light blue colour due to $CuSO_4$.

Small plants produce frequent batches of extremely concentrated waste when baths are being emptied after plating (dipping). Stationary (fixed) rinsing, following plating, produces medium concentrated wastes, and continuous or semi-continuous rinsing produce wastes of decreasing concentrations.

Large plants produce wastes at a virtually continuous rate. In a very well-managed waste handling plant the concentrated (hot) wastes from plating and stationary rinsing are segregated from the concentrated sequential rinsing. In some plants, some of the chemical substances from the "hot" wastes are recovered.

Waste Treatment

Alkaline cyanide wastes can be treated with iron salts to form the complex $Cu_3Fe(CN)_4SO_4$ which is then removed by precipitation and sedimentation. An alternative treatment is to use active chlorine to produce the following chemical reaction (not stoichiometric):

$Cu_2CN_2 + Cl_2 + NaOH \dashrightarrow N_2 + CuCO_3 + CuCl_2 + NaCl + H_2O$

Both $CuCO_3$ and $CuCl_2$ form a precipitant at elevated pH and can be removed by sedimentation. Such treatment can produce an effluent with less than 0.1 mg l^{-1} copper and levels below 0.05 mg l^{-1} can be achieved in well managed plants.

Acid sulphate wastes can be treated with lime to produce the following chemical reaction:

$CuSO_4 + Ca(OH)_2 \dashrightarrow Cu(OH)_2 + CaSO_4$
$Cu(OH)_2$ is insoluble and forms a precipitant.

Lime treatment of copper wastes produces an effluent with less than 0.5 mg l^{-1} of copper and in well managed plants concentrations of 0.05 - 0.1 mg l^{-1} can be achieved after filtration.

Recovery of copper involves in-plant measures for waste stream segregation and flow reduction. Recovery processes include evaporation, ion exchange and electrolytic techniques. Copper containing sludges are usually dried by evaporation and disposed either is specially designed centres for toxic sludges (rare in the Mediterranean area), or in landfill and old quarries in locations where groundwater and surface water contamination can be prevented. However, most of the solid wastes are disposed of without proper control.

It should be stressed that the copper ion is toxic and its salts are largely soluble and thus toxic; copper sulphite is a well-known algicide. Most copper precipitants will remain relatively insoluble in a weak alkaline environment, but will tend to be redissolved in an acidic environment such as found in anaerobic sediments and landfills where biodegradable organic matter is present.

(b) Electrical wire treatment

Electrical wire plant capacity can vary from 500 to 2000 tonnes of wire produced per year, with a few exceptions of larger plants. When wires are drawn from the melted copper they are pickled with sulphuric acid to remove surface layers of copper oxides. Sodium carbonate is used for neutralization.

Wastes

Wastes from this process contain copper sulphate and copper carbonate together with sodium sulphate. It forms a turbid solution containing dissolved copper sulphate, suspended solids, and an orange sludge of copper carbonate.

Approximately 2 to 5 m^3 of wastes are produced per tonne of wire processed. Flow reduction, which is advisable for metal recovery, can reduce this amount to between 1.5 to 2.5 m^3 per tonne of wire. The raw wastes contain 50-100 mg l^{-1} of copper sulphate and 50-100 mg l^{-1} of copper carbonate.

In smaller plants the operation is intermittent and discharges are made for a few hours per day or on certain days in a week. Larger plants have a continuous or semi-continuous flow of effluent.

Waste treatment

Well-managed plants recover copper from the wastes by electrolytic methods; also, the copper carbonate can be dried and sold as a by-product. Following such treatment the final effluent contains less than 0.5 mg l^{-1} of copper and with careful use of established techniques, an effluent with less than 0.05 mg l^{-1} can be produced.

(c) Copper ornamental industry

Copper ornaments, jewellery and souvenirs are "blackened" in small shops or larger copper ornament industries. Although limited in size, this industry is a significant waste producer because it is difficult to control. Coated copper products are washed with sulphuric acid and reduced forms of sulphur and sulphide containing substances such as $K_2S_2O_2$, K_2S etc.

Wastes

Copper oxides and copper sulphate are present in the wastes, together with oils, detergents and salts. Concentrated bath wastes can contain between 100 and 300 mg l^{-1} of copper while sequential rinse waters can contain between 5 to 20 mg l^{-1}. Mixed raw wastes can contain 20 to 100 mg l^{-1} of copper.

The wastes are turbid and acidic and although most of the copper is in solution they contain suspended matter and a greyish sludge. Approximately 5 m^3 of wastes are produced for one tonne of copper products. Wastes are usually discharged in intermittent batches of concentrated bath wastes and rinse waters.

Waste treatment

Following waste treatment with neutralization by lime and precipitation of copper hydroxide, the final effluent may contain less than 0.5 mg l^{-1} of copper and in a well managed waste treatment less than 0.2 mg l^{-1}.

(d) Electronic printed circuit industry

This is an industry consisting mainly of medium and small size establishments producing 1000 to 6000 m^2 of printed circuit per year. However several major electronic firms have opened large factories with capacities of at least 10000 m^2 of printed circuits per year. It should be noted that the trend is to reduce the size and increase the sophistication of printed circuits, so that surface area is not now an adequate measure for assessing plant capacity or waste discharge volume.

Wastes

About 15 to 30 m^3 of wastes are produced per square metre of printed circuits. Copper discharged in wastes might reach 2 to 4 kg per m^2 of printed circuits. Wastes contain mainly copper associated with other metals such as chromium, tin, zinc, nickel and cadmium. Pickling of copper components in chromic acid produces an especially problematic waste containing acidic mixtures of $CuCrO_4$ and Cu_2CrO_4 and CrO_4. Process wastes from plating baths and stationary rinsing can contain 80 to 150 g l^{-1} copper while total plant wastes can contain 100 to 250 mg l^{-1}. The waste is usually a clear bluish acid solution, which is discharged in batches from small establishments. The discharge is virtually continuous in large establishments with occasional peaks in concentration due to spills, emptying and cleaning.

Waste treatment

Copper is removed by pH adjustment, precipitation and settling as described above. Following treatment, the copper concentration in the effluent is usually less than 1 mg l^{-1} and with careful use of established treatment methods 0.1-0.2 mg l^{-1} can be achieved.

(e) Other industries with wastes containing copper

Copper wastes may also originate from the following processes and uses: copper alloys, wood preservation, pulp and paper mills, paper and paper board mills, production and use of chemical catalysts, antifouling paints, alloys, fertilizer manufacture, petroleum refining and algicides, and agricultural uses.

2.2.5 Sewage and sludges

One of the main sources of zinc and copper in the Mediterranean is the discharge of domestic and/or mixed domestic/industrial sewage and sludges. In several cases the runoff from urban areas is, at least in part, combined with sewage. At many sites in the Mediterranean Basin the sewage is discharged untreated to the sea, whereas elsewhere, despite the fact that sewage sludge dumping is not widely practiced here, primary (raw), secondary (activated) or digested sludges can reach the sea. In other cases, sludges are combined with other wastes in landfills without any particular precautions taken for containment and therefore zinc and copper can leach to the soil, groundwaters, and even to the sea.

Raw sludge is normally taken directly from the primary sedimentation tanks. It is known that as much as 70% of the total metals in raw sewage are removed by primary sedimentation; the levels of metals in the primary sludge have been found to be ten to twenty-fold greater than that in raw sewage (Lester et al., 1979).

2.2.6 Zinc and copper binding in sludges

Primary sedimentation has little effect on reducing the levels of dissolved metals in sewage (Oliver and Cosgrove, 1974). Secondary (activated sludge) treatment offers three possibilities for binding metals (Brown and Lester, 1979):

a) physical trapping of precipitated metal (mainly as hydroxyl compounds), in the sludge floc matrix,
b) binding of soluble metal to bacterial extracellular polymers, and
c) accumulation of soluble metal within the bacterial cell cytoplasm.

Although these three basic mechanisms could apply to all metals and types of sludge, Frea et al. (1971) suggest that under anaerobic conditions, such as those occurring in sludge digestion, polymers are hydrolyzed and the bound metals then released back into solution. However, under anaerobic conditions zinc has the tendency to form soluble sulphides. Tan et al. (1971) studied digested sludges and found that after centrifugation the solid fraction contained high levels of zinc ions, most probably retained by cation exchange and adsorption mechanisms (Stover et al., 1976), whereas the supernatant possessed virtually none. Foster (1985) studied the interaction between digested sludge and zinc and concluded that in anaerobically digested sludge, zinc binding is mainly due to chemisorption by weakly acidic functional groups such as carboxyl and hydroxyl units, involving cation exchange. The complexation of zinc on sludge does not seem to depend significantly upon temperature or the source of the sludge; it is site specific and there is essentially only one type of site on the digested sludge surface. Treatment with EDTA affects this surface in 3 ways: a) by destroying a number of sites, b) by modifying the remainder and, c) by exposing and/or producing additional (but limited) number of new sites.

Chen et al. (1974) carried out an extensive study of particle sizes within primary and secondary effluents and digested sludge from the Hyperion Wastewater Treatment Plant, Los Angeles, USA, and found out that virtually all (90%) of zinc was retained by a 0.2 µm filter. At least half of the metal was found to be associated with particles between 0.8 and 8.0 µm. Stover et al. (1976), found that zinc was preferentially bound to organic material in digested sludges.

Baldwin et al. (1983) made a thorough study of digested sewage sludge and its principal components formed by dispersion and sedimentation in water. Using X-ray microanalysis, they concluded that zinc, as well as copper, was bound to the recently formed microbial detritus portion of the organic sludge.

Holtzclaw et al. (1978), studied the incorporation of metals from sludge into soils, and suggested that most of the zinc (as well as Al and Fe) could be in the precipitable fraction of NaOH-extracted sludge and in the fulvic acid fraction of the organic component. This agrees at least in part with the observations of Lagerwerff et al. (1976), that zinc was more leachable from sludge than most other metals (e.g. Pb, Cu).

2.2.7 Fate of zinc and copper after the discharge of sewage and sludge into the sea

Knowledge of the fate of metals, and in particular of zinc and copper in sewage sludge after disposal to sea, is essential for an understanding of how these metals enter food chains and become incorporated into the tissues of marine organisms. An extensive study carried out by Rohatgi and Chen (1976) concluded that under aerobic conditions in seawater, some metals, particularly copper and zinc tended to be released from suspended particles. This was due to oxidation of organic matter and/or zinc and copper sulphides, formation of ionic pairs of zinc and copper chlorides and complexes with organic ligands as well as desorption of zinc and copper ions from suspended solids. The latter depended on dilution ratios and on the pH of the seawater which had been adjusted to between 7.6 and 8.2.

In another study, Rohatgi and Chen (1976) observed that a significant amount of zinc and copper contained in a sewage effluent became solubilised and therefore biologically available. However, many authors suggest that for most metals studied, including zinc and copper, relatively little solubilisation occurs (Norton et al., 1981; Norton et al., 1984).

A number of studies on the form of heavy metals in sewage sludge after disposal at sea (Jenkison, 1972; Faisst, 1980; Gibbs, 1982; Chapman, 1986), suggest that even fine particles (<10 µm) which probably contain most of the zinc and copper, could coagulate, flocculate and settle before much leaching of the metal could occur.

The settling time depends on the size of particles and the water circulation. In most of the cases studied by Draxler (1979) in the New York Bight, more than 60% of the sludge discharged reached the bottom within an hour. Using radioactive tracers, Talbot and Chegwidden (1982), observed sludge particles in the water column up to 8h after dumping in the Thames Estuary, which could then settle well away from the original dumping site (Norton et al., 1981). It should not be forgotten, however, that the latter site is in a tidal system that promotes dispersal whereas in the low tidal regime of the Mediterranean the vast majority of sludge particles will settle within less than one to two hours. This does not exclude the possibility that a relatively small but ecologically important percentage of them remain in the water column for many hours. Therefore, it is important to understand properly the biological and physical effects of zinc, copper and other metals contained in the sludge on benthic and pelagic environments.

Grunseich and Duedall (1978) showed that in seawater the decomposition of sewage sludge by bacteria and fungi was promoted by aerobic conditions and higher temperatures. This implies that these organisms may accumulate zinc in the organic fraction and, when ingested, possibly pass it on to filter feeders in the water column. As a consequence, rapidly sinking or slowly decomposing particles containing zinc and/or copper, such as plant debris, larger flocs and mineral grains, would become available to benthic organisms in the near vicinity of the discharge. Franklin (1983) has shown that, in general, the acute toxicity of metal-contaminated sewage sludge to adult marine animals is low, although at high concentrations shrimp larvae can be harmed.

In addition to the relatively well studied effect of metal containing sludges on benthic communities, there is now some evidence that planktonic communities may also be affected by sewage and sludge discharges because the size and nature of the fine organic flocs could be a suitable food source for plankton. Particulate zinc and copper associated with organic matter may then enter marine food chains within the water column provided that the particles are the right size and the metals are retained by the organisms.

Phytoplankton can accumulate soluble zinc and copper and there have been many studies of metal uptake by herbivorous zooplankton (Davies, 1978). The evidence suggests that this is probably the major route of metal uptake. Zooplankton at sludge dumping sites may, therefore, regularly ingest metal- enriched organic matter and/or phytoplankton. In time, this may lead to the development of metal-resistant species or strains and, in turn, introduces the possibility of a long-term accumulation of zinc and copper in marine planktonic food chains via this route. This includes those fish which feed primarily on plankton.

2.3 Atmospheric inputs of zinc and copper in the Mediterranean

2.3.1 Concentrations and flux data

Studies by Chesselet et al. (1979) and Buat-Menard et al. (1980) have shown that heavy metals in suspended particles of the open Mediterranean waters could not be attributed solely to crustal weathering and particles of planktonic composition and suggested that anthropogenic atmospheric inputs could form potentially significant sources. However, general data on atmospheric fallout cannot be divided into natural and anthropogenic sources with any confidence.

The fact that zinc and copper as well as lead and cadmium are contained in the smallest particles of the atmospheric aerosol, suggests that they were injected at relatively high temperatures into the atmosphere as very small particles formed during the processes of volatilisation and condensation.

This implies that zinc and copper may be directly transported to the Mediterranean from inland sources. The long-range atmospheric transport of particulate matter from continental sources to the open N.W. Mediterranean has been confirmed by Bergametti et al. (1989a) who carried out a continuous daily 24-hour aerosol sampling programme at a coastal location in Northwestern Corsica between 1985 and 1986 and used a three dimensional air mass trajectory analysis to evaluate the data.

In the Western Mediterranean the average atmospheric zinc level is 26 ng m^{-3} (GESAMP, 1989). Bergametti et al. (1989a) give a geometric mean atmospheric concentration, based on one year daily aerosol sampling, of 19.1 ng m^{-3} for zinc and 2.1 ng m^{-3} for copper for the open N.W. Mediterranean. The actual values, however, fluctuate considerably with time. During two cruises, mainly conducted in the Western Mediterranean the atmospheric concentrations of zinc and copper were measured by Arnold (1985) and Dulac et al. (1987) who concluded that considerable changes of up to one order of magnitude can be observed in less than 48 hours. Peak concentrations were observed near highly populated and industrial areas.

The marked temporal variability in the atmospheric concentrations of the elements in the Western Mediterranean was the main reason for a continuous aerosol sampling being undertaken in North Western Corsica between 1985 and 1988. The results from this study (Bergametti et al., 1989a; Remoudaki et al., 1991a, 1991b) suggest that a seasonal pattern occurs for elements of continental origin derived from either natural (eg. Al, Si) or anthropogenic (eg. Cu, Zn, S, Pb) sources. This pattern is inversely related to the frequency of the rainfall, so that the highest concentrations are found between May and October. Arnold et al. (1983) have estimated that the mixed natural and anthropogenic atmospheric input of zinc and copper in the Western Mediterranean is around $11x10^3$ tonnes/y and $1x10^3$ tonnes/y, respectively.

The total annual deposition flux of zinc into the Western Mediterranean basin was calculated recently to be higher at $17x10^3$ tonnes/y, corresponding to 21% of the European man-made emissions (GESAMP, 1989). The total annual deposition flux of copper given by the same source is $2.1x10^3$ tonnes/y corresponding to 11% of the European man-made emissions. If these values are extrapolated to the whole basin, the total atmospheric input for Zn is $42.5x10^3$ tonnes/y and for Cu $5.3x10^3$ tonnes/y.

Bergametti (1987) has estimated a flux of $40x10^3$ tonnes/y of zinc for the whole basin, based on continuous monitoring at a permanent station in the Western basin during 9 months in 1985.

However, such an extrapolation cannot be considered as accurate because of the strong temporal and spatial variability of these total atmospheric fluxes as suggested by Remoudaki et al., 1991a, and 1991b. For an accurate evaluation of the above fluxes these authors suggest that simultaneous and continuous sampling should be carried out at different sites located at the coastal zone and in the open sea. Also, it has been reported that the mineral aerosol fluxes over the Eastern Mediterranean are at least five times higher than those over the Western part and that the fluxes of pollutant elements are lower (UNEP, 1989) although the available data are insufficient for accurate assessments.

Dust samples have been collected at the seawater-air interface in order to investigate the atmospheric input of particles and metals to the Mediterranean Sea (Guerzoni et al., 1987); nine sampling stations were distributed in three distinct areas, namely Western Mediterranean (WM), Southern Adriatic (SA) and Eastern Mediterranean (EM). Average amounts of the total (soluble + insoluble) atmospheric dust loading were different in three areas, with values of 35, 19 and 51 µg m^{-3} respectively. The concentrations of zinc and the estimated fluxes of dry deposition are given in Table 6.

Table 6

Concentration and deposition fluxes of atmospheric zinc in three Mediterranean areas (W.M.=Western Mediterranean) (E.M.=Eastern Mediterranean, S.A.=South Adriatic).

	Areas	mean	max	min
Concentration of zinc in atmospheric particulates (dry deposition) (ng m^{-3})	W.M. E.M. S.A.	18.9 9.1 5.9	32.2 11.8 8.9	4.9 5.6 4.0
Estimated dry deposition fluxes from the atmosphere to the sea surface (ng cm^{-2} y^{-1}):	W.M. E.M. S.A.	595 372 185	1013 286 280	154 176 126

The zinc concentrations are higher (32.2 ng m^{-3}) in "coastal" atmospheric particulates around Southern Italy and Spain, probably related to local input from industrial areas. This figure for zinc is comparable to the total non-atmospheric input from rivers and direct discharges of effluents.

The estimate by Guerzoni et al. (1989) of the mean flux for dry deposition of zinc was 354 ng cm^{-2} y^{-1} (ranging between 126 and 1013). Fluxes for dry deposition based on a deposition velocity of 1 cm sec^{-1} are shown in Table 6. The highest value of 1013 ng cm^{-2} y^{-1}, was found in the Western Mediterranean, whilst the Southern Adriatic had the lowest value (126 ng cm^{-2} y^{-1}).

The available data for zinc and copper show that the atmospheric input for these elements into the Western Mediterranean Sea is comparable to that found for some other European regional seas (GESAMP, 1989; UNEP, 1989). For example, the total atmospheric fluxes to the North Western Mediterranean derived from aerosol concentration data and scaled to measured Pb fluxes are 420 ng cm^{-2} y^{-1} for Cu and 3400 ng cm^{-2} y^{-1} for Zn (Bergametti, 1987; GESAMP, 1989). By comparison, fluxes to the North Sea are 100-440 ng cm^{-2} y^{-1} for Cu and 500-2300 ng cm^{-2} y^{-1} for Zn and to the Baltic Sea 290 ng cm^{-2} y^{-1} for Cu and 1100 ng cm^{-2} y^{-1} for Zn (GESAMP, 1989).

Using data for measured total (wet+dry) atmospheric deposition fluxes of copper from Remoudaki et al. (1991b), a total annual deposition flux of 400 ng cm^{-2} y^{-1} can be calculated for the Western Mediterranean. However, such an extrapolation based on measurements made at a single sampling site to represent the atmospheric input to the open sea cannot be considered as valid. Remoudaki (1990) and Remoudaki et al. (1991a, 1991b) showed that atmospheric deposition fluxes of pollutants (eg. Pb, Cu) to the open North Western Mediterranean follow a seasonal pattern with high values in the summer depending mainly on precipitation frequency. These authors suggest that atmospheric deposition fluxes of pollutants (eg. Pb, Cu) may have a significant spatial variability with high values in the coastal zone close to European sources during the winter (the rainy period) and lower values for the open sea during the same season. This is mainly due to the scavenging of the aerosol particles by precipitation at the coastal zone in winter. Thus, aerosol particles may be localised and atmospheric fluxes to the open sea in winter may be low.

2.3.2 Mineral dust transport over the North Western Mediterranean

Before 1987, the transport of Saharan dust over the Mediterranean region was poorly documented although some authors studied one or two dust events from a meteorological, mineralogical or chemical point of view (Ganor and Mamade, 1982; Bucher et al., 1983; Prodi et al., 1983; Tomadin et al., 1984; Chester et al., 1984; Loye-Pilot et al., 1986; Dulac et al., 1987).

Bergametti et al. (1989a, 1989b) identified twenty episodes of Saharan dust transport over the N.W. Mediterranean during the period February 1985-April 1986 by the abrupt increases in the daily atmospheric concentrations of the elements Al, Si and Fe measured at Corsica. Air mass trajectories calculated for each observed atmospheric concentration have confirmed the African origin of these dusts. The meteorological situations favourable for dust transport to the W. Mediterranean are shown in Figure 2.

The frequency of Saharan dust inputs over the Western Mediterranean sea seems to be at a maximum during spring and summer. Moreover, Remoudaki (1990) identified nineteen periods of abrupt increases of the atmospheric concentrations of Al, Si and Fe between October and December 1987. The emission and transport of dusts over the W. Mediterranean during these periods have been confirmed by the observations done from satellite imagery METEOSAT UV-IR. The main conclusion of the above studies is that one single dust event of a few days duration can account for about 30% of the annual mineral dust deposition rate. Consequently, it is clear that the interpretation of the aeolian signal in the W.Mediterranean sediments does not simply reflect mean atmospheric circulation patterns.

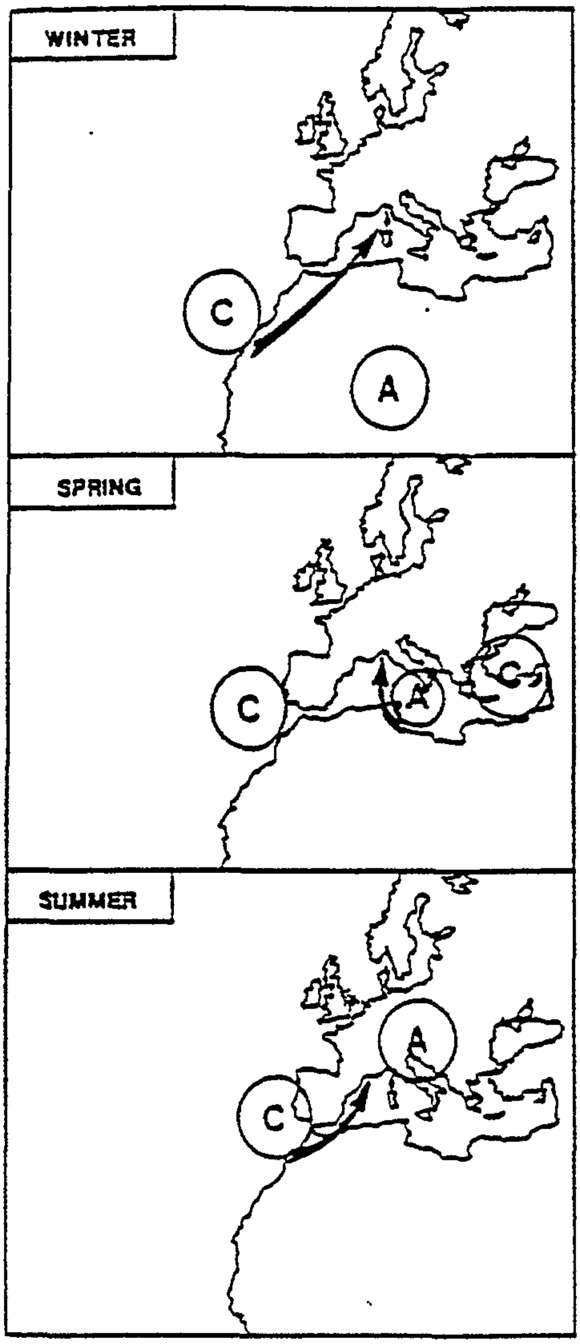


Fig. 2 Meteorological situations favourable for dust transport to the Western Mediterranean Sea (A: high pressure; C: low pressure; the arrows indicate the air-flow direction) from Bergametti _et al._ (1989a)

The above studies also showed that atmospheric concentrations and fluxes of copper, lead and zinc are not influenced by these sporadic and intense Saharan dust transport events. However, atmospheric concentrations and fluxes of elements of mixed origin (crustal and anthropogenic) such as iron and manganese can be controlled by these sporadic events of Saharan dust emissions in the Western Mediterranean atmosphere.

2.3.3 The N.W. Mediterranean coast: a case study

Gomes et al. (1988) used both measured concentrations and a Gaussian semi-box plume model to estimate the emissions of zinc and copper from the large industrial area of Fos near Marseille (Fig. 3).

The deposition patterns relate to the specific conditions of diffusion and transport which were mainly dominant during any one season. Analyses made for other seasons may produce different patterns, due to changes in meteorological conditions and industrial emission rates. Year to year variations mainly depend on precipitation frequency because the annual mean concentrations show little variation from year to year.

The estimated atmospheric dry deposition rate from Fos emissions over the Mediterranean Sea is for zinc (13.8 µg m^{-2} day^{-1}) 497 ng cm^{-2} y^{-1} and for copper (0.70 µg m^{-2} day^{-1}) 25.2 ng cm^{-2} y^{-1}; this can be compared to 1080 ng cm^{-2} y^{-1} for Zn and 93.6 ng cm^{-2} y^{-1} for Cu as the average total deposition over the W. Mediterranean suggested by Arnold et al. (1983). These calculations show that for copper and zinc the predicted average dry deposition rates due to Fos, at its maximal deposition zone in Mediterranean, are of a similar magnitude to the average total deposition reported for the Western Mediterranean. Moreover, the contribution of the dry process to the total deposition is estimated to be 10-20% in the Mediterranean. However, the values given by Arnold et al. (1983) are probably underestimate because of the short duration of the cruises. If the values given by Bergametti (1987) are used a total deposition of 3400 ng cm^{-2} y^{-1} for zinc and of 400 ng cm^{-2} y^{-1} for copper for the North Western Mediterranean is obtained, which are an order of magnitude higher than the values given for dry deposition from Fos.

Another important result was the relatively minor influence of the wind speed on the dry deposition compared to the distance from the source. Estimates for the dry deposition of zinc in g km^{-2} day^{-1} were:

μ= 5m s^{-1}, $Fmax_{40}$............... 45.2 $Fmax_{130}$............. 15.2
μ=13m s^{-1}, $Fmax_{40}$............... 36.4 $Fmax_{130}$............. 13.5

where:
μ = annually averaged wind speed,
Fmax = distance from source area where the measurement took place (40km, 130km)

In another paper, Gomes et al. (1985) calculated that the contribution of the Fos-Berre daily zinc emissions to the atmosphere (2.3 tonnes/day) was 13.7% of the overall zinc emissions of France (16.8 tonnes/day) and suggest (Gomes et al., 1988) that the northern coast of the Western Mediterranean is the main receptor area for zinc and copper, especially during northerly wind conditions. Obviously, higher levels are observed near the "hot spots"

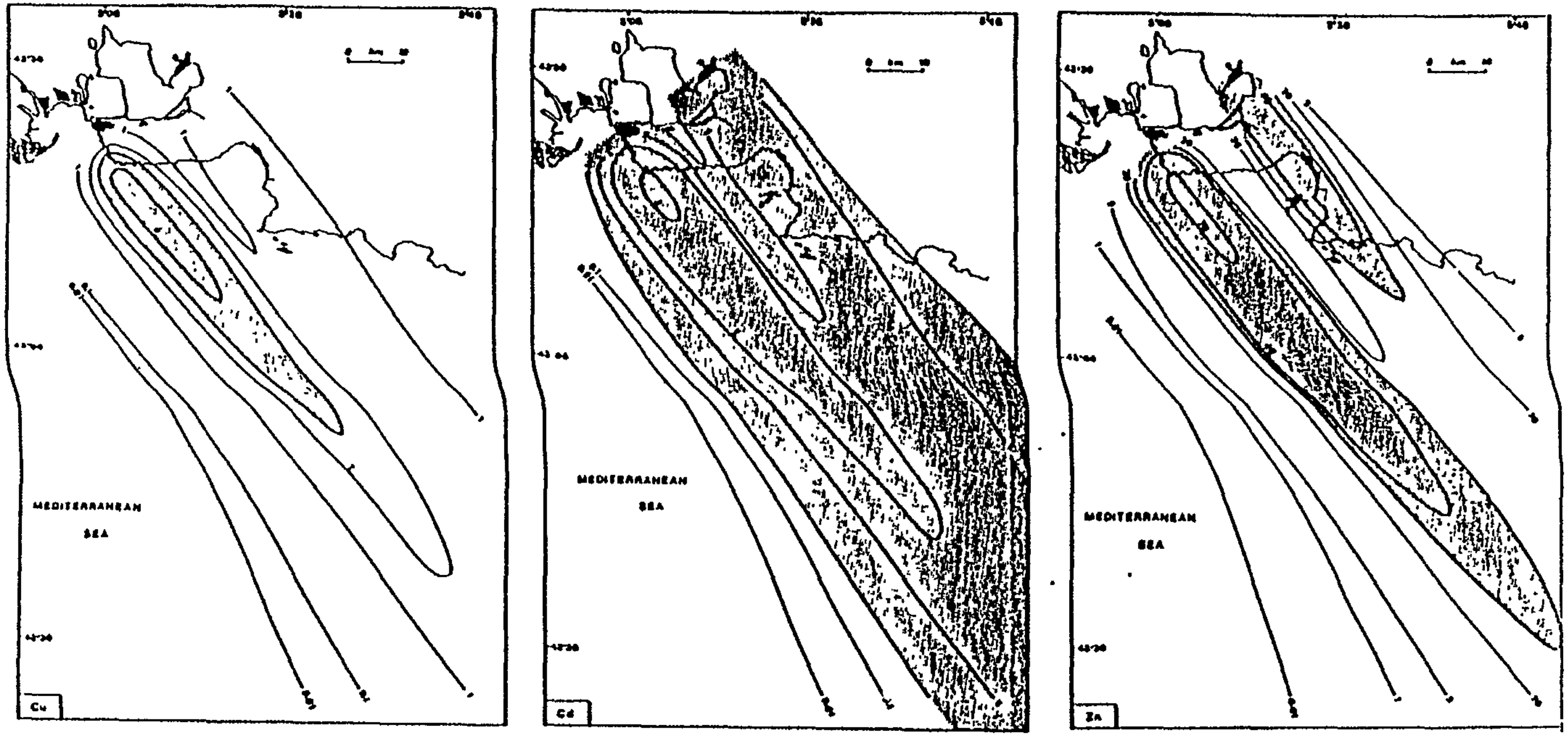


Fig. 3 Calculated average daily dry deposition of copper and zinc over sea. Results from the model (in µg m^{-2} day^{-1}) with prevailing N-NW wind (Gomes et al., 1988)

although in some cases such as the Gulf of Lions, and at a deep sea station sampled in the framework of the EROS-2000 project, the high metal content and aromatic hydrocarbons determined in the sediment surface, combined with a series of magnetic parameters indicative of anthropogenic sources of particles, provide strong evidence that industrial particles heavily laden with zinc, copper and other metals, transported via the atmosphere could affect the sediments of offshore sites to a significant extent (Scoullos et al., 1989).

The effect of the industrial activities in the Fos area on offshore waters was studied by Fukai and Huynh Ngoc (1976) who found that the mean concentrations of zinc and copper were 7 and 20 times higher near Fos than in most other Mediterranean coastal waters.

2.3.4 Summary and preliminary conclusions for zinc and copper atmospheric inputs

Despite the increasing recognition of the important role of episodes, scavenging processes and meteorological phenomena in the transport of particulate matter through the atmosphere and its deposition on Mediterranean seawaters and sediments, there is still a paucity of relevant data. However, the available data indicate that the average total atmospheric flux of zinc to the surface of the Mediterranean Sea is about 42.5x10^3 tonnes/y.

Both the dry and total deposition rates are expected to differ considerably in the various parts of the Mediterranean. Flux calculations (GESAMP, 1989) show that wet deposition is more important than dry, with the ratio of wet to dry for zinc and copper being about 80:20.

Guerzoni et al. (1989) suggested dry deposition fluxes of 595 ng cm^{-2} y^{-1} (154-1013) for the W. Mediterranean, 185 ng cm^{-2} y^{-1} (126-280) for the S. Adriatic and 286 ng cm^{-2} y^{-1} (176-372) for the E. Mediterranean. These values indicate that the major proportion of dry deposition is expected to be precipitated in the W. Mediterranean. This is not unexpected when a single important source at Fos contributes about 500 ng cm^{-2} y^{-1} zinc of dry deposition in the N.W. Mediterranean. The average dry deposition suggested by Guerzoni et al. (1989) was 354 ng cm^{-2} y^{-1}; this flux was an average value based on the considerably differing individual measurements.

Arnold et al. (1983) have calculated an average flux of 93.6 ng Cu cm^{-2} y^{-1}. These values are probably underestimates because of the short duration of sampling programme. The value given by Remoudaki et al. (1991b) of 400 ng cm^{-2} y^{-1} is 4 times higher because it is based on two years of continuous sampling for total deposition.

The dry deposition of copper in the W. Mediterranean attributed to industrial activities in the Fos area is about 25.2 ng cm^{-2} y^{-1} (Gomes et al., 1988) indicating that, at least in the N.W. part, industrial sources contribute less than for zinc. The comparison between the available total and dry deposition fluxes show clearly that wet deposition is the dominant removal process, a finding confirmed also by continuous measurements of the total atmospheric deposition fluxes in the open North Western Mediterranean (Remoudaki et al., 1991a, 1991b). These measurements also show that atmospheric deposition fluxes are increased when precipitation events scavenge an atmosphere sufficiently "loaded" with aerosol particles.

The highest values for metal fluxes (eg. Cu, Pb) are observed in the open N.W. Mediterranean during the dry season. The atmosphere at such a sampling site is loaded with long-range transported particles. When this atmosphere is scavenged by precipitation the fluxes are increased. This generates a seasonal cycle of atmospherically derived fluxes which depends mainly on the frequency of the precipitation periods. Hence the open sea is probably more affected by atmospheric contaminant input during the dry season, whereas the continental coastal regions are probably more affected during the wet season. Therefore, both a spatial and temporal pattern of contaminant deposition to the Western Mediterranean can be expected. This raises some doubts about the validity of extrapolating from the atmospheric deposition fluxes obtained at a single sampling site to the entire basin.

2.4 Summary and conclusions

The present assessment indicates that zinc and copper loads entering the Mediterranean are significant and are considerably higher than those reported in the past.

The major differences result from the inclusion of marine (via Gibraltar and Bosphorus) and atmospheric inputs, which were not taken into account in previous assessments. Similarly, the fact that zinc and copper mining was increased in the Mediterranean by 40% and 23% respectively between 1975 and 1984, had led (Scoullos, unpublished data) to roughly re-assess zinc industrial and domestic effluent discharges estimated in UNEP/ECE/UNIDO/FAO/ UNESCO/WHO/IAEA (1984) to $6x10^3$ tonnes/year and $2.3x10^3$ tonnes/year. However, this amount is not the one necessarily discharged today directly into the sea and it is expected to be reduced in the coming years due to the installation and operation of more sludge and waste treatment plants. For the load carried by rivers there seems to be a major difference between the calculations made UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA (1984) and those of Dorten et al. (1991); although the latter are provisional and produced on the basis of a very limited number of samples, they differ significantly from the former. The results of these assessments are summarized in Table 7.

It is clear that although both the marine and atmospheric inputs into the Eastern Mediterranean were assessed indirectly, they are of the same order of magnitude. This has been confirmed in the N.W. part of the Mediterranean. The atmospheric inputs are also considerably higher than the riverine and direct discharges, and thus could have a strong effect on concentrations in offshore waters and even in deep sea sediments.

Because of the very restricted use of pollution prevention and abatement technologies in the area, there is a clearly significant potential for a drastic reduction of the loads described in this section. Filters to reduce industrial emissions to the atmosphere and primary sedimentation of effluents could reduce discharge loads by 70%, and secondary effluent treatment (eg. by activated sludge) could reduce it by 10-20 fold. Better management of the currently available technologies for the treatment of industrial effluents, sludges, and tailings, and emissions to the atmosphere, could reduce the inputs to one tenth of their present levels.

Table 7

Zinc and copper loads (in tonnes x 10^3 per year).

Inputs	Zinc	Copper
Inputs through the straits of Gibraltar	23.5(b)	9.2(b)
Inputs through the straits of Bosphorus	0.08-1.3(b)	0.5-11 (b)
Load by direct effluent discharges:		
Domestic	1.9(a)	2.3(c)
Industrial	5(a)	6(c)
Loads carried by rivers:		
Anthropogenic	18(14-22)(a) 0.6-1.6(b)	0.2-0.6(b)
Background	4(a)	
Atmospheric inputs (mixed)	42.5(b)	5.3(5-10)(b)

(a) UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA (1984)
(b) Dorten et al. (1991)
(c) Scoullos, unpublished data

Although the installation of such efficient effluent treatment processes will reduce the coastal discharges, and thereby reduce local pollution problems, a need for a more general reduction of inputs would require stringent controls to be placed on discharges to inland waters and to the atmosphere.

If such improved remedial measures are extended to inputs from the Atlantic coasts and around the Black Sea, marine inputs to the Mediterranean could also be reduced significantly.

3. LEVELS OF ZINC AND COPPER IN THE MEDITERRANEAN

3.1 Data quality assurance and intercalibration

It is well known that one of the major problems encountered in the measurement of trace metal concentrations in air and seawater, and to a lesser extent in sediments and biota, is the uncertainty in the accuracy and precision of the chemical analysis (quality control). FAO/UNEP recognized that insufficient analytical quality control may jeopardize the success of the MED POL projects, and accepted the recommendation of the 1975 Expert Consultation to sponsor an analytical quality control programme (MED POL XI "Intercalibration with the IAEA's International Laboratory for Marine Radioactivity" at Monaco) (FAO/UNEP, 1975). As part of this project, some sediments samples and samples of various marine organisms were prepared and distributed for the intercalibration exercise (e.g. Fukai et al., 1978; IAEA, 1978; IAEA, 1985; Mee and Oregioni, 1991).

According to the most recent (September 1991) report (Mee and Oregioni, 1991) on the intercomparison of trace element measurements in deep sea marine sediments (SD-M-2/TM), the largest of this kind ever, the coefficients of variation (non-parametric total 95% confidence interval expressed as a percentage of the median) for both zinc and copper were less than 10% (Fig. 4).

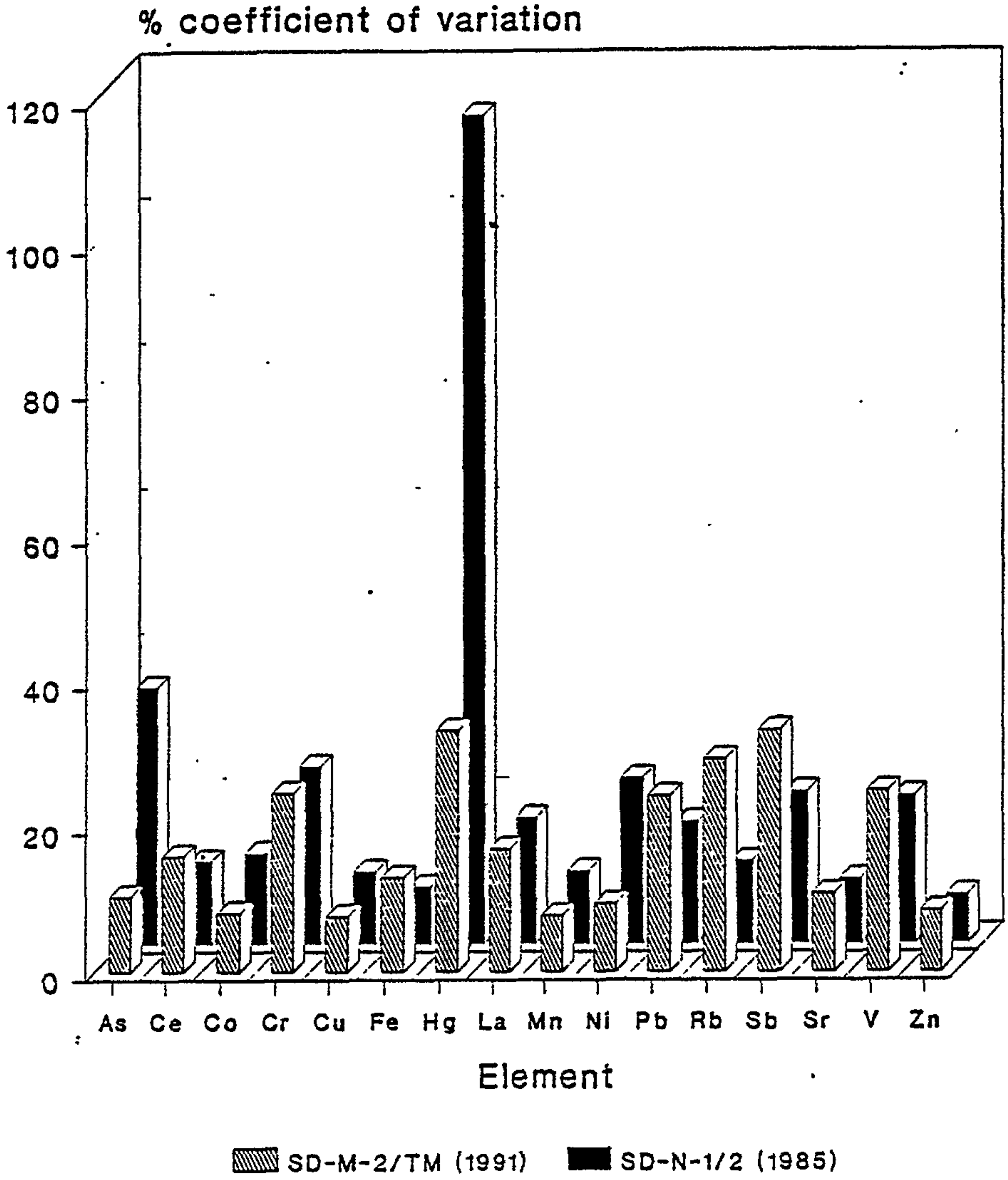


Fig. 4 Data quality for selected metals in deep sea sediments; two intercomparisons

This report states that both copper and zinc provide examples of extremely well-grouped data, with good agreement between the different instrumental techniques. The data spread for partial digestion (Fig. 5) closely mirrors that of total measurements in both cases, suggesting that different pretreatment techniques do not exert a strong influence on the accuracy of the measurements. The zinc histograms were slightly skewed towards higher values suggesting reagent contamination or poor calibration; zinc is particularly common as a contaminant in laboratory glassware which has been in contact with latex rubber, etc. In the case of zinc, the spread of data was far less satisfactory for NAA and XRF than for AAS or ICP-AES but the relatively small numbers of samples analyzed in this manner during the intercalibration exercise do not allow for a very thorough statistical comparison of the results.

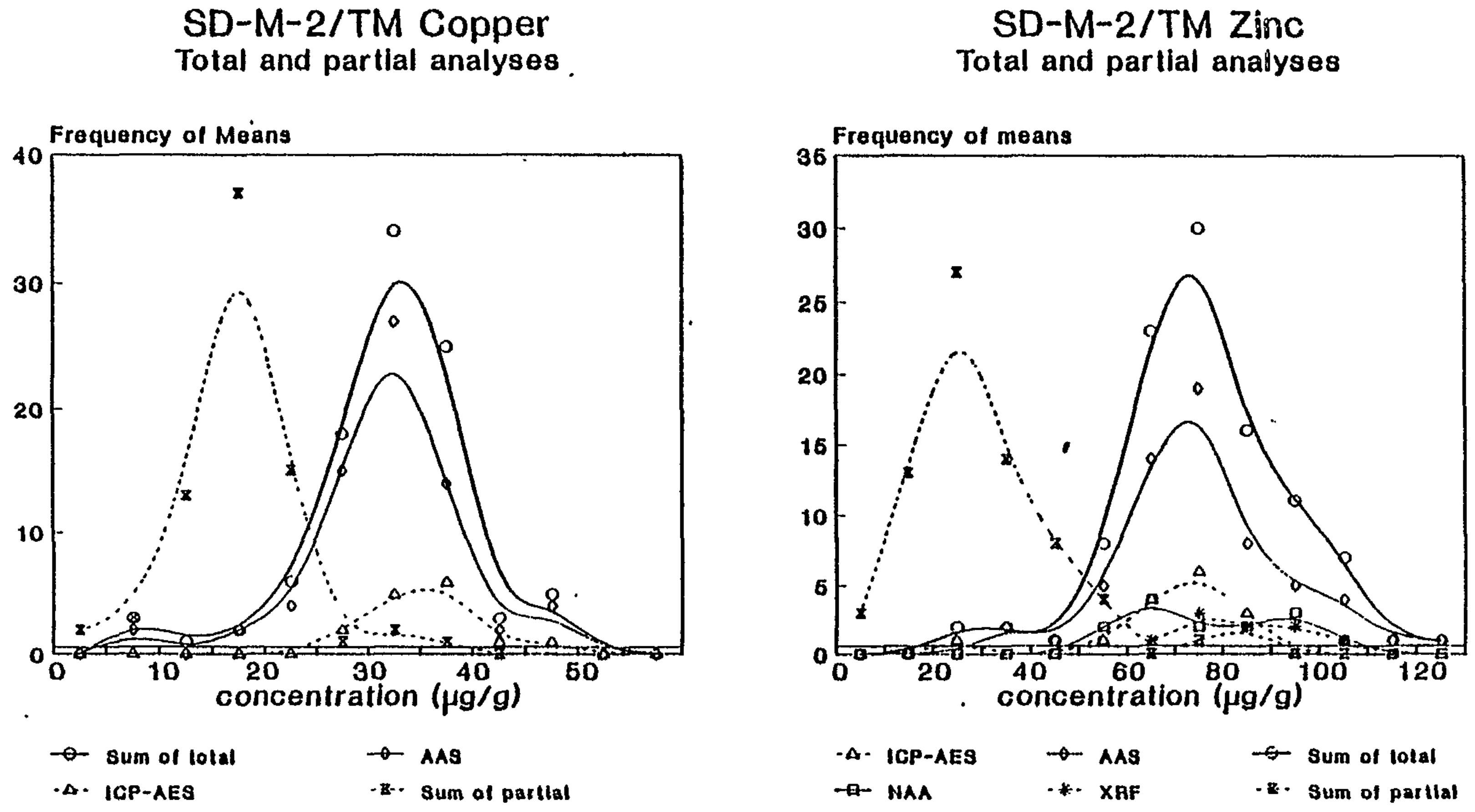
IAEA has announced its intention to repeat the exercise with sediment from polluted coastal areas which will require additional attention by the analysts because of the interactions between high concentrations of organic matter and heavy metals.

Unfortunately there are no intercalibration standards which could be used for analysis at the low concentrations found in sea water, rainwater and air. This is regrettable because since the zinc and copper concentrations in waters and air are low, the uncertainties surrounding the data are high.

Intercalibration has four important aspects: (a) participation increases the confidence in the analytical data published, (b) it improves the analytical techniques used, since very often errors in the analytical procedures can only be detected through participation in an intercalibration or by a comparison with a certified standard, (c) it improves the knowledge about alternative approaches and promotes innovation and cooperation between laboratories, (d) it allows for the identification of the weakest laboratories and groups which need systematic scientific, technical and eventually financial support to improve their infrastructure and performance.

New analytical techniques with increasing sensitivity and specificity make it possible to measure trace elements in very low concentrations. However, the results from small scale intercomparisons carried out between laboratories show in general that the data on seawater from different authors are not easily comparable since the differences in the zinc and copper concentrations reported may be significant. This uncertainty increases with decreasing concentrations. Thus the uncertainty surrounding the open sea water concentrations, which are in the ng l^{-1} range, is usually greater than that of the polluted coastal waters which is frequently one or even two orders of magnitude higher and even greater than that of the much higher levels (µg kg^{-1}) in sediments and biota. Errors are more frequently made by unexperienced or poorly equipped laboratories but they can also be committed by experienced laboratories, mainly with water and/or biological samples.

When examining the historical sea water data for zinc and copper it may seem that the older values are much higher than today. It is true that there is now a greater awareness of the limitations of certain analytical methods and of sample contamination risks which has increased the accuracy of analytical determinations. Nevertheless, it is not possible to state generally that analyses carried out in recent years are necessarily more accurate than



The frequency intervals
are 5 µg/g

The frequency intervals
are 10 µg/g

Fig. 5 Data spread for analyses of zinc and copper digestion of sediment samples older ones, nor that the lower trace element levels now found are always or necessarily the correct ones. It is possible that the higher historical values were correct.

3.2 Zinc and copper in the air

Relatively very few measurements exist for metal concentrations in the air. The concentrations of zinc and copper in the atmosphere over the Mediterranean are only partially known, mainly in the N.W. region, as reported in section 2.3.

The average zinc level for the W. Mediterranean is around 20-25 ng m^{-3}. GESAMP (1989) reported a value of 26 ng m^{-3} and Bergametti et al. (1989a) gave geometric mean atmospheric concentration of 19.1 ng m^{-3}. The corresponding concentration for copper is around 2 ng m^{-3} over the open Mediterranean.

Guerzoni et al. (1987) reported the following concentrations of zinc for atmospheric particles collected in the Western Mediterranean, the Eastern Mediterranean and the Southern Adriatic: 18.9 ng m^{-3}; 9.1 ng m^{-3} and 5.9 ng m^{-3}, respectively.

Detailed information and a discussion of the atmospheric concentrations and inputs have been given in section 2.3.

3.3 Zinc and copper in seawater

As stated above, heavy metal analysis in sea water can be subject to serious errors arising from the sampling, preconcentration and analytical methods used. The improvement of techniques and the reduction of sample contamination by using clean methodology and laboratories, and ultra-clean reagents, has contributed to a general decrease in the concentrations of heavy metals reported in the literature since the mid-seventies (Bruland et al., 1978a, 1978b).

Therefore copper and zinc are now found in oceanic waters in concentrations that are significantly lower than those previously measured. It was also found that these metals occur in well defined distributions in the world oceans (Bruland and Franks, 1979). However, as also stated above, it cannot be concluded that all the earlier data are incorrect.

The amount of reliable data on the metal distribution in sea waters, not only within Mediterranean but throughout the world's oceans is still limited and the present document allows merely for a state-of-the-art overview of the available knowledge in a field in which rapid advances are still being made. In order to understand and comment on the available data and particularly on the vertical distribution of zinc and copper in the Mediterranean, it is useful to summarise the information available for other oceans.

Both zinc and copper are depleted in the surface layers, as are the nutrients nitrate, phosphate and silicate. Usually the profile of zinc shows a very good correlation with silicon and indicates the existence of a regeneration of zinc at greater depths where the release of zinc in associated with the degradation of hard skeletal material derived from plankton. The profile of copper in open oceans (eg. the Pacific) shows, in general, a surface minimum concentration and an increase with depth (Boyle et al., 1977; Bruland, 1980), a phenomenon interpreted as the result of vertical advection of bottom waters high in copper and diffusive mixing with overlying intermediate water. Copper analyses of pore water show that oceanic sediments are able to enrich the overlying bottom waters with copper (Klinkhammer, 1980). Study of the copper profiles indicate the existence of scavenging mechanisms in deep and intermediate waters. Similar scavenging may also take place for zinc. However the distribution of zinc is strongly influenced by the internal biogeochemical cycle, making measurements of its removal processes more difficult.

Heavy metal concentrations, especially in coastal waters, can depend on factors such as input variability, mixing of different water masses, transport and dilution processes and biological activity. Thus, the interpretation and comparison of heavy metal concentrations in seawater is rather difficult. Furthermore, different analytical methods usually determine different fractions of the total heavy metal concentration. Therefore, in comparing heavy metal data, the values for total, dissolved and particulate forms have to be considered.

Data prior to 1983 have been reviewed by UNEP (1978) and UNEP/FAO (1986b). In Table 8 more recent data on concentrations of copper and zinc in the Mediterranean waters are summarized. The analytical methods used by authors are also included since these can influence the results obtained.

3.3.1 Zinc levels

The reported concentrations of zinc in the Mediterranean waters vary considerably, ranging from 0.02 µg l^{-1} in offshore stations to 450 µg l^{-1} in heavily polluted harbours. Table 8 summarises all the relevant data within a regional classification.

It is extremely difficult to conclude what the actual zinc levels are in the Mediterranean. The majority of measurements far from point sources seem to range between 0.1 and 8 µg l^{-1}. The higher values correspond mainly to coastal regions and in a small number of cases those in offshore waters have been attributed by some authors to seasonal phenomena. According to Huynh Ngoc and Fukai (1979) the average dissolved concentration in the Mediterranean is 2±0.2 µg l^{-1}. Kremling and Peterson reported a much lower Mediterranean average (of 0.40±0.16 µg l^{-1}) which was considered by the authors to be "close" to the oceanic values. The results obtained within the framework of the EROS 2000 project by Morley et al. (1990), provide an overall range of concentrations between 0.150 and 0.242 µg l^{-1}. These authors also obtained some useful information about the vertical distributions of zinc and copper in deep and coastal waters of the N.W. Mediterranean. The winter samples generated results that were generally inconsistent with the oceanographic features, attributed by the authors to contamination of the sampling system by zinc. The sampling procedures used in the summer (July 1989) using Kevlar line and manual sampling from an inflatable craft produced much lower zinc concentrations.

Table 8

Zinc and copper in offshore and coastal waters.

LOCATION	METHOD	Zn (µg l^{-1})			Cu (µg l^{-1})			REFERENCES
		mean	min.	max.	mean	min.	max.	
Med (open)	Freon extr./AAS	0.40			0.21			Kremling & Peterson (1981)
Med (coastal)			0.016	11		0.02	0.49	Reviewed by Bernhard (1983)
Med (open)		2.3	0.1	7.9				Fukai & Huynh Ngoc (1976)
W Med (central)	DPASV (Diss.)	-			0.130	0.045	0.153	Ferrara & Serriti (1989)
Alboran (bottom)	(Part.)	-			0.170			Boyle et al. (1985)
Alboran (deep)	(Part.)	-			0.131			Boyle et al. (1985)
Alboran (surface)	(Part.)	-			0.111			Boyle et al. (1985)
Alboran	DPASV (Diss.)	-			0.095	0.080	0.130	Ferrara & Seritti (1989)
N.W. Med (open)	ASV	2.7			0.4			Huynh Ngoc & Fukai (1979)
N.W. Med (open)	ASV	1.2			0.10			Huynh Ngoc & Fukai (1979)
N.W. Med (open)		-			0.11			Boyle et al. (1985)
N.W. Med (open)	Dowex/Extr./AAS	-			0.48			Frache et al. (1980)
N.W. Med (coastal)	ASV		1	9		0.1	22	Fukai & Huynh Ngoc (1976)
N.W. Med	-	3.0	0.5	7.9	-			Fukai & Huynh Ngoc (1976)
Ebro delta, Spain	-		51	104	-			Obiols & Peiro (1981)
Var lagoon, France	APDC extr./AAS	-			4.1			Chabert & Vicente (1981)
Italian estuaries	Filtration/ASV	-				0.11	0.95	Breder et al. (1981)
Lagoons, Spain	Freon extr./AAS		3.3	4.3	-			De Leon et al. (1983)
Ligurian coasts	Filt./Dowex/AAS (Diss.)	-				<0.010	7.4	Baffi et al. (1983, 1984)
	(Part.)	-				<0.05	0.58	Baffi et al. (1983, 1984)
Monaco	APDC/Extr./AAS		1	2		0.4	0.8	Veglia & Vaissiere (1986)
Gulf of Fos (surf.)	-	46	6.0	120	-			Benon et al. (1978)
(bott.)	-	48	3.2	400	-			Benon et al. (1978)
Gulf of Fos	-		83	377	-			Arnoux et al. (1981a)
Cote d' Azour	-		55	110	-			Cenciarini & Fernex (1980)
Gulf of Lions,								
shallow	AAS	-	0.152	0.242	0.184			Morley et al. (1990)
offshore	AAS				0.118			Morley et al. (1990)
Ligurian Sea	Dowex A-l/AAS	-			1.4			Frache et al. (1980)
Ligurian Sea (coast.)	(Diss.)	-			0.23	0.11	0.38	Breder (1987)
Ligurian Sea	AAS	-	1	2		0.4	0.8	Veglia & Vaissiere (1985)

LOCATION	METHOD	Zn (µg l^{-1})			Cu (µg l^{-1})			REFERENCES
		mean	min.	max.	mean	min.	max.	
S.W. Med (open)	ASV	-				0.06	-0.13	Laumond et al. (1984)
S.W. Med	ASV	1.4	0.1	4.1	-			Fukai & Huynh Ngoc (1976)
Tyrrhenian (open)	ASV	0.9			0.18			Huynh Ngoc & Fukai (1979)
Tyrrhenian Sea (open)	ASV	-				0.13	0.19	Nurberg et al. (1977)
Tyrrhenian	-	1.0	0.2	2.3	-			Fukai & Huynh Ngoc (1976)
Tyrrhenian (coast.)	DPASV (Diss.)	-			0.090	0.065	0.140	Ferrara & Seritti (1989)
Tyrrhenian (coast.)	DPASV (Part.)	-			0.065	0.020	0.125	Ferrara & Seritti (1989)
Tyrrhenian (coast.)	DPASV (Diss.)	-			0.070			Breder (1987)
Tyrrhenian (coast.)	DPASV (Part.)	-			0.060			Breder (1987)
River Tiber mouth	AAS		1.4	3.3		0.2	0.6	Pettine et al. (1982)
Archipel. of Tuscany	DPASV (Diss.)	-			0.097	0.072	0.165	Ferrara & Seritti (1989)
Apulian region,Italy	-	1.5			-			Blondi et al. (1986)
Punta Ala- Piombino	DPASV (Diss.)	-			0.443	0.280	0.740	Breder (1987)
Adriatic Sea (coast.)	NAA		1	36	3.4			Marijanovic et al. (1983)
Adriatic Sea (coast.)	NAA					0.6	50	Grancini et al. (1976)
Central Med (open)	ASV	1.8			0.7			Huynh Ngoc & Fukai (1979)
Central Med (open)	-	-			0.15			Boyle et al. (1985)
Sicilian coasts	(Diss.)		0.2	16		0.25	7	Alpha et al. (1982)
	(Part.)		1	17		0.12	4	Alpha et al. (1982)

LOCATION	METHOD	Zn (μg l^{-1})			Cu (μg l^{-1})			REFERENCES
		mean	min.	max.	mean	min.	max.	
Aegean Sea (open)	ASV	3			0.3			Huynh Ngoc & Fukai (1979)
Aegean Sea	-		20	40	-			Aubert et al. (1979)
Aegean Sea	-	5.3	4.7	5.8	-			Fukai & Huynh Ngoc (1976)
Aegean Sea (Eastern)	(Diss.) Pre/Chelex100	5.6	4.8	8.9	0.7	0.5	1.0	Scoullos & Dassenakis (1986)
Gulf of Elefsis	(Diss.)	18	4.2	85	1.51	0.93	2.85	Scoullos (1981)
	(Part.)	2.4			0.91			Scoullos (1981)
S.Euvoikos Gulf	100/AAS (Diss.)	13	4.9	34	1.9	0.7	5.4	Scoullos & Dassenakis (1983)
	(Part.)	2.7	0.7	5.0	1.0	0.4	1.8	Scoullos & Dassenakis (1983)
Saronikos Gulf	(Diss.)	18			-			Scoullos et al. (1992)
Saronikos Gulf	(Part.)	2.4			-			Scoullos et al. (1992)
	NAA		2.4	32		0.5	1.4	Zafiropoulos (1983)
Nothern Greece	ASV		3.7	18		1.0	3.5	Huynh Ngoc & Zafiropoulos (1981)
Ionian Sea	APDC-MIBK		13	23	-	0.7	2.1	Fytianos & Vassilikiotis (1983)
Cretan Sea	-	1.4	0.7	2.4	-			Fukai & Huynh Ngoc (1976)
Cretan Sea	-	1.5			-			Fukai & Huynh Ngoc (1976)
Saronikos (inner)	(Part.)	10	0.5	19	-			Kalogeropoulos et al. (1990)
Saronikos (outer)	(Part.)	4.8	0.5	14	-			Kalogeropoulos et al. (1990)
Saronikos (polluted)	(Part.)	19	9.0	4.1	-			Kalogeropoulos et al. (1990)
Saronikos (offshore)	(Part.)	5.0			-			Kalogeropoulos et al. (1990)
Amvrakikos Gulf	-		1.5	5.2	-			Scoullos et al. (1990)
Gulf of Elefsis	-	-				0.2	0.8	Scoullos et al. (1990)
Gulf of Geras, Lesvos, Greece	(Diss.)	4.05	1.3	6.1	3.2	0.9	9.8	Scoullos et al. (1983)
	(Part.)	1.55	1.1	1.7	1.7	1.0	2.7	Scoullos et al. (1983)
	(Diss.)	-			1.2	0.8	0.9	Scoullos & Dassenakis (1982)
					2.1	0.6	6.2	Scoullos & Dassenakis (1982)
Black Sea		1.9	0.4	12	-			Spencer & Brewer (1969)
S.E. Med (open)	ASV	0.9			0.04			Huynh Ngoc & Fukai (1979)
Alexandria, Egypt	APDC-MIBK Extr./AAS	210			70			El-Sayed & El-Sayed (1981)
Alexandria Harbour	-	211	58	450	-			El-Sayed & El-Sayed (1981)
Tel-Aviv, Yaffa								
(summer)	-		22	85	-			Amiel & Navrot (1978)
(winter)	-		20	47	-			Amiel & Navrot (1978)

Profiles for the upper 500 m of the water column at the deep water stations (20 and 25) are shown in Fig. 6a. While the extent of depletion in the surface layer noticed by Morley et al. (1990) in the Western Mediterranean is much less marked than in oceanic regimes, these data do show a significant degree of recycling of zinc, in contrast with the behaviour of other metals removed through phosphorous recycling. Vertical profiles for zinc concentrations at a shelf station are shown at Fig. 6b. Concentrations are similar to those in the deeper waters except for higher values attributed by the authors to the influence of Rhône river water near the river outfall and in the upper water column to the west.

It appears that results from earlier studies may have been significantly affected, to varying degrees, by contamination problems. To reject previous data completely is a very easy solution but even strictly scientifically such a rejection is inappropriate. Many of the high coastal concentrations previously reported were for severely polluted embayments and estuaries or areas affected by sewage outfalls with localised high concentrations of zinc. In some cases, it is precisely in these polluted areas with high concentrations where important biogeochemical mechanisms become more obvious and better understood. Therefore, some parts of previous studies can be used, particularly if new ones confirm the general trends for each system studied, but bearing in mind that contamination during sampling and analysis can easily occur so that the data should be treated with a proper caution. In addition, any generalization that low concentrations are a result of high quality analyses, and vice versa, should be avoided as being scientifically wrong both in principle and in practice.

3.3.2 Copper levels

The copper concentrations found in the open waters of the Mediterranean as reviewed by UNEP (1978) and UNEP (1986) ranged from less than 0.03 to 3 µg l^{-1}.

Huynh Ngoc and Fukai (1979) reported the average dissolved copper concentration in Mediterranean offshore waters to be 0.33±0.09 µg l^{-1}. Nurberg et al. (1977) has reported lower values (0.13-0.19 µg l^{-1}) for the Tyrrhenian Sea, and Laumond et al. (1984) a range of 0.06-0.13 µg l^{-1} for the Western Mediterranean.

Kremling and Peterson (1981) reported an average of 0.21±0.07 µg l^{-1} for the Mediterranean open waters which is very similar to oceanic values obtained under similar conditions.

More recent reports suggest that the actual copper concentrations in the Mediterranean may be even lower. Boyle et al. (1985) reported mean values of 0.11 and 0.15 µg l^{-1} for the Alboran Sea and the Central Mediterranean respectively. According to these authors these values are slightly higher than those for the Atlantic.

Morley et al. (1990) reported concentrations of 0.099 µg l^{-1} for stations at water depths of 1000 m or more in the N.W. Mediterranean, but higher values for shelf stations in winter.

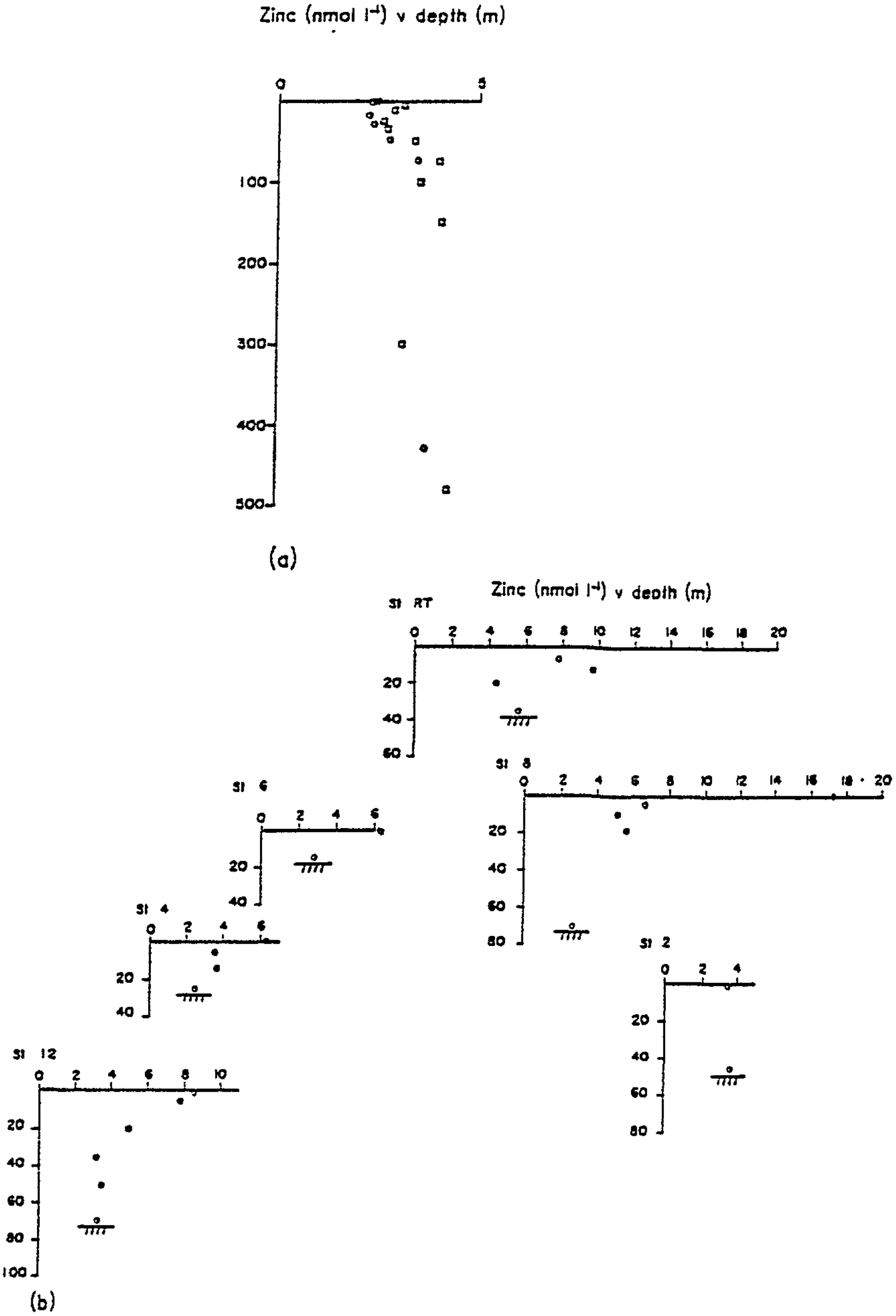


Fig. 6 Profiles of dissolved zinc concentrations in nmols (1 nmol = 0.065 µg Zn) in (a) Upper water column at 2 deep water stations in July 1989 (depths are nominal (wire out) values); (b) Shelf stations (<100 m), July 1989. From Morley <u>et al.</u>, 1990

Spivack et al. (1983) commented on the results of the NORDA cruise carried out in August and September 1980 by the U.S.N.S. Barlett using a laminar flow clean bench and a modified cobalt-APDC coprecipitation method for analysis of both filtered and unfiltered samples. They found no significant difference between filtered and unfiltered (through a 0.4 µm Nucleopore filter) samples. They confirmed that most of the West Mediterranean samples had higher copper concentrations than those of the Atlantic sampled under the same conditions.

Outside the Straits of Gibraltar the copper concentrations are below 0.089 µg l^{-1} while all the samples from the Mediterranean were above 0.091 µg l^{-1}. Concentrations increase immediately within the Straits and they remain relatively constant through Alboran and Southern Balearic Seas. In the central Balearic, there is a rise in concentrations of copper. The highest concentrations in the W. Mediterranean were found in the Tyrrhenian Sea with increasing concentrations towards the Straits of Messina (Fig. 7). These differences are paralleled by changes in salinity which increase with higher copper concentrations. Everywhere in the Mediterranean there are higher concentrations of copper than in other comparatively nutrient-depleted waters of the open ocean.

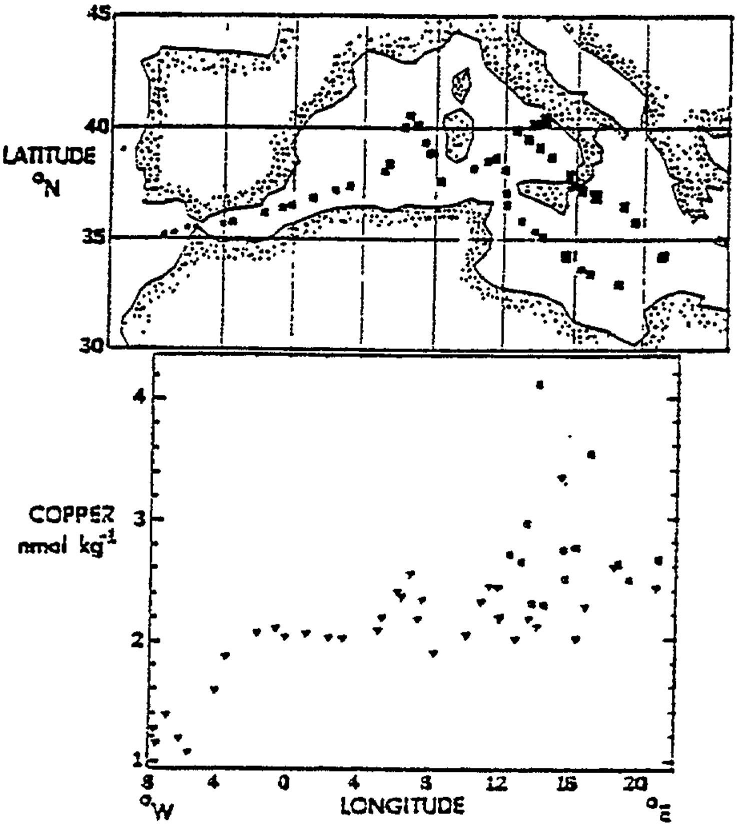


Fig. 7 a) Concentration of copper in the Mediterranean. Length of symbol perimeter proportional to concentration. b) Actual copper concentrations in nmols (1 nmol = 0.063 µg Cu). (From Spivack et al., 1983)

From the general principles of biochemical cycling, a general depletion of copper in surface waters and enrichment with depth would be expected. However, the actual vertical distribution of copper in the Mediterranean are not so simple (Spivack et al., 1983; Morley et al., 1990). Advection-diffusion models with scavenging have been used by Boyle et al. (1977) to explain and model deep copper distributions in other parts of the world where the surface concentrations in oligotrophic oceans are usually lower (between 0.032 and 0.089 µg l^{-1}) than those reported for the Mediterranean.

However, the data for copper reported by Morley et al. (1990) for the N.W. Mediterranean show little vertical variability in winter below 250 m depth, but there was evidence of increased concentrations in the upper waters. The average concentrations were similar at all the offshore stations in water depths of about 1000 m or more, with an overall mean value of 0.1 (s.d., 0.15) µg l^{-1}. For the shelf stations in winter, the distribution pattern of copper showed a higher concentration (0.419 µg l^{-1}) in the surface waters of a shallow station near the Rhône plume and significantly increased concentrations at stations west of the Rhône input (with an average concentration of 0.172 (s.d., 0.20) µg l^{-1} in the well mixed water column. Seasonal changes in concentrations of copper were not apparent in the same area. However, some higher concentrations (1.143-1.652 µg l^{-1}) were reported for summer (1989), in the surface waters at a station off the Rhône discharge.

Although the importance of biochemical cycling in controlling the distribution of copper in oceanic waters has been repeatedly emphasized, other processes such as its mobilisation from continental shelf sediments, rainout and fallout from the atmosphere and the river transport of weathering products seem to play an important role for the distribution of copper in the Mediterranean and particularly along its coasts. There, most of the high concentrations recorded seem to be real and due to either domestic or industrial point sources.

The fact that the Western Mediterranean sea has higher copper concentrations than similar nutrient-depleted waters in the open ocean, supports the hypothesis that part of the excess trace metals, including copper, may originate from outside the Mediterranean i.e. by metal inputs to coastal waters. This was reinforced by the discovery of a metal-enriched plume in the inflowing waters within the Alboran Sea (Boyle et al., 1985). This additional increase in trace metals from west to east (within the Western Mediterranean) is likely to be due to sources existing in the basin.

Deep waters of the Mediterranean seem to have higher levels of copper than Atlantic open ocean surface waters but not much higher than the levels observed in the surface waters of Central Mediterranean.

Although it is not yet clear whether the higher copper concentrations of the surface layers are derived from natural or anthropogenic sources, their maintenance in the surface layers of the Mediterranean is most likely due to the inefficient removal of trace metal by organisms and the low degree of nutrient recycling within the Mediterranean. Phosphorus atoms, for instance, appear to recycle only 5 times before leaving the Mediterranean via the outflow. This represents a 20-fold reduction in the opportunity for a phosphorus atom to remove trace metals from the Mediterranean compared to that in the open ocean (Boyle et al., 1985). It is a phenomenon which, if confirmed, seems to be one of the root causes of the observed enrichment of copper and other metals in the Mediterranean.

In a carefully conducted sampling programme (Martin et al., in press) relatively high concentrations of 21.7 and 10.14 nM (1.37 and 0.64 µg l^{-1}) were found in the Sicilian channel and in the Messina straits respectively, especially in the benthic (500m) waters. This might indicate a volcanogenic origin or a greater remobilization of copper at the sediment water interface linked to the longer residence times of water in the eastern Mediterranean basin.

This value was 10 times higher than those measured in the central western Mediterranean where generally ranged from 0.084 to 0.144 µg l^{-1} with a lowest recorded value of 0.055 µg l^{-1}.

Vertical profiles show a minimum concentration of copper (0.05-0.76 µg l^{-1}) present in the surface waters at Gibraltar and at a nearby area corresponding to Atlantic water.

The concentrations reported for semi-enclosed embayments, estuaries and other coastal areas of the Mediterranean vary widely but they are significantly higher than those reported for offshore waters. Maximum copper concentrations reported from different polluted coastal areas of the Mediterranean range from 0.5 to 50 µg l^{-1} and are usually localised around point sources. In the coastal areas of Alexandria and in the Adriatic, concentrations as high as 70 µg l^{-1} and 50 µg l^{-1} respectively have been reported (Grancini et al., 1976; El-Sayed and El-Sayed, 1981).

In the coastal waters near Cadiz (Spain), copper concentrations of up to 8.6 µg l^{-1} have been reported. These are believed to be the result of copper mining activities in the area (UNEP, 1978). In shallow areas receiving untreated mining discharges (eg. Lavrion, Greece), particulate copper of up to 10 µg l^{-1} has been measured (Scoullos, 1981). The activities in this latter area were stopped in the mid 1980s.

3.4 Zinc and copper in sediments

Zinc and copper concentrations in various sediment fractions have been studied extensively in Mediterranean coastal areas. In contrast, relatively few data exist for sediments from the open Mediterranean.

Sedimentation processes deposit heavy metals contained in anthropogenic particles, together with terrigenous and biogenic material, on the sea bed. These processes are very important in river deltas, and also in other areas receiving discharges of domestic sewage and industrial effluents, sludges and solid wastes. Another contribution to the sediments, relatively poorly studied, is that of atmospheric particles and aerosols. The concentrations of heavy metals in sediments will thus depend not only on pollution inputs but also on other factors such as the natural background levels of the area and its catchment basin, the geomorphology, the prevailing water circulation, the organic carbon content, the mineralogical characteristics and grain size of sediment components and the sedimentation rates.

The concentrations of zinc and copper found in sediments depend in part on the method of analysis used. The first step is the solubilization of the sample. A wide variety of reagents, usually acids, has been used by different investigators ranging from total solubilization by $HF-HCLO_4-HNO_3$ to simple extraction by dilute HCl. Also, some investigators analyze the whole sediment sample, others the fraction of less than 200, 63 or 5.5 µm. It is obvious that data on zinc and copper in sediments are not easily comparable, due to various methodologies used.

The distribution of heavy metal concentrations in the whole sediment is a very useful first step towards identifying areas affected by natural and anthropogenic inputs. However, if this is not followed by an analysis of the easily extractable metal fraction, the results may be misleading in identifying areas contaminated by industrial or urban activities. Several authors studying heavy metal concentrations in sediments found that these depend on the composition of the fine sediment fraction, the specific surface areas, and the accumulation level in the less than 63 µm fraction (pelite). Donazzolo et al. (1984a and 1984b) reported that 74-86% of the total concentration of zinc and copper is bound in the pelite fraction in sediments of the Northern Adriatic.

The relationship between heavy metal concentrations in sediments and the mineralogical characteristics or grain size was also recognized in earlier work in the Mediterranean area (Grancini et al., 1976; Scoullos, 1981; Fascardi et al., 1984).

The differing contribution of factors such as grain size and mineralogical characteristics and organic carbon content will have a significant influence on the natural background levels. Differences caused by these factors make it difficult to compare the heavy metal concentrations in sediments from different sites, even those within the same region.

Scoullos (1979, 1981) has suggested that, in order to obtain a better understanding of the copper and zinc distributions in sediments, a series of leaching reagents should be employed on the same sample. Samples should be taken from various depths of undisturbed mini-cores.

Scoullos (1979, 1981) has studied extensively the zinc and copper partitioning among various sediment fractions, by employing sequential extraction methods on a series of physically separated components. The smaller sized particles are enriched with zinc and copper. The easily extractable fraction leached with $MgCl_2$ was compared to the non-lattice held inorganic fraction leached with ARR (acetic-hydroxylamine hydrochloride), the non-lattice held "organically" bound fraction (including probably also sulphides) extracted by EDTA, and the total including the non-leachable lithogenous fraction (extracted with HF and HNO_3).

A large number of mini-cores taken from a typical polluted Gulf, the Gulf of Elefsis, near Athens, were analysed. It became clear (Fig. 8) that the top 10 cm of the sediment column is particularly enriched with zinc and copper, in some cases by 10 times above the natural background range of 60 to 80 µg g^{-1} dry weight for total zinc contained in the <63 µm fraction. At two sites, located outside shipyards and major industrial complexes, zinc values as high as 2440 and 1500 µg g^{-1} DW were found in the top-2cm surface layer of

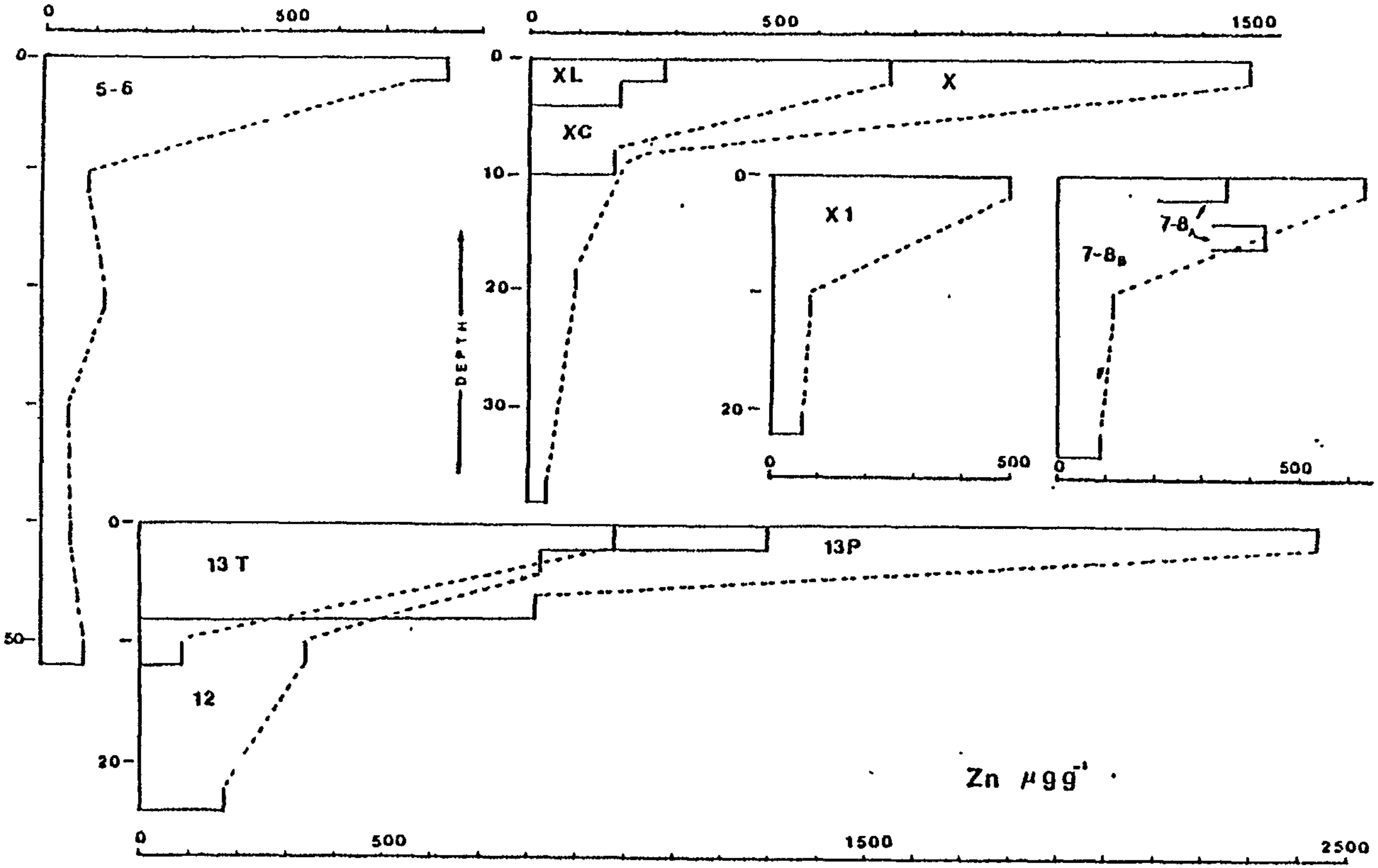


Fig. 8 Typical downcore distributions of zinc in the Gulf of Elefsis (Scoullos, 1981)

the sediment. In the same strata the total copper values reached 150-170 µg g^{-1} DW. The major percentage (60-80%) of the zinc determined in subsurface samples was found to be associated with the non-leachable lithogenous fraction which is not related to pollution. This fraction provided a lower contribution (49-55%) in the upper 10 cm of the sediment column. The non-lattice-held inorganic fraction of zinc, usually associated with Fe and Mn oxides and carbonate minerals, represented approximately 36% of the total zinc content, whereas the organically bound and at least part of the zinc leached from sulphides with EDTA, represented 12% of the surface and a higher percentage (up to 22%) in subsurface strata. The easily leached by $MgCl_2$ fraction represents a small, but not negligible, percentage which usually ranges around 1% but at certain depths of the sediment column it reached 4.3% of the total zinc determined. Similarly, the easily exchangeable copper which also usually ranges around 1-1.5%, reached 3% of the total at lower depths.

The major difference, however, between zinc and copper in the sediments of Elefsis Gulf is the organically bound fraction which for copper represents the major form (39-88% of the total) with the maximum values being found in the top 12 cm of the sediment column. These findings confirm the ability of copper to form stable complexes with organic ligands and/or to be coprecipitated together with organically rich particles. The non-leachable lithogenous fraction contributes significantly, approximately 35-40% in the subsurface sediments, whereas the ARR extracted fraction fluctuates between 13-20% for the majority of samples.

Cosma et al. (1979, 1982, 1983) have also used a range of extraction methods for sediment analyses. Reagents such as EDTA, NH_2OH, HCl-CH_3COOH and 0.5N HCl can extract amounts of copper ranging between 10 and 48% of the total. In comparing the values found by various authors summarised in Table 9, it is evident that zinc and copper concentrations vary significantly, with extremely high concentrations occurring in coastal sediments from areas receiving industrial effluents, sludges, solid wastes and domestic sewage, and low concentrations in areas reflecting the Mediterranean background values. The concentrations reported by researchers thus depend not only on the actual degree of heavy metal pollution in the area, but also on the extraction techniques used, as well as on the proximity of stations to source inputs. In some cases the very high values reported may not be representative of the entire areas studied but only of a very small and restricted region. The scientific importance of such values relies on the fact that they do exist in the natural environment, even if they are extreme values which represent only a small area within heavily polluted sites.

Examples of such high values of zinc (DW) are those reported for surface sediments at Portman and other coastal sites in Spain (up to 6480 µg g^{-1}); in the vicinity of Marseille (2550 µg g^{-1}); in the Gulf of Elefsis and the upper Saronikos Gulf, Greece (2100-2400 µg g^{-1}); in the Venice lagoons (up to 5930 $µg^{-1}$); at various sites in the Ligurian sea, the Kastela bay, Croatia (1300 µg g^{-1}), and the inner Izmir bay, Turkey, as well as at places in Egypt such as the lake Mariut, the Abu Kir bay, and the Alexandria harbour. Most of these sites also have high copper concentrations, with maximum values reported for the W. Harbour of Alexandria (1890 µg g^{-1}) and the bay of Izmir (870 µg g^{-1}).

Table 9

Zinc and copper concentrations in Mediterranean sediments.

LOCATION	METHOD	Zn (µg g^{-1} DW)			Cu (µg g^{-1} DW)			REFERENCES
		mean	min.	max.	mean	min.	max.	
Mediterranean								UNEP (1978)
Var lagoon, France	HF-$HClO_4$-HNO_3	-			15			Chabert & Vicente (1981)
Coastal lagoon, Spain	<63 µm Conc. HNO_3		500	6200		10	94	De Leon et al. (1983)
River Ebro Delta	HNO3		33	104		7.9	21	Obiols & Peiro (1981)
River Ebro	-	-				7.9	21	De Leon et al. (1983)
River Rhône Delta	HNO_3-$HClO_4$		90	104		20	55	Added et al. (1981) Cauwet & Monaco (1983) Badie et al. (1983)
Marseille	<200 µm HCl-HNO_3		120	2550		29	34	Arnoux et al. (1981b)
Cannes	<63 µm HNO_3-H_3PO_4-HCl		50	300		15	80	Ringot (1983)
Gulf of Nice	HNO_3-HCl	-				<2.1	32	Flatau et al. (1983)
Italian estuaries	HNO_3-HCl	-				33	53	Breder et al. (1981)
Ligurian Sea	HF-$HClO_4$		60	970		14	145	Cosma et al. (1979-82-83)
N.W. Med (offshore)	HNO_3-HCl		130	260		30	49	Arnoux et al. (1983)
Gulf of Fos	<63 µm HCl-HNO_3, 3:1		83	337	-			Arnoux et al. (1981a)
Cortiou (Marseille)	<63 µm HCl-HNO_3, 3:1		150	2000	-			Arnoux et al. (1981b)
Catalonia coast	HNO_3	-				7	299	Modamio (1986)
Gulf of Lions	-	60				50	200	Nolting (1990)
Coast of Spain	-		27	1050		4	230	De Leon et al. (1985)
El-Harrach, Algeria	HNO_3-HCl	125			-			Chouikhi et al. (1988)
Cartagena, Spain	-	1145			226			De Leon et al. (1985)
Portman, Spain	-	6481			110			De Leon et al. (1985)
Valencia, Spain	-	337			118			De Leon et al. (1985)

LOCATION	METHOD	Zn (µg g^{-1} DW)			Cu (µg g^{-1} DW)			REFERENCES
		mean	min.	max.	mean	min.	max.	
Cagliari lagoon	HCl 0.4N	-				10	70	Contu et al. (1988)
Tyrrhenian (offshore)	HNO_3		20	56		10	44	Frignani & Giordani (1983)
Oblia Gulf (Sardinia)								
(outer)	-		40	105	5			Contu et al. (1988)
(shore)	-	-			22			Contu et al. (1988)
(inner gulf)	-	-			16			Contu et al. (1988)
Cagliari Gulf (harbour)	-		60	65	-			Contu et al. (1988)
Calgiari Gulf (outer)	-		10	25	-			Contu et al. (1988)
Gulf of Trieste	-		27	650		9	139	Majori et al. (1979)
Gulf of Trieste	-	205			44			Majori et al. (1979)
Gulf of Venice	HNO_3		48	450		34	37	Angela et al. (1981)
Gulf of Venice(min-max)	HNO_3 8N		60	870	-			Angela et al. (1981)
Gulf of Venice(average)	HNO_3 8N		90	200	-			Angela et al. (1981)
Venice lagoons		215	19	3000	-			Pavoni et al. (1988)
Venice lagoons			61	5930	-			Contu et al. (1988)
Kastela Bay, Croatia (surf.)	-	1300			-			Stegnar et al. (1981)
Kastela Bay, Croatia (sub.)	-		23	85	-			Stegnar et al. (1981)
Kastela Bay, Croatia	NAA <100 µm		53	1300		14	42	Stegnar et al. (1979)
River Po Delta	HNO_3		24	244		1.3	50	Fascardi et al. (1984)
Mali Ston, Croatia	NAA		40	100		13	22	Vukadin et al. (1985)
Zadar, Croatia (surf.)	NAA	90.5			21.8			Zvonari & Stegnar (1987)
Sibenik, Croatia (surf.)	NAA	182.6			49.0			Zvonari & Stegnar (1987)
Split, Croatia (surf.)	NAA	125.1			31.0			Zvonari & Stegnar (1987)
Dubrovnik, Croatia (surf.)	NAA	160			69.5			Zvonari & Stegnar (1987)
Middle Adriatic (offshore)	NAA	24.0			27.4			Zvonari & Stegnar (1987)
Northern Adriatic	-		1.7	870		2.3	52	Donazzolo et al. (1984b)
Adriatic Sea (offshore)	HNO_3		54	78		15	30	Frignani & Giordani (1983)
/Adriatic Sea	-	0.043			-			Vukadin et al. (1985)
Ionian lagoons (surf.)	<0.45mm HCl 2N	60	30	80	23	8	32	Voutsinou-Taliadouri et al. (1987)
Patraikos Gulf,Greece	$HF-HNO_3-HClO_4$					23	100	Varnavas & Ferentinos (1983)
Patraikos Gulf,Greece	<0.45 HCl 2N	72	280	430	35			Voutsinou-Taliadour et al. (1987)
Patraikos Gulf,Greece	-	55			24			Voutsinou-Taliadouri (1983)
Patraikos Gulf,Greece	-		104	430		23	101	Varnavas & Ferentinos (1983)
Kalamata Bay, Greece	$HF-HNO_3-HClO_4$	-				11	56	Varnavas et al. (1987)
Gulf of Catania	HNO_3		25	236		3.8	2.5	Castagna et al. (1982)
Central Med	HNO_3		55	78		24	29	Frignani & Giordani (1983)
Sicily channel coast	-	81			55			Moussa & El-Sayed (1990)

LOCATION	METHOD	Zn (µg g^{-1} DW)			Cu (µg g^{-1} DW)			REFERENCES
		mean	min.	max.	mean	min.	max.	
Thermaikos-Kavala Gulf, Greece	<63 µm HNO_3-$HClO_4$		10	28		0.6	1.1	Fytianos & Vassilikiotis (1983)
Evoikos Gulf, Greece	<61 µm 0.5N HCl	20			9			Scoullos & Dassenakis (1983)
Evoikos Gulf, Greece	<55 µm 0.5N HCl		7	95	-			Angelidis et al. (1981)
S.Evoikos Gulf, Greece	HCl 2N		25	44		3.4	15	Satsmadjis & Voutsinou-Taliadouri (1984)
Geras Gulf, Greece	<61 µm 0.5N HCl		12	390		8	160	Scoullos et al. (1983)
Saronikos Gulf, Greece	<55 µm 0.5N HCl		5	1360	-			Angelidis et al. (1983)
Saronikos Gulf, Greece	HCl 0.5N	83			-			Kalogeropoulos et al. (1989)
Saronikos Gulf(Piraeus)	-	2500			364			Angelidis et al. (1983)
Saronikos Gulf(Outfall)	-	1800			58			Angelidis et al. (1983)
Saronikos Gulf								
(fertiliser Plant)	-	1520	840	2100	-			Kalogeropoulos et al. (1990)
(sewage outfall)	-	430	220	260	-			Kalogeropoulos et al. (1990)
(inner)	-	91	81	110	-			Kalogeropoulos et al. (1990)
(outer)	-	83	68	100	-			Kalogeropoulos et al. (1990)
Thermaikos Gulf, Greece	<45 µm HNO_3					10	50	Voutsinou-Taliadouri (1983)
Thermaikos Gulf, Greece	-	105	8	240	28			Voutsinou-Taliadouri (1983)
Axios River	NaOH 0.1N	-			46	35	50	Samanidou et al. (1988)
Pagassitikos Gulf, Greece	<45 µm HNO_3	130			30			Voutsinou-Taliadouri (1983)
Pagassitikos Gulf	-							
Pagassitikos Gulf	-	130			35			Voutsinou-Taliadouri (1983)
Pagassitikos Gulf	-	30			32			Chester & Voutsinou (1981)
East Aegean (offshore)	-	58			21			Voutsinou-Taliadouri (1983)
Gulf of Elefsis (max)	45 µm HNO_3	40			20			Voutsinou-Taliadouri (1983)
Gulf of Elefsis (surf.)	HF-HNO_3	2440			168			Scoullos (1979, 1981)
Gulf of Elefsis (sub.)	HF-HNO_3		125	1500		23	150	Scoullos (1979, 1981)
Kaloni Bay, Greece	HF-HNO_3	100				20	50	Scoullos (1979, 1981)
Kaloni Bay, Greece	HCl 50% v/v		30	103	-			Varnavas (1990)
Izmir Bay	-	103			48			Varnavas (1990)
Izmir Bay (Gulbahce)	HNO_3	277			105			Uysal & Tuncer (1985)
Izmir Bay	HNO_3	76			28			Uysal & Tuncer (1985)
	-		53	866		33	866	Yaramaz et al. (1990)

LOCATION	METHOD	Zn (µg g^{-1} DW)			Cu (µg g^{-1} DW)			REFERENCES
		mean	min.	max.	mean	min.	max.	
Erdemli, Turkey	HNO_3-$HClO_4$-HF	65			31			Balkas et al. (1979)
Alexandria	-	180			48			El-Sokkary (1979)
Alexandria Harbour	HNO_3-HCl	53			27			El-Sayed et al. (1981)
W. Harbour Alexandria	HNO_3-$HClO_4$		23	470		30	1890	Saad et al. (1981)
E. Harbour Alexandria	-	53	12	174	-			El-Sayed et al. (1981)
Gulf of Veneta, Egypt	-	-				34	37	Angela et al. (1981)
Abu Kir Bay, Egypt	HNO_3	100			12			Saad et al. (1981)
Abu Kir Bay, Egypt	HNO_3 2N	102	9	758	-			Saad et al. (1981)
River Nile Delta	HF-HNO_3		2	120		5	77	Moussa (1983)
River Nile Delta	HCl 1N		20	100		6	74	Tomma et al. (1981)
Nile (continent. shelf)	-	48	20	100	-			Tomma et al. (1981)
Nile Delta (shelf)	HF-HNO_3	89	2	119	33	5	77	Moussa (1983)
River Nile	-	108	62	216	52	31	70	Emelyanov et al. (1978)
Nile Delta (shelf)	HF-HNO_3	-			34			Moussa (1985)
(sand)	HF-HNO_3	-			10			Moussa (1985)
(mud)	HF-HNO_3	-			58			Moussa (1985)
Cilician basin	HF-HNO_3-$HClO_4$		54	81		33	50	Ozkan et al. (1980)
Cilician basin	-	76			40			Shaw & Bush (1978)
Lake Brullus, Egypt	-	40	21	55	18	10	29	Moussa (1985)
Lake Maryut, Egypt	-		70	2960		16	500	Wahby (1979)
Lake Edku, Egypt	-	81			55			Moussa & El-Sayed (1990)
Lake Manzalah, Egypt	-		60	80	-			Abdel-Moati & Dowidar (1988)
Lebanon coast	<1.75mm, HNO_3-$HClO_4$	60	13	155	-			Shiber (1980)
Haifa Bay (Israel)	<250 µm HNO_3 conc.65%		7.8	97		1.3	36	Krumgalz & Fleisher (1985)
Haifa Bay (Israel)	$NH_2OH.HCl$-CH_3COOH	-			1.6			Roth & Hornung (1977)
Haifa Bay (Israel)	HNO_3		68	105		41	78	Krumgalz et al. (1989)
Israel (coastal)	-		2.1	18	-			Contu et al. (1988)
Eastern Med	-	-				5	50	Moussa (1977)
Libyan coastline	HNO_3		2.3	27		8.7	42	Hamouda & Wilson (1989)
Mersin Bay, Karaduvar	HNO_3	152	66	466	23	9	50	Bodur & Ergin (1988)
Mersin Bay, Pozcu	HNO_3	96	25	209	16	8	26	Bodur & Ergin (1988)
Mersin Bay, harbour	-	250			136			Ozkan (1978)
Mersin Bay, Lamas	-	65			31			Ozkan (1978)

Relatively few offshore samples have been analysed. Offshore sediments have zinc concentrations ranging usually between 20 and 80 µg g^{-1} DW (Frignani and Giordani, 1983; Voutsinou-Taliadouri, 1983). However, Shaw and Bush (1978) reported average zinc concentrations in deep sea sediments of around 117 µg g^{-1} DW.

In sediment cores the zinc levels usually range between 20 and 85 µg g^{-1} DW. Even in heavily polluted areas such as the Gulf of Elefsis, the subsurface background level for total zinc was <20 µg g^{-1} (Scoullos, 1981). Indeed, as a background concentration for total zinc in Mediterranean sediments the value of 20 µg g^{-1} DW could be considered as a good approximation. Similarly, for copper, Frignani and Giordani (1983) reported a range of 10-44 µg g^{-1} DW and Voutsinou-Taliadouri (1983) an average of 20 ± 7 µg g^{-1}. Core sample analysis gave total copper values ranging from 15 to 30 µg g^{-1} DW (Scoullos, 1979; Cauwet and Monaco, 1983; Donazzolo et al., 1984). Shaw and Bush (1978) reported average values of copper in deep sea sediments of the Cicilian basin of 42 µg g^{-1} DW. Background copper concentrations in Mediterranean sediments are therefore in the range of 10-30 µg g^{-1} DW with a commonly found average value of 15 µg g^{-1}. Many authors, however, who have used weak acids for extraction have reported considerably lower values, some even at <1 µg g^{-1}.

3.5 Zinc and copper levels in biota

Zinc and copper concentrations in marine biota depend on environmental factors such as the concentrations of these metals in seawater and sediments, on the position of the organism in the food chain, its age and weight/size, sex, on the season of sampling and on the chemical speciation of zinc and copper to which the organisms are exposed. Both zinc and copper are essential elements, with different species having different requirements for them. Also, different mechanisms exist for the regulation of these metals in organisms, including their transport, storage and excretion of surplus metal (see also section 4). Therefore, various biological species in the same environment may have quite different zinc and copper concentrations in their tissues. Also, various individuals within a species may contain different levels and, of course, the various tissues of the same species can attract different proportions of the body burden. This means that for a valid comparison of zinc or copper in biota from different localities, the same tissue of the same biological species of similar size/age, collected during the same season should be compared. In practice, most of the comparisons have been made between samples of the same species and tissues with relatively little attention given to other parameters.

3.5.1 Zinc and copper in plankton

Fowler (1977) studied the concentrations of trace metals in zooplankton particulate products in the Mediterranean and concluded that the moults and faecal pellets contain relatively high concentrations of heavy metals and that their deposition may play an important role in marine biochemical cycles.

Relatively few data have been published on zinc and copper concentrations in plankton and particularly for open ocean or "pelagic" species, although their crucial role in the food web, their importance in terms of their total biomass and their ability to accumulate and transport metals in various ways has been well documented (Martin and Knauer, 1973; Leatherland et al., 1973; Fowler, 1977). Aubert et al. (1974), found a bioconcentration factor of 3400 in plankton exposed to 0.03 mg l^{-1} of zinc for 8 days.

The results of a systematic study in the Mediterranean carried out during the periods 1974-75 and 1977, were summarized by Fowler (1986). The sampling stations used, the relevant cruise, and the year are shown in Fig. 9. Mixed microplankton (using nets of various mesh (60-500 µm)) as well as species of macroplankton and necton were sampled. The results of the microplankton analysis for zinc and copper are summarized in Table 10, together with results obtained by Zafiropoulos and Grimanis (1977), Hardstedt-Roméo and Laumond (1980) and Hardstedt-Roméo (1982).

Concentrations of copper and zinc measured simultaneously in plankton and surface waters showed no clear correlation with geographical trends except at one station in the S. Ionian sea, where high copper concentrations in plankton coincided with the highest value of copper in the seawater (0.74 µg l^{-1}) recorded along Fowler's cruise tract. Although some of the spatial variability in the metal levels in microplankton could be undoubtedly attributed to differences in the metal concentrations in the seawater, much of the variation should be attributed to natural differences in species composition throughout the Mediterranean. For example, samples from the S.W. basin of the Mediterranean taken by Fowler (1986) contained far greater numbers of diatoms than those collected from the Aegean and Ionian seas.

It is known that metal concentrations vary considerably among different species of zooplankton and phytoplankton. It is noteworthy that, in nine times out of ten, zinc and copper concentrations were significantly higher in microplankton collected with a 132 µm mesh net than that taken by a 60 µm one, indicating that differences existed between organisms collected with different mesh sizes. In general, the phytoplankton fraction of the total biomass was greater in the samples obtained with a 60 µm mesh (Fowler, 1986).

The figures reported by Hardstedt-Roméo (1982) show slightly higher concentrations (in µg g^{-1} dry weight) for phytoplankton (Zn 262, Cu 34.0) in comparison with copepods (Zn 227, Cu 24.1). Also, for macroplankton, no uniform offshore-inshore gradients were observed for zinc and copper concentrations in the euphausid Meganyctiphanes norvegica. Table 11 summarizes zinc and copper concentrations found in macroplankton. Levels differed by no more than a factor of 4 for any group of organisms studied and for most of the groups the degree of variation was considerably lower.

Fowler (1977) noted that zinc concentrations were higher in the moults of Euphausiacea than in the whole animal, whereas for copper the reverse was true. Copper was also less concentrated in the moults of the Decapoda Pasiphaea than in the muscle tissue (Fowler, 1974). The author suggested that the surface area is probably not of major importance in the concentration of this metal by planktonic crustacea. The narrow range of variation for zinc in Euphausiacea to Decapoda may be due to a homeostatic regulation of this element in macroplankton as suggested by Hamanaka and Tsujita (1981) who measured zinc concentrations in different crustaceans. In

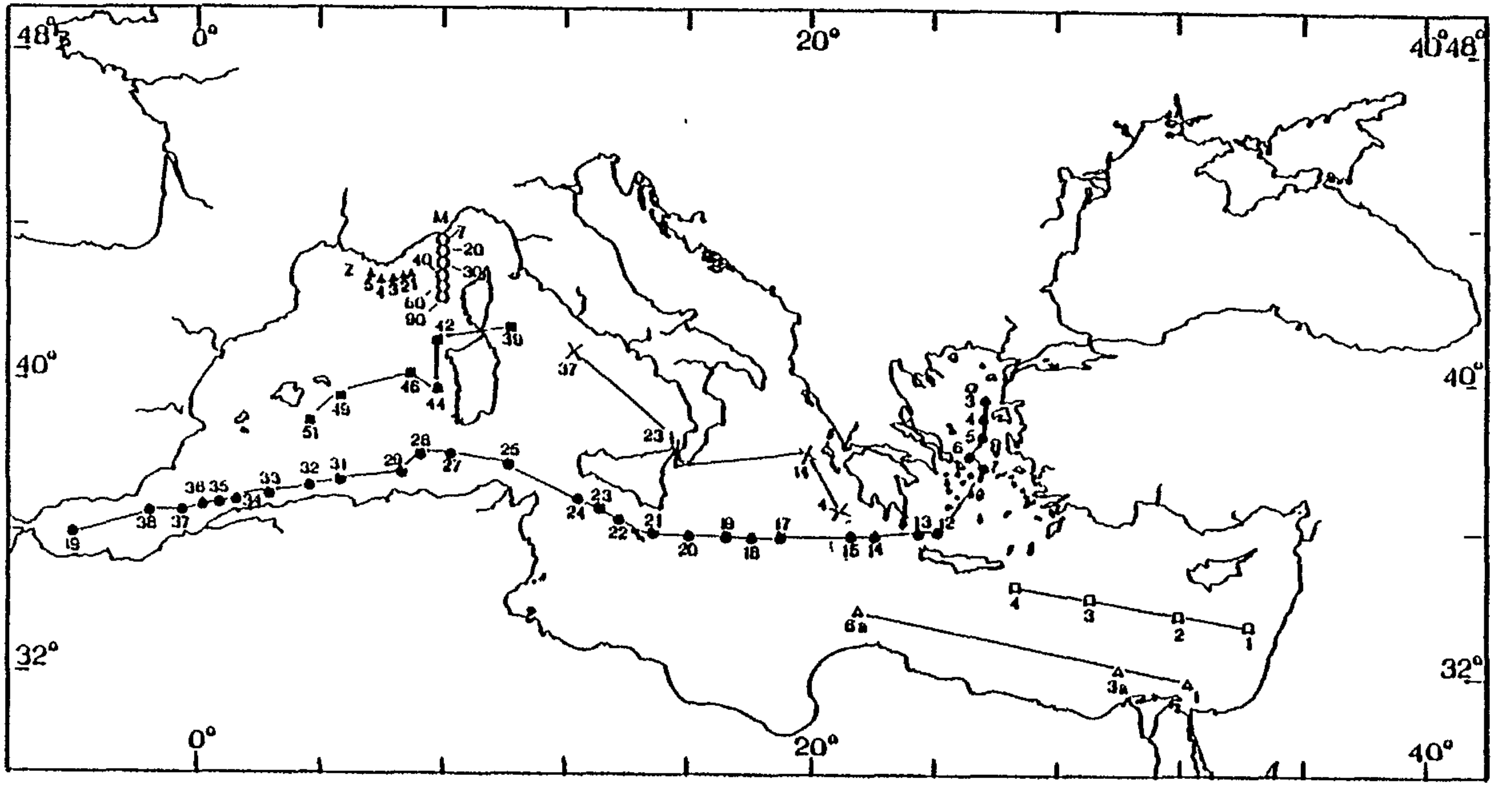


Fig. 9 Sampling stations in the Mediterranean. Chain 1975 (●), Shikmona 1977 (□), Atlantis II 1977 (△), Hayes 1977 (x), Cornide de Saavedra 1977 (■), Monaco transect 1974 (O), Hyères transect 1974 (▲)

Table 10

Zinc and copper concentrations in Mediterranean microplankton.

	MESH (µm)	Zn (µg g^{1} DW) mean (min-max)	Cu (µg g^{1} DW) mean (min-max)	REF.
Microplankton (May-June 1974)				Fowler (1986)
Monaco	132	424 (246-596)	16.6 (15.1-20.7)	
Hyeres	132	413 (334-584)	24.1 (19.2-35.9)	
Microplankton				Fowler (1986)
Chain Cruise 121				
(May 1975)	60	385 (79-1276)	42.6 (11.8-96.0)	
Open Med	132	446 (286-769)	39.1 (13.3-172)	
Microplankton Copepods **<u>Acartia</u> <u>clausi</u>**				Zafiropoulos & Grimanis (1977)
Gulf of Elefsis	250	1270 (800-2500)	55.3 (34-107)	
Microplankton 1977				Fowler (1986)
Eastern Med	280	201 (96-271)	17.6 (15.8-20.2)	
Ionian	60	296 (294-298)	43.9 (33.1-54.7)	
	280	159 (136-183)	30.3 (21.8-33.1)	
Tyrrhenian	60	207	37.1	
	280	118 (118-119)	23.8 (15.3-32.3)	
N.W. Med	500	100 (74-139)	17.7 (6.6-37.1)	
Open Med 1977		176 (74-298)	25.4 (6.6-54.7)	
N.W. Med (coastal)	200	268 (52-745)	32.6 (5.9-126)	Hardstedt-Roméo & Laumond (1980)
Phytoplankton (Porto Vecchio, Corsica)		262	34.0	Hardstedt-Roméo (1982)
Copepods		227	24.1	

general, the levels of zinc and copper for the majority of the Mediterranean pelagic species of plankton analysed fall within the range of values reported for the same groups of organisms from other geographical areas. Although based on a limited number of data, there appears to be no evidence of higher metal loads in any of the Mediterranean species studied.

There is a trend in the Mediterranean for a well defined reduction in metal concentration between microplankton and pelagic carnivores, a finding similar to those reported for other pelagic communities. (Martin and Knauer, 1973; Leatherland <u>et</u> <u>al.</u>, 1973; Hamanaka and Tsujita, 1981).

Table 11

Zinc and copper concentration in pelagic macroplankton.

	Zn µg g^{1} DW mean(min-max)	Cu µg g^{1} DW mean (min-max)	Ref.
EUPHAUSIACEA			Fowler (1986)
Euphausia spp.			
Open Med	108 (68-228)	32.9 (25.0-41.4)	
Eastern Med	106 (58-140)	30.9	
Ionian Sea	84	-	
Tyrrhenian Sea	89 (57-120)	33.7 (31.5-36.0)	
Northwestern	39	43	
Meganyctiphanes norvegica			Fowler (1986)
Ionian sea (1977)	39	-	
Tyrrhenian (1977)	144	-	
Open Med (1974-75)	85 (66-112)	65.6 (58.6-71.1)	
M. norvegica and Euphausia spp.			Fowler & Oregioni (1976)
Mediterranean	98 (66-228)	47.7 (25.0-71.1)	
M. norvegica and Stylocheiron longicorne			Roméo & Nicolas (1986)
East Corsica	59 (44-71)	25.4 (19.8-32.9)	
M. norvegica			Hardstedt-Roméo (1982)
Porto Vecchio, Corsica	61	26.5	
S. longicorne	58	23.9	
AMPHIPODA			Fowler (1986)
Phrosina semilunata			
Mediterranean	150 (109-190)	24.3 (21.6-26.7)	
DECAPODA			Fowler (1986)
Sergestes spp.	68 (60-79)	27.7 (20.2-31.6)	
Gennadas elegans	69 (63-73)	38.7 (24.5-49.7)	
S. articus			Roméo & Nicolas (1986)
Corsica	51 (37-61)	17.7 (12.6-28.9)	

Roméo and Nicolas (1986) suggested that zinc concentrations decrease sharply from copepods to higher crustaceans, whereas copper decreases from phytoplankton to copepods (see Fig. 10).

The "enrichment factors" in zooplankton organisms remained lower than that for phosphorus. Therefore, compared to phosphorus, there was no enrichment but in fact a reduction in both copper and zinc up the food chain.

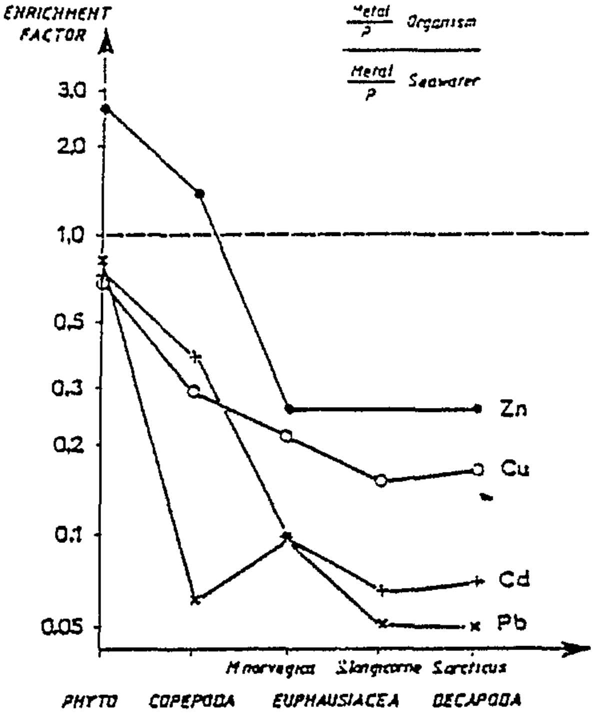


Fig. 10 Enrichment factors based on metal: phosphorus ratios, for pelagic organisms. (Roméo and Nicolas, 1986)

Krishnaswami _et al._ (1985), Fowler (1985) and Roméo _et al._ (1987), have studied the gelatinous macroplankton in the Mediterranean. The samples collected in May 1984 in the N.W. Mediterranean (the Villefranche-sur-Mer Bay) contained representatives of Tunicates, Cnidarians (Hydromedusae, Siphonophores and Scyphomedusae), Ctenophores and Molluscs. Table 12 from Roméo _et al._ (1987) summarises the results.

The highest values for both zinc and copper were found by Krishnaswami _et al._ (1985) in the tunicate _Thalia democratica_ from the N.W. Mediterranean. However, the findings of Roméo _et al._ (1987) indicate that the mean zinc concentrations in tunicates were low, significantly lower than in cnidarians. According to these authors, zinc seems to be preferentially concentrated in organisms rich in collagen which constitutes their mesoglea, such as cnidarians, ctenophores and the gelatinous molluscs, rather than in organisms such as tunicates which are rich in tunicin.

3.5.2 Seaweeds

Relatively few data are available on zinc and copper levels in Mediterranean seaweeds, most probably because no seaweed species had been included in the monitoring programmes, despite their wide distribution and importance in the cycling of trace metals, particularly in nearshore shallow ecosystems.

Table 12

Zinc and copper concentrations (µg g^{-1} DW) in gelatinous macroplankton organisms from different sources. The results were calculated on P/dry weight ratios given by Roméo et al., 1987.

LOCATION	SPECIES	Zn	Cu	REF.
N.W. Med	**TUNICATES:THALIAC-EANS** Thalia democratica Salpa maxima	93-312 35.6	17.0-22.4 7.3	Krishnaswami et al. (1985)
Med	Salpa maxima Pyrosoma atlanticum	26-54 64-180	7.6-10.4 8.7-13.4	Fowler et al. (1985)
N.W. Med	T. democratica and S. fusiformis	17	3.4	Roméo et al. (1987)
Med	**CNIDARIANS:HYDROMEDUSAE** Abylopsis tetragona	25	-	Fowler et al. (1985)
N.W. Med	**HYDROMEDUSAE:** **CNIDARIANS:SCYPHOMEDUSAE**	65	2.7	Roméo et al. (1987)
Adriatic	Pelagia noctiluca	29-76	5.4	
N.W. Med	Pelagia noctiluca **CTENOPHORES:** Beroe ovata	46 97	2.0 7.1	Roméo et al. (1987)

a) Algae

Zinc is an essential trace element for algal growth and metabolism and while copper is a micronutrient for many of them it can be toxic at high concentrations.

Zinc and copper levels in Adriatic seaweeds collected in the rocky eulittoral and sublittoral at the Piran and Rovinj area (Istrian coast) were studied by Munda (1990). The water concentrations measured during spring there were zinc ca. 60 µg l^{-1} and copper ca. 2 µg l^{-1}. The results showed that brown algae had zinc concentrations ranging between 40 and 74 µg g^{-1} DW and copper concentrations between 2 and 10 µg g^{1}. The eulittoral fucoids accumulate more zinc than the sublittoral ones. The accumulation of the metal in Scytosiphon lomentaria increases towards the end of the vegetative period. Elevated copper concentrations were found in Dictyotales (3-8 µg g^{-1} DW) and Scytosiphonales (9-22 µg g^{1}), and these were related to pollution at the sampling sites.

In general the nature of metal accumulation in brown algae is rather irregular and the metal remains strongly bound (Morris and Bale, 1975).

Munda (1990) found relatively high zinc concentrations (DW) in red algae: Porphyra leucosticta 23 µg g^{1}, Pterocladia capillace 60-73 µg g^{1}, Ceramiales ciliatum 23 µg g^{1}, Laurencia obtusa 17 µg g^{1}, compared to copper where its concentration was elevated only in Gelidium pusillum (15 µg g^{-1}).

Scoullos et al. (1989 and unpublished data) have studied the seasonal fluctuations of zinc and copper concentrations in sea waters and in Ulva lactuca in samples collected the Saronikos Gulf, Greece The concentrations of zinc and copper in Ulva lactuca tissues are shown in Table 13. Algal samples were collected from nine stations at three sites of the Saronikos Gulf, and at monthly intervals from February 1985 to March 1986.

Table 13

Concentration of zinc and copper in Ulva lactuca
tissues from the Saronikos Gulf (1985-1986).

Station	Zn	Cu
	µg g^{-1} (dry weight)	
Piraeus		
P_1	60.5 - 306.0 (*) (170 ± 58)	6.5 - 23.0 (**) (13.9 ± 4.8)
P_2	49.8 - 1549.0 (*) (427 ± 453)	8.8 - 53.4(**) 18.0 ± 12.1)
Aspropyrgos (**)		
A_1	82.6 - 509.0 (197.5 ± 130)	10.4 - 41.7 (19 ± 7.6)
A_2	78.4 - 379.0 (224 ± 103)	3.7 - 35.0 (18 ± 8)
A_3	33.0 - 621.0 (186 ± 159)	4.3 - 29.4 (14 ± 6.5)
Loutropyrgos (**)		
L_1	44.5 - 805.0 (207 ± 193)	
L_2	73.9 - 1293 (285 ± 363)	
L_3	68.5 - 302.0 (127 ± 88)	
L_4	45.2 - 258 (142 ± 68)	

(*) Scoullos et al. (1989) and (**) Unpublished data.

There was quite good correlation between zinc concentrations in algal tissues and the total zinc content of seawater (dissolved and particulate). The maximum zinc concentrations were observed mainly in August and September, whereas the values of the concentration factor (C_{Ulva}/C_{diss}) were higher in April.

Elevated copper concentrations were observed the same period, as for zinc, but also in March and April, when the dissolved copper concentrations were minimum and the particulate copper concentrations were of a maximum.

b) Higher plants

Lyngby and Brix (1989) have studied zinc and other metals during the growth and decomposition of the common mediterranean eelgrass (Zostera marina L.). Although the samples were collected outside the Mediterranean, the data for the distribution of zinc in the various parts of the plant are relevant here. Leaves contained 180 µg g^{-1}, decayed leaves 162 µg g^{-1}, stem 62 µg g^{-1}, roots 134 µg g^{-1} and rhizomes 55 µg g^{-1} (DW).

Sanchiz et al. (1990) studied the bioaccumulation of heavy metals in Posidonia oceanica (L.) Delile and Cymodocea nodosa (Ucria) Ascherson, at an uncontaminated site in the east coast of Spain and concluded that zinc concentrations were higher in the plant tissues than in the sediment. Values for both species were quite similar. Zinc concentrations in the different parts of the plant, increased in an order similar to that of Zostera marina: old leaves> old leaves apical> detached dead leaves> old leaves basal> young leaves> root> rhizome (the age of the leaves used is determined by lepidochronological analysis). Panayotidis et al. (1990) who studied the cyclic variations of the copper bioaccumulation in the leaves of Posidonia oceanica concluded that there was a significant negative correlation between the copper concentration and the thickness or density of the leaves, indicating that the copper bioaccumulation cycle in this plant is annual.

Bei et al. (1990) reported that Cystoseira sp. and Padina pavonica collected from the waters around Milos island (Greece), an Aegean area of high hydrothermal activity, had mean zinc concentrations in their leaves ranging respectively between 2.2 and 59.1 µg g^{-1} DW and 21.8 and 37.3 µg g^{-1} DW.

Panayotidis and Florou (1989) reported copper concentrations in a number of seaweeds of the Ionian Sea and the enclosed Amvrakikos Gulf, collected during April and July 1987. The copper concentrations (in µg g^{-1} DW) in Posidonia oceanica from two sites in the Ionian (April) were:

site 1 (Ionian Sea): roots 17.4> young leaves 13.8> old leaves 10.4> rhizomes 8.4
site 2 (entrance of the Amvrakikos): young leaves 12.4> old leaves 8.4> rhizomes 7.8

For Jania rubers (April) site 1: 7.2; site 2: 5.0
For Padina pavonica (April) site 2: 3.2; (July) site 1: 10.4; site 2: 8.4
For Cystoseira sp. (April) site 2: 2.2 and Liagora viscida (July) site 1: 9.8

Inside the Amvrakikos Gulf Cymodocea nodosa from one site had copper concentrations of 5.2 µg g^{-1} in the leaves and >3.0 in the roots (April) whereas in the same site in July the concentrations were 19.2 and 3.2 respectively. The same seaweed was sampled in five sites within the Amvrakikos in July and considerable variations were observed (for leaves, from 6.8 to 59.8 and; for roots 3.6 to 7.2 µg g^{-1}); these differences were attributed to the influence of runoff.

3.5.3 Crustaceans

Relatively very few data exist for zinc and copper levels in Mediterranean crustaceans (see Table 14).

Panayotidis and Florou (1989) reported copper concentrations in Penaeus kerathurus (n=8) from the Amvrakikos Gulf (Ionian Sea) collected during cold and warm periods. The concentrations during the warm period were marginally higher (19 - 25.2 µg g^{-1} DW) than those in the cold one (16.4 - 24.7 µg g^{-1} DW).

Table 14

Average zinc and copper concentrations (µg g^{-1}) in crustaceans from the Mediterranean.

Species	No of samples	Zinc mean	Standard Deviation	No of samples	Copper mean	Standard Deviation
Nephrops norvegicus (1)	279	15(fw)	2.8	303	5.7(fw)	1.9
Parapenaeus longirostris	19	11(fw)	3.4	22	8.5(fw)	8.0
Penaeus kerathurus (1)	22	22(fw)	16	12	5.2(fw)	2.7
Carcinus mediterraneus (1)	13	41(fw)	29	-	-	-
Decapoda (2)			(range)			(range)
Segrestes articus	5	51(dw)	37-61	5	17.7(dw)	12.6-28.9
Sergestes spp	6	68(dw)	60-79	6	27.7(dw)	20.2-31.6
Gennadas elegans	3	69(dw)	63-73	3	38.7(dw)	24.5-49.7

(1) from UNEP/FAO (1986a) (concentrations in fresh weight);
(2) from Fowler (1986) (concentrations in dry weight).

3.5.4 Molluscs

Mytilus galloprovincialis has been designated as an obligatory species in the MED POL monitoring programme and this explains the abundance of data for this species throughout the Mediterranean. However, concentrations in mussels are difficult to compare when samples are taken at different seasons and locations. Fowler and Oregioni (1976) studied the variation of heavy metal levels in Mytilus galloprovincialis and reported that maximum concentrations occurred in the spring. They suggest that this is probably a result of the reproductive state of the mussels but also of the high particulate metal loads in the sea water caused by increased winter runoff. Majori et al. (1979) and Fowler (1985) report significant variations of trace metal concentrations in Mytilus galloprovincialis. Borchardt et al. (1988) suggest that the metal content in mussels is highly dependent on season, size and body condition.

Tables 15, 16 and 17, show the wide range in concentrations of both zinc and copper in Mytilus galloprovincialis from the Mediterranean region. In Table 15 it is apparent that the mean concentrations of zinc in the various Mediterranean regions in Mytilus galloprovincialis range from 17-45 µg g^{-1} wet weight. Overall ranges are between 2.5 and 97.7 µg g^{-1}, whereas the mean for the entire Mediterranean is 27 µg g^{-1} wet weight. Similar levels have been reported for M. edulis in the North Sea (ICES, 1974, 1977a, 1977b).

Table 15

Zinc concentrations in Mytilus galloprovincialis µg g^{1} (fresh weight) (UNEP/FAO, 1986a).

Region	No of samples	Min	Max	Mean	Standard Deviation
II	26	13.00	60.20	28.0	10.7
IV	84	3.15	63.00	34.0	11.2
V	58	2.50	64.25	17.0	12.0
VIII	21	9.20	97.70	45.0	24.6
All regions	179			27.0	13.0

Table 16

Copper concentrations in Mytilus galloprovincialis µg g^{1} (fresh weight) (UNEP/FAO, 1986a).

Region	No of samples	Min	Max	Mean	Standard Deviation
II	55	0.504	4.80	1.50	0.90
IV	85	0.070	6.00	1.90	1.10
V	58	0.163	4.40	1.00	0.90
VIII	13	0.750	2.80	1.60	0.60
All regions	179			1.30	0.70

Individual values of zinc for Mytilus galloprovincialis are shown in Table 17 and range between 12 and 644 µg g^{1} dry weight which agree with the above range assuming a wet/dry weight ratio of 6.

Copper concentrations are considerably lower with means ranging from 1.0-1.9 µg g^{1} wet weight. The mean value for the entire Mediterranean is 1.3 µg g^{1} wet weight (Table 16). These values are within the ranges reported for Mytilus edulis in the North Sea (0.6-9.4 µg g^{1}) (ICES, 1977a, 1977b).

The copper values in Table 17 for Mytilus galloprovincialis range from 2.4 to 154 µg kg^{-1} dry weight, and agree with the data in Table 16, the highest values being reported for the Ligurian Sea (off Monaco) and the Turkish coast.

Martinèiæ et al. (1987) studied copper accumulation in native mussels Mytilus galloprovincialis (L.) and its correlation with free and labile complexes of dissolved copper in the seawater of the Limski Kanal (N. Adriatic). A significant seasonal variation in the copper content of the soft part of the mussel and in the organs (with the exception of the foot and the kidney) was found. The highest concentrations of copper (1.59 µg g^{1} wet weight, in total soft tissues, in mantle 1.51 µg g^{1}, in gill 1.94 µg g^{1} and in viscera 2.2 µg g^{-1}) were associated with the concentration of bioavailable copper (mainly ionic) in the ambient water. Particulate matter in the water column stimulates water transport and thus influences copper accumulation and its distribution between the organs. The equilibration of copper within the different organs (with the exception of labial palps) is relatively rapid (less than 30 days).

Table 17

Zinc and copper concentrations in Mytilus galloprovincialis and other molluscs from selected Mediterranean areas (in µg g^{-1} dry weight).

Species	Zn	Cu	Region	References
	µg g^{-1} (dry weight)			
1. Mytilus galloprovincialis	97 - 644*	2.4 - 154	Ligurian Sea Med II	Fowler & Oregioni (1976)
2. Mytilus galloprovincialis	87 - 137	6.2 - 9.8	Adriatic Sea Med V (Gulf of Trieste)	Majori et al. (1979)
3. Mytilus galloprovincialis	12 - 87	4 - 5	Aegean Sea (Saronikos Gulf)	Grimanis et al. (1979) Papadopoulou & Kanias (1976)
4. Mytilus galloprovincialis	336 - 452	36 - 64	Turkish Coast Med VIII	Uysal (1979)
Recent data:				
6. Mytilus galloprovincialis April (cold period) July (warm period)		 4.1 - 10.9 5.2 - 15.6	Ionian Sea Med VI (Amvrakikos Gulf)	Panayotidis & Florou (1989)
7. Mytilus galloprovincialis	190 ± 44	15.0 ± 16.5	L'Etang de Berre/Fos (FR) MED II	Catsiki & Arnoux (1987)
8. Murex trunculus	540 ± 744	65 ± 21		
9. Venerupis aurea	119 ± 53	13.5 ± 7.5		
10. Venus verrucosa Branchies Masse visc "Reste"	65 ± 20 81 ± 92 57 ± 1 93 ± 34	6.9 ± 1.7 9.2 ± 2.0 8.0 ± 2.0 7.0 ± 1.0	Port-Vendres/Roussilion (FR) MED II	Gnassia-Barelli et al. (1988)
11. Perna perna (L.)	243 ± 25 133 ± 26 174 ± 91	10.9 ± 1.0 13.1 ± 4.2 10.9 ± 1.4	Amiroute (Alger) (ALG) Chenoua (ALG) Sondja (ALG) MED III	Asso (1985)
12. Donax trunculus	126 ± 104**	21 ± 10	All Med Regions	UNEP/FAO (1986a)

Note: * Concentrations of No 1 to 6 are given in ranges; for References of No 1 to 5 see in Fowler (1985);
** No 12 was converted using a wet/dry weight ratio of 6.

In other molluscs (Table 17) the highest concentrations of both zinc and copper were recorded in Murex trunculus from Etang de Berre /Fos (Zn 540 ± 744 and Cu 65 ± 21 µg g^{1} dry weight). The concentrations measured in other molluscs from the same area were also particularly high. Perna perna (L.) collected near Amiroute in Algeria (Zn 243 ± 25 and Cu 10.9 ± 1 µg g^{1} dry weight) and Donax trunculus from various parts of the Mediterranean (Zn 126 ± 104 and Cu 21 ± 10 µg g^{1} dry weight) have the highest concentrations but the associated fluctuations are considerable.

3.5.5 Fish

Tables 18, 19 and 20 summarize the zinc and copper concentrations found in Mullus barbatus (an obligatory species for MED POL monitoring) from various regions and localities of the Mediterranean.

Table 18

Zinc concentrations in Mullus barbatus µg g^{1} (fresh weight)
(UNEP/FAO, 1986a).

Region	No of samples	Minimum	Maximum	Mean	Standard Deviation
II	132	0.10	7.10	4.00	0.97
IV	221	0.40	7.00	4.00	1.00
VII	11	2.70	5.80	4.30	0.86
VIII	40	2.57	6.89	3.50	0.80
IX	12	3.66	7.40	5.10	1.04
X	23	3.06	5.87	4.40	0.65
All regions	453			3.90	0.90

Table 19

Copper concentrations in Mullus barbatus µg g^{1} (fresh weight)
(UNEP/FAO, 1986a).

Region	No of samples	Minimum	Maximum	Mean	Standard Deviation
II	153	0.20	1.30	0.405	0.97
IV	208	0.0025	1.00	0.380	1.00
VII	10	0.36	2.70	0.930	0.86
VIII	60	0.22	1.47	0.600	0.80
X	23	0.069	2.55	0.800	0.65
All regions	444			0.400	0.14

Tables 21 and 22 summarize the zinc and copper concentrations in various marine fish from the Mediterranean and from the Eastern (Levantine) sector. Zinc is present in considerably higher concentrations than copper in Mullus barbatus, but there is a wide spectrum of values for the various species.

Table 20

Comparison of zinc and copper (µg g^{-1} fresh weight) in Mullus barbatus found in several Eastern Mediterranean regions (Hornung and Ramelow, 1987).

Region	Zn	Cu	Reference
Israel	1.8-10.9	0.005-0.19	Hornung and Ramelow (1987)
Italy	2.4-9.5	0.33-1.30	Capelli et al. (1983)
Greece	3.6-6.9	0.30-0.51	Grimanis et al. (1981)
Greece	2.1-7.7	0.16-1.48	Voutsinou-Taliadouri (1983)
Yugoslavia	3.4-5.45	0.43-0.78	Vukadin et al. (1985)
Turkey	3.7-5.98	0.48-0.95	Uysal and Tuncer (1985)
Turkey	4.5*	0.48*	Balkas et al. (1979)
Egypt	---	0.32-0.65	Emara (1983)
Israel	14.9-25.5	3.30-6.40	Roth and Hornung (1977)

(*) average value

Zinc concentrations for Mullus barbatus range from 0.4 to 7.4 µg g^{-1} (fresh weight) whereas the mean regional ones are within 3.5 and 5.1 µg g^{-1} (fresh weight) with higher mean values recorded in the North Levantine and high individual concentrations in samples from the Ligurian and the N.Western part. However, there are no significant regional variations. The overall Mediterranean average (435 samples, excluding the 5% highest values) is 3.9 µg g^{-1} (fresh weight) with a standard deviation of 0.9. The widest zinc variations and the highest concentration of 10.9 µg g^{-1} (fresh weight) were recorded by Hornung and Ramelow (1987) (see Table 20) from the coast of Israel. The same authors have reported in an earlier work (1977) even higher zinc concentrations in Mullus barbatus, ranging between 14.9 and 25.5 µg g^{-1} (fresh weight).

Copper concentrations in Mullus barbatus (see Table 19) range widely from 0.0025 to 2.7 µg g^{-1} (fresh weight) with mean regional values ranging between 0.38 and 0.93 µg g^{-1} (fresh weight) and an overall Mediterranean average (444 samples) of 0.4 µg g^{-1} (fresh weight) with a standard deviation of 0.014.

No significant variations between regions can be established for copper because of the high standard deviations. The widest range, however, was again reported for the Levantine, off the coast of Israel (from 0.005 to 6.4 µg g^{-1} fresh weight) by Hornung and Ramelow (1987). Such a variation requires confirmation and, if genuine, further investigations into its cause will be necessary.

Table 21

Concentrations of zinc and copper in twelve species of fish from far eastern Mediterranean. Ranges, (averages and standard deviations) are given for composite (C) and individual (I) samples. Total number of specimens in each sample are indicated in parenthesis (From Hornung and Ramelow, 1987).

Species	No of samples	Range of lengths (cm)	Zn	Cu
			$\mu g\ g^{-1}$ (dry weight)	
Mullus barbatus	C(35)	10.9-20.8	6.7 - 58.8 (22.0 ± 8.8)	0.9 - 14.7 (3.7 ± 3.0)
	I(24)	14.0-23.0	8.8 - 47.7 (20.6 ± 8.8)	0.02 - 5.3 (1.8 ± 1.3)
Upeneus moluccensis	C(15)	9.6-17.7	10.7 - 36.2 (19.3 ± 6.3)	0.48 - 8.32 (3.1 ± 2.7)
	I(17)	13.6-20.6	10.2 - 25.0 (16.8 ± 3.9)	(0.35 ± 3.46) (2.0 ± 0.8)
Saurida undosquamis	C(13)	17.0-30.0	11.3 - 20.0 (15.8 ± 2.4)	0.18 - 2.33 (1.4 ± 0.6)
	I(22)	13.1-31.5	10.6 - 30.0 (16.5 ± 5.1)	0.26 - 8.08 (1.5 ± 1.7)
Pagellus erythrinus	C(9)	13.7-17.1	13.4 - 34.5 (23.2 ± 6.0)	0.80 - 4.53 (2.2 ± 1.3)
	I(17)	12.2-20.2	10.0 - 32.3 (22.0 ± 6.1)	0.12 - 3.44 (1.5 ± 0.8)
Pagellus acarne	C(1)	13.8	19.5	2.53
	I(1)	16.2	11.1	2.80
Sphyraena sphyraena	C(2)	21.9-29.5	15.2 - 22.8	1.36 - 5.45
	I(3)	27.1-31.0	4.1 - 23.3	1.03 - 3.44
Sphyraena chrysotaenia	I(2)	26.7-26.7	12.9 - 20.8	3.12 - 3.74
Chelidonich thyslucernus	I(1)	17.9	21.2	3.64
Boops boops	C(3)	15.8-19.8	17.6 - 28.2	0.30 - 2.81
Merluccius merluccius	I(2)	19.4-22.2	15.9 - 12.1	1.50 - 2.40
Trachurus mediterraneus	C(5)	17.8-21.5	12.2 - 31.6	0.30 - 5.57
	I(3)	15.0-26.4	22.6 - 26.8	2.24 - 6.24
Mullus surmuletus	I(1)	13.4	15.0	2.75

The same authors measured copper and zinc concentrations in a number of other fish from the Eastern Mediterranean (Table 21) and examined in more detail the ranges and natural variability of copper and zinc in 4 fish species of economic importance for the area (Mullus barbatus, Upeneus moluccensis, Saurida undosquamis, Pagellus erythrinus). They concluded that zinc concentrations generally decrease with the length of the fish but the correlation was not significant; copper did not show any such tendency. Metal concentrations in these fish species seemed to generally decrease with the depth sampled but again the correlations were not significant.

Amiard et al. (1987) in a comparative study of bioaccumulation patterns of trace metals, did not observe any correlation between zinc concentrations in fish tissue and in sea water.

Table 22

Average zinc and copper concentrations in marine fishes from all Mediterranean regions µg g^{-1} (fresh weight) (UNEP/FAO, 1986a).

Species	No of samples	Zinc mean	Standard deviation	No of samples	Copper mean	Standard deviation
Engraulis encrasicolus	75	18.0	6.7	97	0.99	0.66
Mugil auratus	66	10.6	15.0	31	0.70	0.96
Mullus surmuletus	24	10.0	14.0	20	0.60	0.54
Upeneus moluccensis	13	2.9	1.1	-	-	-
Sarda sarda	-	-	-	27	2.1	1.7

From the data in Tables 21 and 22 it is clear that very wide interspecies variations occur in the concentrations of both zinc and copper. Mediterranean average values for zinc as low as 2.9 µg g^{-1} fresh weight for Upeneus moluccensis to as high as 18.0 ± 6.7 µg g^{-1} fresh weight for Engraulis encrasicolus or above 30.0 µg g^{-1} (dry weight) for Saurida undosquamis and Sphyraena sphyraena etc. occur in the literature.

Similarly for copper the Mediterranean average ranges between 0.60 ± 0.54 µg g^{-1} (fresh weight) for Mullus surmuletus to 2.1 ± 1.7 µg g^{-1} (fresh weight) for Sarda sarda (see Table 22) whereas in the Eastern Mediterranean (see Table 21) values higher than 3.0 µg g^{-1} (dry weight) have been reported for several species.

The main characteristic in most of the studies is the very wide fluctuations in the values for individual fish. Samples are often collected without taking into account the sex and size of the fish and the season of sampling. Panayotidis and Florou (1989) reported the following copper concentrations for four fish species during "cold" and "warm" periods from Amvrakikos Gulf (Ionian Sea):

	Range of Cu concentrations (µg g^{-1} dry weight)		
	No samples	Cold per.	Warm per.
Mullus barbatus (L.)	13	1.0-2.0	1.4-2.6
Sardina pilchardus (W.)	10	2.0-2.3	2.6-4.0
Mugil cephalus (L.)	10	1.4-1.6	1.0-3.0
Mugil auratus (R.)	14	1.4-2.2	1.0-3.2

It is apparent that the range and maximum values are higher during the warm period (July).

Apostolov et al. (1985) reported copper and zinc concentrations in the flesh and liver of the edible fish Gobius niger in a comparable study including samples from the Varna Bay (Bulgaria) and the Saronikos and Petalion

Gulfs (Greece) (see Table 23). Capelli and Minganti (1987) found that copper and zinc levels were higher in the liver of Sarda sarda than in other organs.

Table 23

Average concentration (µg g^{-1} wet weight) of copper and zinc in the flesh and liver of Gobius niger from Varna Bay, Bulgaria and Saronikos and Petalion Gulfs, Greece.
(from Apostolov et al., 1985).

Station	Specimen per composite sample	Mean length (cm)	Cu flesh	Zn	
				flesh	liver
Varna Bay					
1	20	10	0.326±0.029	10.00±0.60	59.35±3.56
2	20	10.5	0.956±0.086	10.60±0.64	47.90±2.87
3	19	10	1.040±0.094	9.37±0.56	36.10±2.16
4	18	9.5	0.587±0.053	7.74±0.46	---
Saronikos Gulf					
1	10	10	0.228±0.023	4.84±0.28	12.60±0.88
2	12	9.5	0.180±0.018	3.82±0.23	10.90±0.76
Petalion Gulf					
3	20	10.5	0.202±0.020	4.14±0.25	11.90± 0.83

The level in the samples of the Varna Bay were higher than those determined in the Greek gulfs. However, the concentrations are comparable to those reported for other benthic fishes, even to those from areas considered to be less polluted and clearly not dangerous for human health. Zinc concentrations in the liver seem to be 3 to 6 times higher than in flesh.

3.5.6 Birds and marine mammals

No data are available on zinc and copper concentrations in birds and marine mammals from the Mediterranean.

3.6 Levels in ecosystems under the influence of anthropogenic activities

The previous sections have shown that, except for a few cases, there seems to be little correlation between zinc and copper concentrations in marine organisms and the pollution status of their environment. This may be due in part to the occurrence of wide natural fluctuations. It may be also that the way in which the research and monitoring programmes were designed and conducted was insufficient to provide all the necessary features for reliable assessments of this kind.

Amiard-Triquet et al. (1987) examined the relationship between copper and zinc concentrations in seawater and gastropods as well as the importance of the transfer of these metals in short food chains (algae grazing gastropods) and attempted to establish the natural fluctuations. Three species of algae (Fucus seratus, Ulva lactuca, Porphyra sp.) and 15 specimens of flat top shells (Gibbula umbilicalis) and of edible winkle Littorina littorea) were collected monthly. In experimental studies the gastropods were exposed for 4, 8 or 16 days to a range of high zinc concentrations. The authors concluded that in many cases it will be difficult to attribute the metal concentrations in living organisms to either natural causes or to a pollution source unless the pollution is excessive. The ratios between maximum and minimum concentrations observed under the above conditions are comparable to those calculated from the data of several authors (see Table 24) who have studied the fluctuations due to natural factors and/or pollution.

Table 24

Variation in the ratio between the highest and the lowest trace metal concentrations according to the origin of the fluctuations investigated by different authors.

Species	Origin of fluctuation	Concentration (max/min)		Calculated from the data of
		Cu	Zn	
Ulva lactuca	Temporal	6.4	6.3	(1)
Ulva lactuca	Regional	2.0	1.8	(2)
Porphyra sp.	Temporal	4.6	5.3	(1)
Fucus serratus	Temporal	7.1	5.7	(1)
Fucus serratus	Temporal	1.9-2.2	2.3-3.6	(3)
Fucus serratus	Regional	1.4	3.7	(3)
Fucus vesiculosus	Individual	-	1.4-4.1	(4)
Fucus vesiculosus	Temporal	-	2.7	(4)
Fucus vesiculosus	Temporal	1.3-4.0	1.8-2.9	(3)
Fucus vesiculosus	Temporal	-	1.8-2.0	(5)
Fucus vesiculosus	Regional	7.0	44.4	(3)
Fucus vesiculosus	Regional	-	6.6	(5)
Fucus vesiculosus	Temporal+ regional	73.3	16.6	(6)
Gibbula umbilicalis	Temporal	3.0	1.3	(1)
Littorina littorea	Temporal	3.0	1.5	(1)
Littorina littorea	Regional	4.9	1.7	(7)
Littorina littoralis	Temporal+ regional	7.0	15.1	(6)

(1) Amiard-Triquet et al., 1987; (2) Talbot and Chegwidden, 1982; (3) Fuge and James, 1973; (4) Stenhagen-Schneider, 1981; (5) Cullinane and Whelan, 1982; (6) Bryan, 1983; (7) Bouquegneau and Martoja, 1982.

The correlations between the metal concentrations in algae and in gastropods are shown in Table 25. The number of significant correlations is limited, contrary to the observations of Bryan (1983) on closely allied species. The possible cause of this discrepancy, according to Amiard-Triquet et al. (1987), is the extent of the metal contamination at the two sites, being low in the bay studied by Amiard-Triquet et al., and high in the estuaries studied by Bryan. The significant positive correlations which may support this hypothesis are that the responses of both algae and gastropods to environmental fluctuations are similar, and the fluctuations of metal concentrations in grazing gastropods reflect the fluctuations in the food which may be their main environmental source of metals.

Table 25

Correlation coefficients between the trace metal concentrations
in molluscs and algae calculated from all the available
sampling data. (n=26)

	Fucus	Ulva	Porphyra
Copper			
L. littorea	-0.59 (**)	-0.41 (*)	-0.31
G. umbilicalis	+0.22	+0.14	+0.25
Zinc			
L. littorea	+0.69 (**)	+0.40 (*)	+0.23
G. umbilicalis	+0.12	+0.07	+0.19

(*) significant correlation (P<0.05)
(**) highly significant correlation (P<0.01)

Table 26 gives a comparison between the metal levels in primary producers and herbivorous species. The level of copper is considerably higher in the gastropods than in their food and the cause of this difference remains unknown. The concentrations of zinc are of the same order of magnitude in the grazing gastropods and F. serratus and they are lower in the other two species of algae. The ability of the winkles and top shells to regulate the zinc concentration in their whole soft tissues has been established but such regulation is initiated above a certain threshold concentration, the level of which decreases with increasing duration of exposure. Similarly, it has been postulated that L. littoralis possesses some ability to regulate copper and zinc (Young, 1975; Bryan, 1983).

In conclusion, as a consequence of the essential trace metals being regulated, the levels of copper and zinc in gastropods will be partly independent of the concentrations in their ecosystems, at least in moderately polluted areas. Acute pollution episodes within these systems may remain undetected since short-term exposures to high levels of zinc do not cause a significant change in concentration in G. umbilicalis and L. littorea.

Table 26

Bioconcentration factors (BCFs) of copper and zinc in algae and molluscs (BCF= ratio of mean metal conc. in the organism to mean metal conc. in seawater).

Species	Cu	Zn
Fucus serratus	2500	8200
Ulva lactuca	1700	3700
Porphyra sp.	3600	4700
Gibbula umbilicalis	79900	8600
Littorina littorea	55900	9900

Catsiki and Florou (1985) studied the concentrations of several metals, including copper, in benthic species and fish living in the Gulf of Geras, Lesvos isl. The Gulf receives the effluents from a large tannery and Scoullos et al. (1981, 1982) have reported that high metal concentrations, particularly chromium, are present in the waters and sediments of the Gulf. Copper was identified by Scoullos et al. as one of the metals whose distribution was not affected so much by this pollution source as by agricultural practices.

Copper concentrations in the species collected are given in Table 27. Although the authors concluded that the tannery effluents do not contribute to the pollution of the Gulf with copper (copper concentration in the effluents are ~30 ppm), elevated copper concentrations were measured in some of the benthic species collected from the vicinity of the waste outlets. The copper concentrations in the fish species, and particularly in Mullus barbatus, are within the lower limits of the Mediterranean average.

Krumgalz and Fleisher (1984) attempted to identify useful bio-indicators of copper and zinc pollution in the Haifa Bay (Israel). They examined sediments and a number of gastropods and bivalves and concluded that, for both copper and zinc, gastropod molluscs bioaccumulated more than bivalves. However, there was no significant correlation between the metal concentrations in the animal tissues and in the sediment apart from a relatively good correlation for copper in the gastropod Arcularia gibbosula.

Uysal and Tuncer (1985) studied the levels of copper and zinc in sediments and fish species from the Izmir Bay. Although they did not attempt to correlate the two, the highest values (Table 28) in D. annularis were recorded in the inner Bay where copper and zinc concentrations in sediments ranged from 33 - 866 mg kg^{-1} (dry weight) and 53- 8660 mg kg^{-1} respectively whereas in the Gulbahce Bay the concentrations in the sediments were for copper 12-56 mg kg^{-1} and for zinc 16-135 mg kg^{-1}. However, such a trend was not reflected in M. barbatus tissue concentrations.

Table 27

Copper in benthic animals and fish species from the Gulf of Geras, Greece. (Catsiki and Florou, 1985).
(A: Close to the tannery B: Far from the tannery)

	Cu (µg g^{-1} DW)	
Benthic species	A	B
Eledone moschata	26.40	23.2
Ostrea edulis	135.80	-
Arca sp.	5.10	-
Murex trunculus	532.00	110.5
Murex brandaris	71.40	53.4
Paracentrotus lividus	6.60	1.6
Dasycladus clavaef	5.00	-
Fish species		
Mullus surmuletus	2.20	
Mullus barbatus	2.60	
Boops boops	3.00	
Trachurus trachurus	2.60	
Gobius sp.	3.60	
Maena chryselis	2.40	
Serranus scriba	2.40	
Diplodus annularis	2.80	
Pagellus erythrinus	2.20	

Table 28

Average heavy metal concentrations (µg g^{-1} fresh weight) in fish from Izmir Bay (from Uysal and Tuncer, 1985).

Species	Location	Cu	Zn
S. scriba	Gulbahce bay	0.70	5.30
D. gibbossus	Gulbahce bay	0.88	4.50
P. erythrinus	Gulbahce bay	0.67	3.50
S. alsedo	Gulbahce bay	0.90	6.70
D. annularis	Gulbahce bay	0.40	8.00
	Inner bay	1.57	12.20
M. barbatus	Gulbahce bay	0.95	5.98
	Inner bay	0.54	4.80

3.7 Summary and conclusions

This Chapter has examined the distribution of zinc and copper in the Mediterranean. Background levels of zinc measured in offshore waters can be as low as 0.02 µg l^{-1} but the normal range found is 1 to 5 µg l^{-1}; this can rise to as high as 450 µg l^{-1} in polluted harbours. Similarly, copper concentrations in offshore waters are about 0.2 µg l^{-1} and can rise to around 50 µg l^{-1} in the vicinity of point source discharges.

A need for caution has been expressed about the accuracy of these measurements because of the ease with which water samples can become contaminated by these metals. This does not apply to the same extent for sediment samples where the concentrations of zinc and copper are much higher. However, for both water and sediment samples the physico-chemical state of each metal should be determined, especially in relation to their bioavailability for marine organisms.

The data presented in this Chapter do not show in general that particularly high concentrations of zinc and copper are being accumulated in Mediterranean organisms. However, the way in which research and monitoring programmes have been designed and conducted in most cases has been insufficient to provide reliable information. Thus, a consideration of the data available together with information on bioconcentration rates and the data on zinc and copper levels in seawaters and sediments reported in Chapter 3, does not exclude the possibility that certain species of commercial value with high zinc or copper concentrations could occur at polluted sites.

4. EFFECTS OF COPPER AND ZINC ON MARINE BIOTA

4.1 Biochemical effects

Trace metals are usually divided into two subclasses. The first includes Zn and Cu together with Fe, Mg, Mn and Co, which are "essential" for the functioning of certain biochemical processes. The second subclass is made up of metals (Cd, Hg, Cr, Pb, etc.) which have no established biological function and therefore comprise the more important contaminants in the aquatic environment. Viarengo (1985) summarised the biochemical properties of zinc and copper in comparison with those of other metals (Hg, Cd, Pb, Ag). This chapter is largely based on his review.

4.1.1 Zinc uptake and effects on cell membranes

The metal uptake mechanism by the cells has not yet been fully elucidated; the evidence indicates that metals cross the cell membranes essentially by a passive transport process although endocytosis may also occur (George and Viarengo, 1985). Studies by Simkiss (1983) suggest that the metal complex goes through the biological membranes as a lipophilic compound, although this simplified model does not seem to be applicable to the uptake of all metals.

Recent studies have demonstrated that correct ratios between zinc in the external medium, zinc bound to the membranes and zinc in the internal environment, are essential in the maintenance of the structure and function of the cell membranes (Bettger and O'Dell, 1981). Zinc ions stabilize the plasma and internal membranes either by binding to structural components or by preventing metal-catalyzed lipid peroxidation (Chvapil, 1973). This is important particularly when compared with other metals such as Cd and Pb, which react with phosphate groups on the lipid bilayer before being complexed by intracellular ligands (George and Viarengo, 1985). Moreover, in fish Hg and Cd are able to disrupt the ionic balance by altering the permeability characteristics of the cell membranes.

4.1.2 Zinc and copper interactions with cytosolic components and effects on intermediate metabolism

When metals cross the cell membrane they react with the cytosolic component, and are usually complexed in different ways (by sulphydrylic binding, chelation, salt formation) to cytosolic compounds such as high affinity specific ligands (metallothioneins), substrates, products of enzymatic activity or enzymes themselves.

Metals can bind to functional groups of proteins, such as imidazole, sulphydryl, carboxyl, amino and peptide groups. Two possible molecular mechanisms for enzyme-related metal toxicity have been identified: (a) the toxic metal displaces a beneficial metal from the active site of the enzyme; (b) the toxic metal binds to a deactivating site of the molecule. It should be noted, however, that the binding of the metallic cations to enzymes could alter their activity, not only by inhibiting but also by stimulating the catalytic function of the enzyme (Eichhorn et al., 1969).

Metals may affect enzymatic activity in different ways, depending on whether their activity is assayed after in vivo exposure to the metal, or by in vitro addition to the incubation mixture.

Data for fish show that copper (and Pb) in vitro inhibits alkaline phosphatase, but that this is stimulated following in vivo exposure. It should be stressed that, irrespective of the metal examined, in vivo exposure of animals to a metal may result in either stimulation, no change, or inhibition of the enzyme activity tested, depending on the duration of exposure and the dosage used (Jackim, 1974), even for enzymes belonging to the same biochemical pathway; this makes the interpretation of the data extremely complicated.

In order to achieve some understanding of the effects of trace metals on intermediate metabolism, the alteration of the activity of rate limiting enzymes induced by heavy metal exposure of the animal was suggested by Livingstone (1982) as a useful starting point.

Variations in the activity of enzymes that catalyze essentially irreversible reactions (rate limiting enzymes) seem to be more appropriate for providing information on the alteration of a particular aspect of intermediate metabolism, since they represent the maximum potential flux related to the metabolic pathway considered. Data are limited, but the case described by Webb (1979) may be a good example. It has been shown that Cd alters glucose metabolism in metal-treated mammals, by affecting the activity of rate limiting enzymes such as glucose-6-phosphatase, fructose-1, 6-diphosphatase, pyruvate-carboxylase etc; however, this effect is achieved mainly by altering the hormonal status of the animals. This emphasizes that care must be taken in interpreting in vivo effects of heavy metals.

Carpene et al. (1984) have studied the effects of zinc on a phosphoryl-transferring enzyme, pyruvate kinase, isolated from the adductor muscle of the Adriatic mollusc Venus gallina. This enzyme is very common in the majority of invertebrates and is generally reported to be a non-equilibrium glycolytic enzyme important for the survival of these bivalves and other organisms which live under intermittently anaerobic conditions.

The pyruvate kinase value of K_1 for Zn^{2+} for pH 7.6 is 1.0 and zinc (as well as Cd) has a serious inhibitory effect on its activity. Nevo et al. (1988) examined samples of the shrimp Palaemon elegans and the marine gastropods Monodonta turbinata collected near Shikmona, an unpolluted site, south of the Haifa Bay. Both dead and live animals subjected to electrophoresis; Palaemon elegans was analyzed for variations in phosphoglucomutase (PGM) and Monodonta for phosphoglucose isomerase (PGI). It was found that copper and zinc at high concentrations mainly inhibited the PGM-M (M= medium migrating allelic isozymes) but at low concentrations (for copper in the range of 0.02 - 0.8 mg l^{-1}) there was an activator effect on the same allozyme (the same effect occurred with PGI-M).

4.1.3 The role of zinc and copper in nuclear metabolism

Metals can interact with nuclear proteins by altering the complex structure of chromatin or the catalytic activity of the enzymes involved in DNA and RNA metabolism. In vitro, metal ions can bind directly to nucleic acids, either to the phosphate groups, ribose-hydroxyl or to the heterocyclic bases (Eichhorn, 1973), which implies that metal cations could affect the correct replication or transcription of DNA, as well as the fidelity of the translation of mRNAs during the process of protein synthesis at the ribosomal level. The in vivo effects of heavy metals on the transcriptional process would indicate that there is a diphasic response in the cell nucleus: metals such as copper (but also Cd and Hg), initially decrease RNA synthesis which subsequently returns to the control level or higher (Viarengo et al., 1982).

Despite the net decrease of RNA synthesis observed initially when metals accumulate in nuclei, the effects of metals on the synthesis of the different messenger RNAs range from inhibition to stimulation, as in the case of the specific messenger RNA that codes for metallothioneins (Andersen and Weser, 1978). The fact that heavy metals are able to induce the synthesis of metallothioneins is considered the most important factor in zinc and copper homeostasis and in the detoxication of the xenobiotic divalent cations Cd and Hg.

4.1.4 The role of Cu-, Zn- and other metallothioneins in marine animals

Metallothioneins are a class of soluble, low molecular weight proteins (about 6800-7000), characterised by their high affinity for heavy metal cations, heat stability, virtual lack of aromatic amino-acids and hystidine and by an unusually high content (30- 35%) of cysteine (Kagi and Nordberg, 1979). These metalloproteins are widely distributed in the animal and plant kingdom. In 1972, metallothioneins were first shown to be present in the tissues of fish exposed to Cd and Hg. Subsequently metallothioneins were reported in metal-exposed marine invertebrates (Roesijadi, 1980), and in particular for decapod crustaceans (Bryan, 1968). White and Rainbow (1986) studied the zinc and copper binding components in the decapod crustacean

Palaemon elegans. Metal binding mechanisms in other crustaceans have been studied by Jennings et al. (1979), Olafson et al. (1979) and Overnell and Trewhella, (1979).

Three low molecular weight, metal-binding components, identified as metallothioneins, have been isolated by White and Rainbow (1986) from the hepatopancreas (an excretory organ) of the shrimp Palaemon elegans. The two larger components P-I (11-15000) were associated with large amounts of copper in field-collected and copper-exposed shrimps and with cadmium in shrimps exposed to elevated cadmium concentrations.

A smaller component, P-III (3500-4500) was associated with zinc although it was also able to complex copper. It was found that copper and zinc are not evenly distributed between individual tissues of P. elegans, the highest concentrations occurring in the hepatopancreas, gills and eyes as shown in Table 29.

Table 29

Mean percentage distributions (SD) of total dry weight and total
body burdens of copper and zinc among tissues of Palaemon elegans.
Data are for pooled tissues from four animals, N=3.
(from White and Rainbow, 1986).

Tissues	Percentage total body dry weight	Percentage total body metal burden	
		Cu	Zn
Cuticle	52.2 (4.7)	39.4 (4.0)	48.4 (4.0)
Muscle	28.0 (3.1)	7.5 (1.2)	17.2 (1.9)
Hepatopancreas	8.0 (1.9)	38.9 (7.2)	17.2 (1.0)
Gill	1.3 (0.1)	3.2 (0.6)	2.1 (0.3)
Eye	1.3 (0.1)	1.3 (0.4)	3.5 (0.6)
Rest	9.2 (2.6)	9.7 (2.9)	11.6 (2.9)

Flatou et al. (1985) determined the organically bound copper, isolated from liver of injured fishes Sparus auratus and Dicentrarchus labrax from the Mediterranean. They found that, for S. auratus, 52.6 µg l^{-1} of copper is bound to compounds of low molecular weight (around 6000) while 34.7 and 22.1 µg l^{-1} of copper were bound to compounds of molecular weight of 15000 and 25000 respectively. The distribution was different for D. labrax: 18 µg l^{-1} and 35 µg l^{-1} were bound to fractions of 8000 and 14000 respectively. The authors concluded that the low molecular weight compounds were most probably metallothioneins and/or polypeptides, whereas those with molecular weights between 10000 and 30000 could be di-,tri-, and tetrameres of metallothioneins and mixtures.

Metallothioneins have also been detected in the tissues of some uncontaminated organisms; their physiological role could be related to the control of zinc and copper metabolism, either through the binding of the excess quantity of divalent cations that penetrate into the cell or by permitting the redistribution of these essential trace metals among the appropriate apoenzymes. Metallothioneins usually are not saturated by a single metal but 6-7 ions of Cu and Zn, and Cd, Hg and Ag, when present, coexist on the same molecule. In Cd-induced thioneins the metal is bound to cysteine residues by trimercaptide bonds but this simple scheme of metal interaction does not seem to apply to (Cu-Zn) or (Cd-Cu-Zn) thioneins (Webb, 1979). When Cd, Hg or excess copper penetrate into the cells they are able to displace zinc from (Zn-Cu) thioneins normally present in the cytosol (Viarengo et al., 1985). This buffer effect of preexisting thioneins represents a first step in the process of heavy metal homeostasis.

If the concentrations of metals taken up into the cell is high and the metals saturate the physiological pool of (Zn- Cu) thioneins, then the excess of cations can stimulate the synthesis of new thioneins either acting at the nuclear level or by stimulating the translation of thionein mRNA at the ribosomal level. In this way, although the concentration of metal in the cell may be abnormally high most of the metal is present in an non-toxic form bound to the neosynthesised thioneins. It is currently assumed (Viarengo, 1985) that only if the rate of influx of metals into the cells exceeds the rate of metallothionein synthesis and/or if the maximum value of thioneins produced in the cell is exceeded by the metals, which can then interact with subcellular components, does cellular toxicity occur.

4.1.5 Effects of copper and zinc on lysosomal biochemistry

Lysosomes, the subcellular organelles involved in the degradation of the food taken up by endocytosis into the cell and principally in the regulation of macromolecular half-life (Moore et al., 1982), are one of the most interesting targets of heavy metals.

Although the acidic pH present in the internal environment of these organelles would not seem ideal for metal accumulation, the data demonstrate that lysosomes are the most important sites of metal compartmentation in the cell (Sternleib and Goldfischer, 1976). In vivo studies of the effects of copper on mussel digestive gland demonstrate that one of the first alterations to be detected at the lysosomal level is the loss of membrane stability (Viarengo et al., 1981; Moore et al., 1984). The destabilisation of lysosomal membranes, which as an extreme consequence of damage could involve leakage of hydrolytic enzymes into the cytosol of the cell, is usually interpreted as an uncontrolled activation of the catabolic activity of the organelles. Studies on mammals, however, indicate that a decrease of lysosomal stability probably represents only an initial transient stage of increased protein catabolism; treatment of animals with Cd or Hg may lead to an inhibition of lysosomal proteolytic enzymes such as acid phosphatase and to a longer half-life of cellular proteins (Mego and Chain, 1975).

Not all heavy metals exert damaging effects on lysosomes. Various studies indicate that zinc, in particular, is able to stabilize the lysosomal membranes (Sternleib and Goldfischer, 1976) and has stimulatory effects on lysosomal enzymes (Webb, 1979).

Copper and zinc are important in the lipid peroxidation mechanisms but in a different way. The term lipid peroxidation covers a complex sequence of biochemical reactions classified by Bus and Gibson (1979) as three sequential steps: a) the initiation process which comprises the generation of lipid radicals, b) the series of propagation reactions in which peroxidation continues and the presence of free radicals is maintained and c) the termination reactions in which free radicals are destroyed. During the termination reaction adjacent fatty acids are joined by abnormal bonds, probably altering the structure of enzymes and their catalytic activity; moreover, lipid peroxy radicals produced in the propagation reactions could abstract hydrogen atoms from neighbouring proteins, resulting in lipid-protein and protein-protein cross-linking. The accumulation of this kind of reaction product leads to the formulation of lypofuscin granules, often detected in the cells of metal-exposed animals (Sternleib and Goldfischer, 1976; George and Viarengo, 1985). Copper plays an important role in the initiation step of lipid peroxidation and it was found that trace amounts of metal ions catalysed the propagation reactions (Bus and Gibson, 1979). Contrary to the effects of copper, cadmium etc, zinc inhibits the process of lipid peroxidation (Chvapil, 1973). There are several data indicating that zinc and copper act antagonistically for this reaction, and that the activity of metal ions in lipid peroxidation is probably dependent upon the balance between zinc and copper or other metals, rather than on the absolute concentrations of copper or cadmium etc. themselves. These results also help in the understanding of the role of zinc in membrane stability and in enzyme activity protection.

Lobel (1987) reported that it became apparent from several studies that there is a considerable "inherent" variability (unexplained residual variability) in the ratio of zinc to the other heavy metals in the kidney of unpolluted mussels with as much as 40-fold variation between individual kidneys. This was not due, according to the author, to variability in the quality of lypofuscin granules which act as storage reservoirs for zinc prior to excretion, which then raises the question of whether this large variability was an effect on the ability of individual mussels to preserve their membrane integrity when subject to pollutant stress.

Lysosomes also play an important role in the catabolism and elimination of metallothioneins. Several studies on metal detoxification in the digestive gland of mussels exposed to copper and cadmium have shown that, as with other cytosolic proteins, (Cu-Zn) (Cd-Zn) thioneins are taken up by the lysosomes (George, 1983; Viarengo et al., 1983). Once inside these organelles they follow different metabolic pathways, probably related to the particular metals associated with the apoprotein. During the detoxification period, the thioneins present in the digestive gland cell of copper-exposed mussels are accumulated as an insoluble polymer in the lysosomes and subsequently eliminated by exocytosis.

Using a reducing solution, it is possible to solubilize more than 80% of the copper present in an insoluble form in the organelles. It has been found that most of the solubilized metal is associated with a low molecular weight protein showing the general characteristics of metallothioneins (Viarengo et al., 1983). (Cu-Zn)thioneins, due to the acidic environment of the lysosomes, probably lose part of the zinc, but not the copper; subsequently the metalloproteins that became rich in free sulphydrylic groups tend to polymerize by disulphide bridges.

The metal trapped in the lipofuscin granules, which are always present in the lysosomes of copper-exposed mussels, probably accounts for the remaining 20% of metal present in the organelles in an insoluble form (Moore, pers. comm.). This particularly efficient double way of elimination of copper via lysosomes is consistent with the short biological half time of this metal in the digestive gland cells of mussels (7-8 days). By contrast, experiments on cadmium detoxification processes have demonstrated that the biological half time of this metal in mussel digestive gland cells is 6-7 months longer than that of copper (Viarengo et al., 1985). This may be related to the finding that even after only 1 month of detoxication most of the cadmium present in the digestive gland cells is bound to thioneins (80-90%), and the decrease of cadmium in the tissue essentially follows the slow diminution of Cd-thionein content. This fact seems to imply that there is a "closed cycle" of (Cd-Zn) thioneins, in which the metalloproteins are taken up into the lysosomes and metals released from the metallothioneins which are then hydrolyzed.

The complex role of thioneins and lysosomes in heavy metal homeostasis is summarized in Fig. 11 (Viarengo, 1985). The scheme of metal homeostasis presented is consistent with most of the data for animals irrespective of their phyla. However, great differences exist among different sub-groups of animals (and different tissues of the same organism), in particular with regard to the elimination by exocytosis of the metal-rich residual bodies. In vertebrates, for example, this form of elimination is not properly utilised in liver hepatocytes and is absent in the cells of the nervous system, and the accumulation of the metal there is associated with serious diseases (Sternleib and Goldfischer, 1976).

However, different methods of storage and detoxification of heavy metals have been developed especially by aquatic invertebrates, i.e. metal compartmentation in membrane limited vescicles as well as the formation of inorganic endocellular precipitates. These metal sequestration mechanisms are extremely important in metal homeostasis of many invertebrate groups and the literature has been reviewed by Coombs (1980).

Betaines such as homarine have been proposed as low molecular weight Zn-binding ligands (Dall'Aglio, 1971; Coombs, 1974). Wong and Rainbow (1987) isolated a non-proteinaceous Zn-binding ligand of low molecular weight (ca. 300) from a hepatopancreas extracts of the crustacean Carcinus maenas. The complex is highly polar, lacks nitrogen and aromatic groups, and it was thought to consist of a dicarboxylic acid with complex aliphatic backbone or of several related carboxylic acid species. It is probable that the ligand is a TCA-metabolite since it is widely accepted that most organisms have large pools of TCA-metabolites possessing carboxylic functional groups.

4.1.6 Effects of copper and zinc on the endoplasmic reticulum

It has been shown that cadmium, mercury and copper in the cells of metal-exposed organisms are able to reduce the rate of protein synthesis (Viarengo et al., 1980), not only by reducing the rate of RNA synthesis as reported above, but also by influencing the attachment of polyribosomes to the rough endoplasmic reticulum and probably damaging the ribosomes themselves. Zinc also has an adverse effect and the important role of this cation (and Mg) in the maintenance of the structure and function of polyribosomes and in general, of the endoplasmic membranes, is well known.

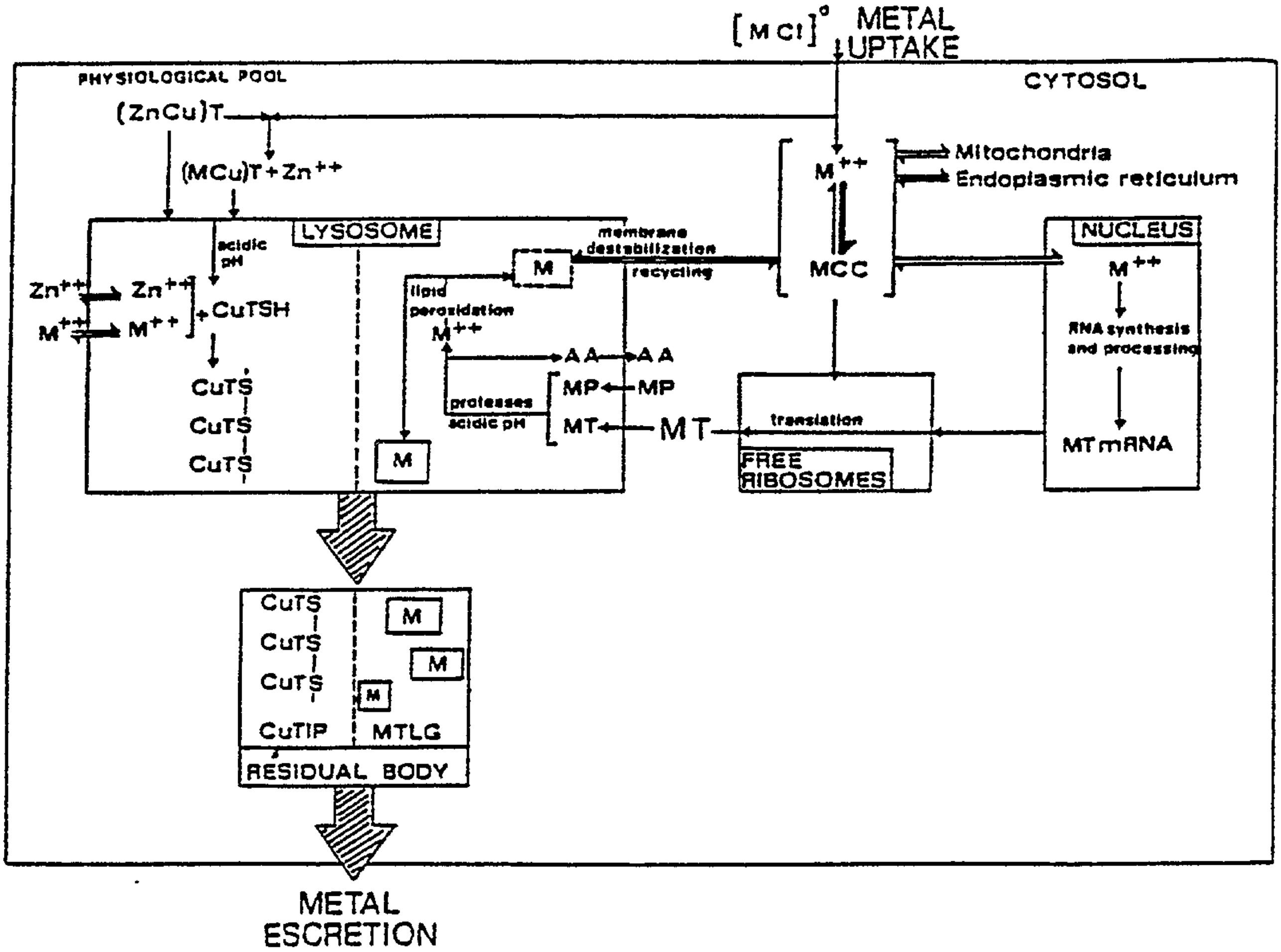


Fig. 11 Proposed scheme of the role of metallothioneins and lysosomes in metal homeostasis. M^{2+} = divalent metal cation; MCC = metal bound to cytosolic components; MT = metallothioneins; MP = metal bound to enzymatic and structural proteins; AA = amino acid; M = metal weakly bound to lipid peroxidation products; M = metal bound to lypofuscin granules in a non-interchangeable manner; CuTiP = Cu-thionein insoluble polymer; MTLG = metals trapped in lypofuscin granules

4.1.7 Effects of copper and zinc on ATP synthesis

It is well-known that mitochondria, the organelles responsible for aerobic ATP production, are able to accumulate high concentrations of Ca by an active transport process. Zinc and many other metal cations, such as Fe^{3+}, Mn^{2+}, Cd^{2+} and Hg^{2+} are actively accumulated by these organelles (George, 1982). There is evidence that copper is taken up by a passive process (Zaba and Harris, 1978). Results of *in vitro* and *in vivo* studies have demonstrated that extremely low concentrations of heavy metals can inhibit oxidative phosphorylation. These data indicate that mitochondria may be considered as one of the most important targets of heavy metals in cells.

4.1.8 Summary

This review of biochemical effects provides an insight into the mechanisms used by marine organisms to translocate and detoxify zinc and copper ions that are surplus to their biological requirements. The presence of such processes indicate that organisms may be able to adapt to elevated levels of these metals in the environment. However, when environmental concentrations rise above a certain level, these processes will become overloaded and consequent damage will be caused to tissues and ultimately to the organism. The state of knowledge about biochemical effects is at present insufficient to predict the concentrations at which such overloading will occur for the various groups of marine organisms. These critical levels can only be measured by long-term toxicity tests on the whole organism, taking into account all the factors that are known to affect accumulation, translocation and detoxification.

4.2 Other effects

It is well known that high concentrations of heavy metals in the water have a direct disruptive effect on the external cell membranes or cell walls of organisms, causing rapid mortality. While acute toxic effects are of some biological interest, the longer-term effects caused by lower concentrations are more important in the setting of water quality standards for environmental protection.

However, many research workers have carried out marine toxicity tests without due regard to the chemistry of the test substance in sea water. For example, the solubility of zinc in seawater is 1.2 mg l^{-1}, so that higher concentrations will be present as a precipitate and not as free ions. Also, copper can readily form soluble complexes with organic substances in the water; these are much less toxic than the ionic forms and so the toxicity of the total dissolved copper content is reduced. Therefore, the true toxic concentrations may be lower than the nominal ones recorded. The following sections focus on those experiments that demonstrate harmful effects on organisms at zinc and copper concentrations of <1 mg l^{-1}.

4.2.1 On algae

Scoullos et al. (1989) and Scoullos and Caberi (1991) have studied the effects of zinc, copper and other metals on the seaweeds Ulva lactuca and Enteromorpha, in samples collected from the Saronikos Gulf, Greece, and in mesocosm enclosures placed in the Gulf of Elefsis (Caberi, 1990).

Free floating, mature growths of Ulva lactuca were used by Caberi (1990). In three mesocosms, trace metal concentrations were adjusted to high levels: 30,60,300 times for zinc (between 200 to 2000 µg l^{-1}) and 10, 20, 100 times for copper (between 15 to 150 µg l^{-1}) higher than those of the local environment, whereas in the fourth (reference mesocosm) the concentrations were kept at about the natural levels. All other factors (T, S%., pH and DO) were kept identical with those of the natural environment of the area. However, the existence of the mesocosms themselves had some impact on the conditions. Nutrients showed a slight increase within the mesocosms and in the mesocosm with the highest metal concentrations, lethal effects were observed.

No algae were alive after 15 days. Algal degradation resulted in indirect changes of pH and DO and also to the production of relatively large quantity of particulate matter. The trace metal content of the latter was very high, and considerably higher than the content of the algal tissues, indicating that this organic matter acts as an effective scavenger of metal ions. Similar conclusions were reached by using different methodologies by De Filippis et al. (1981) and Haritonidis et al. (1981) who have reported that zinc and cadmium respectively tend to accumulate rapidly in dead algal cells.

Stromgren (1979a, 1979b; 1980a, 1980b) investigated the relationship between the percentage reduction (z) in growth rate and the product of time (x) and concentration (y) in copper and zinc treated fucoid algae (Fucus, Ascophyllum and Pelvetia): z=Kxy. He found at least 60% reduction in growth rates at copper concentrations above 33 µg l^{-1} during the course of an 11 day in vitro incubation.

The effect of copper on the early stages of the kelp Laminaria saccharina was studied by Chung and Brinkhuis (1986) using 5, 10, 50, 100 and 500 µg Cu l^{-1} in the plants culture medium. Copper toxicity is believed to be related mainly to the concentration of the free cupric ion, as chelating agents detoxify Cu-spiked seawater. The authors found that the density of meiospore release was reduced in concentrations higher than Cu >50 µg l^{-1} in treated sorus materials. Settlement and germination were not affected by the range of copper concentrations up to 500 µg l^{-1}. Development of gametophytes and gametogenesis were delayed in copper concentrations >50 µg l^{-1}. Growth of sporophytes in terms of length increase or relative blade area increase was inhibited by copper concentrations >10 µg l^{-1}. The critical concentrations of copper which inhibit the development of gametophytes and young sporophytes is between 10 and 50 µg l^{-1}.

According to Braek et al. (1976), copper and zinc acted synergistically to the dinoflagellate Amphidinium carteri and the diatom Thalassiosira pseudonana, while the same metals acted antagonistically towards the diatom Phaeodactylum tricornutum. Mixtures of the metals may be additive in producing acute but interact in rather unpredictable ways in producing chronic effects.

Data reviewed by the UK Water Research Centre (WRC, 1984a) showed that effects of zinc on algal growth were not found at concentrations <50 µg l^{-1}. Data on the toxicity of copper (WRC, 1984b) were more variable; for a range of species the lower concentrations that limited growth were between 5 and 6000 µg l^{-1}.

4.2.2 On crustacea

4.2.2.1 Zinc

The LC_{50} values for the brine shrimp (Artemia salina) is 100 µg l^{-1} zinc within an exposure time of 150 hours (Brown and Ahsanullah, 1971).

Bagshaw et al. (1986) studied the effects of zinc on the hatching of Artemia larvae. The results are summarized in Table 30. In all cases the total number of embryos that developed up to at least the emergence stage was similar to that in the controls, i.e. zinc did not affect development before emergence (which is the last step before hatching).

Table 30

Effects of zinc on the hatching of Artemia larvae
(from Bagshaw et al., 1986).

ZINC CONCENTRATION µg l^{-1}	EXPOSURE TIME			
	24h		48h	
	% EMERGED	% HATCHED	% EMERGED	% HATCHED
Control	8.7±4.3	56.1±8.1	5.1±3.2	64.7±7.7
1360 µg $ZnCl_2$ l^{-1}	65.1±4.9	4.0±2.8	59.8±7.8	6.3±5.9
136 µg $ZnCl_2$ l^{-1}	51.7±7.4	12.9±5.8	40.2±19	20.6±7.8
13.6 µg $ZnCl_2$ l^{-1}	31.8±15.1	24.1±10.2	22.3±7.7	49.7±6.1

The hatching stage of Artemia development is highly sensitive to the presence of zinc which seems to inhibit the rupture of the hatching membrane. The developing post-gastrula embryos are protected by an impermeable chitinous shell and suffer little or no apparent damage. The emerging pre-nauplius larvae are sensitive to zinc which may affect their further development. After hatching, however, the nauplius larvae are far less sensitive to heavy metal toxicity. Thus, 1360 µg l^{-1} $ZnCl_2$ produced no significant mortality in hatched nauplii.

Hardouvelis (1988) studied the survival and fertility of four successive generations of the harpacticoid copepod, Tisbe holothuriae, after exposure to three sublethal zinc concentrations (70, 10 and 7 µg l^{-1}).

At 70 µg l^{-1} zinc, a concentration equal to 1/10 of the LC_{50}, the population size was reduced to zero after the first generation, whereas the population size of the fourth generation was not affected by a zinc concentration of 7 µg l^{-1}. The highest mortalities were found at 70 µg l^{-1} zinc for the first generation and at 10 µg l^{-1} for the fourth, while nauplii proved to be more sensitive than the copepodites.

An increase in zinc concentration from 0-70 µg l^{-1} decreased the percentage of animals with egg-sacs. At 70 µg l^{-1}, only 0.38% of the population produced a third egg-sac whereas in the other concentrations, a greater number of animals produced up to 5 egg-sacs. The percentage of the population producing egg-sacs decreased from generation to generation at the 10 µg l^{-1} level, something that was not observed at the 7 µg l^{-1} level and in the controls. The results show that zinc is harmful not only at high zinc concentrations, but also at lower sublethal concentrations and especially after prolonged exposure of the population to the pollutant.

4.2.2.2 Copper

The acute toxicity of copper to Artemia salina was found to be 480 µg l^{-1}. Similar toxicities have been found for copper and other small crustaceans (Moraitou-Apostolopoulou, 1978; Moraitou-Apostolopoulou and Verriopoulos, 1982).

De Nicola Giudici et al. (1989) studied the effects of acute and chronic exposure to copper and cadmium on the isopod crustacean Idothea baltica collected from the bay of Naples. Acute toxicity tests showed that copper, an essential metal, was more toxic than non-essential cadmium. Similar results were found with toxicity studies on other crustaceans (Bryan and Hummerstone 1971; Ahsanullah et al., 1981a, b; Negilski et al., 1981). Furthermore, females of Idothea baltica showed a significantly higher tolerance than males did. Males had a significantly higher tolerance than juveniles. When the adults and juveniles were exposed to metal concentrations higher than 1 mg l^{-1}, there was a marked levelling in the LT_{50} curves. This may suggest the existence of a threshold concentration above which there is no further significant increase in toxicity. Formation of organo-metal complexes might reduce the free ion levels in the solution (Moraitou-Apostolopoulou, 1978). Moreover, the slopes of the LT_{50} curves were not parallel, which indicates that copper and cadmium have different mechanism of action, as previously reported (Ahsanullah et al., 1981b; Negilski et al., 1981).

Demographic parameters, viability, sex ratio, and growth, were strongly affected by long-term exposure to 0.5 mg l^{-1} of both metals. Growth was reduced, survival at the 120th day dropped to about 10% and females markedly exceeded the males. The toxic effect on males occurred mainly in the first 2 months of development, before the juveniles attained sexual maturity. Therefore Idothea baltica populations may be unable to survive long-term exposure to 0.5 mg l^{-1} copper.

In juveniles exposed to 5 µg l^{-1} copper, growth and sex ratio were similar to those found in control animals, while survival was dramatically reduced at the 120th day (about 60%). Exposure to copper during embryonic and juvenile development had the greatest toxic effect; exposure during embryonic development only was the less toxic of the two. In juveniles exposed to copper the mortality rate was high during the first 3 months; once sexual maturity was reached, survival did not differ significantly from the controls. This indicates that the first months of development are the most sensitive stage.

In conclusion, a long-term exposure to 5 µg l^{-1} copper can halve an Idothea population.

Direct interference with heart action by copper ions has been reported by Kerkut and Munday (1962). A concentration of 25 µg l^{-1} copper inhibited contraction of excised Carcinus maenas hearts and the respiratory rate of the heart muscle fell by 34%.

Eisler and Hennekey (1977) reported a 96hr LC_{50} of 400 µg l^{-1} for copper for the adult crab, Pagurus longicarpus.

Verriopoulos et al. (1986), studied the acute toxicity of 4 toxicants (Cu, Cr, oil and oil dispersant) to adult Artemia salina acting individually and jointly (in combinations of 2, 3 or 4 chemicals). The individual toxicity tests showed that copper was the most toxic:

Cu > Oil dispersant > Cr > Oil

In the copper mixtures the toxic effects was less than additive (Cu+Cr, Cu+Oil) which indicates antagonism between the components. In the 3 and 4 pollutant mixtures with copper the toxicity was markedly less than additive.

Moraitou-Apostolopoulou and Verriopoulos (1982) demonstrated an obvious synergism of the effects of three metals (Cu, Cd, Cr) to Tisbe holothuriae when acting in mixtures of two. The mixture of the three metals were more toxic than that of the individual metals acting separately, but lower than that of two metal mixtures. It seems that the mode of joint action of pollutants can depend on the organism tested.

The WRC review (1984a) confirms that 100 µg l^{-1} zinc was the lowest effect concentration recorded for crustaceans up to that time; for copper (WRC, 1984b) no effects had been recorded below 10 µg l^{-1}.

4.2.3 On polychaetes

A zinc concentration of 1000 µg l^{-1} resulted in a 13 hour LC_{50} in the polychaete Ophryotrocha (Brown and Ahsanullah, 1971).

The WRC review (1984a) reveals that polychaetes are relatively resistant to zinc, with lowest effect concentrations being generally >1 mg l^{-1}. Copper is more toxic (WRC, 1984b) with effects being recorded at >40 µg l^{-1}.

4.2.4 On echinoderms

Inhibition of larval development was observed with Paracentrotus lividus at a zinc concentration of 30 µg l^{-1} (Bernhard and Zattera, 1975).

The WRC review (1984a) contains little information on the toxicity of zinc to the various life stages of this group of organisms; in general, effects have not been recorded at concentrations <1 mg l^{-1}. In contrast, copper (WRC, 1984b) is toxic to larval development at concentrations >10 µg l^{-1}.

4.2.5 On molluscs

Because molluscs are generally found in inshore areas and estuaries where discharges of wastes are likely to occur, a considerable amount of information has been obtained on their reaction to chemicals, particularly the heavy metals.

4.2.5.1 Effects on burrowing and crawling

Amiard and Amiard-Triquet (1986), studied the natural and metallic pollution factors which may influence the burrowing activity of the bivalve molluscs Cardius edule (L.). A partial inhibition was observed for copper and zinc at concentrations of 0.1 mg l^{-1} and for 2.5 mg l^{-1} respectively. For copper this concentration is similar to the 96hr LC_{50}, whereas for zinc it is two times lower.

4.2.5.2 Effects on shell growth

The effect of copper and zinc on the shell growth of Mytilus edulis has been measured by a laser diffraction technique, accurate to 3µm, by Manley et al., 1984. The results show that within three days 10 µg l^{-1} added copper has a significant inhibitory effect on shell growth. Longer term experiments have been undertaken which show that the effects of 10 µg l^{-1} copper become more severe as the exposure time increases. Recovery of near normal shell growth occurs on transfer to clean sea water even after a 14 day exposure to this concentration. The effects of zinc on shell growth are less severe. Thus, 75 µg l^{-1} zinc had no apparent effect on the shell growth whereas 200 µg l^{-1} decreased the growth by 20-30% of that shown by the control over a three day period.

4.2.5.3 Effects on valve closure and heart rate

Mussels are able to detect and respond to increased levels of copper in their environment. Manley (1983) measured a threshold detection response of 20 µg l^{-1} and complete valve closure at 200 µg l^{-1}. He described the threshold detection responses as an intermittent movement of the shell valves, along with periodic opening and closing of the exhalent siphon. This behaviour, which he called "testing behaviour", decreased in frequency as copper concentration increased above the threshold concentration until a concentration was reached above which the animals did not open. Heart rates recorded before and during the addition of copper showed immediate short-term changes. These changes are most likely the result of "testing behaviour" or valve closure. Long term effects of copper on heart rate are rare. Davenport (1977) studied heart rates of mussels exposed to a cyclical copper regime for 6 days. Grace and Gainey (1987) reported that long-term changes in heart rates appeared at copper concentrations ranging between 50 and 400 µg l^{-1} and the time necessary to effect these changes increased as copper concentrations decreased; at the highest concentration (400 µg l^{-1}), a decrease in rate and irregularities in rhythm were detected after 2h exposure.

The most frequent change noted apart from a straightforward decrease in rate, was a pattern consisting of a series of beats followed by a pause and then another series of beats (burst activity). The same phenomenon was observed also after 10 days exposure at the lowest concentration of copper (50 µg l^{-1}); moreover burst activity appeared in both open and closed animals. In some of the animals exposed to the two lower concentrations, burst activity disappeared after several days and regular beating resumed, indicating that no irreversible damage had occurred.

The final change in heart rate was a completely irregular rhythm pattern. This occurred in mussels exposed to the three higher concentrations and appeared around 3-4 days after exposure; in addition, all mussels exposed to the two higher concentrations of copper (200, 400 µg l^{-1}) died within 5-7 days of exposure.

4.2.5.4 Effects on filtration rates

Oxygen uptake and feeding in bivalves are dependent on a flow of water across the gills. Water is drawn into the mantle cavity through the inhalant aperture; it passes between the gill filaments into the subrabrachial cavity and is ejected through the exhalant aperture. The difference in area between the large inhalant and small exhalant aperture results in a low inflow and a fast outflow speed.

The flow of water through a bivalve can be measured as the filtration rate (the volume of water cleared of particles per unit time) or as the pumping rate (the volume of water passing through the animal per unit time). The two parameters are almost identical in most circumstances as there is virtually a 100% retention of particles >2µm in diameter.

Filtration in Perna perna, Choromytilus meridionalis, Crassostrea margaritacea and Crassostrea gigas is reduced by 50% by zinc and copper in the ranges 750-2000 µg l^{-1} and 60-160 µg l^{-1} respectively (Watling, 1981; Watling and Watling 1982). The zinc and copper concentrations which cause total inhibition of pumping, and the zinc concentrations which cause measurable decreases in pumping, are clearly higher than recorded environmental levels even in polluted Mediterranean areas.

A series of investigations focussed on the cause of the response of M. edulis and other bivalves to copper. Abel (1976) and Howell et al. (1984) investigated the effects of some pollutants on the filtration rate of groups of mussels using the algal removal method. Abel (1976) produced dose-response curves for copper and zinc showing a gradual decrease in filtration with increasing metal concentration. He reported EC_{50} for filtration of 150 µg l^{-1} copper using intact animals after immediate exposure, while Manley (1983) found an EC_{50} of 30 µg l^{-1} copper in intact animals after immediate exposure. Davenport and Manley (1978) found that valve closure in mussels not exposed to copper resulted in lowered filtration rates as well as decreased heart rates; they suggested that the apparent immediate effects of copper are due to the previously mentioned "testing behaviour"; however, Howell et al. (1984) cut the adductor muscle to prevent valve closure and obtained an EC_{50} of 94 µg l^{-1} copper. Filtration rates measured by Grace and Gainey (1987), from animals kept for 5 days after exposure to copper yielded an EC_{50} of 2 µg l^{-1}, which is much lower than those previously reported and close to concentrations recorded in several polluted localities in the Mediterranean.

Other data

The WRC review (1984a) indicates that harmful effects of zinc on molluscan larvae can occur at concentrations >40 µg l^{-1}, and for copper (WRC, 1984b) this value was >5 µg l^{-1}. Gould et al. (1988) reported the very strong inhibition effects of copper on the production of gametes and the spawning of the scallop Plactopecten magellanicus.

4.2.6 On fish

Steele et al. (1973) studied the effect of sublethal exposure to copper on the diel activity of sea catfish, Arius felis, after 72 h static exposure to copper (0.0, 0.05, 0.1 or 0.2 mg l^{-1}). He did not find any significant differences in activity between control fishes and those exposed to 0.05 mg l^{-1} Cu. Fishes in the 0.1 and 0.2 mg l^{-1} Cu-exposure groups reacted to a similar extent with significantly greater activity compared to that of the controls and the fish in 0.05 mg l^{-1}. Hyperactivity of fish following sublethal exposure to copper may have been induced by a general excitation of behaviour, by irritation of external chemo- or mechanoreceptors and/or by avoidance behaviour of the fish. The diel cycle remained but at proportionally increased levels of activity, probably attributable to an effect of the metal on the neural control centres.

Studies on the toxicity of methylmercury and copper to the blue gourami Trichogaster trichopterus indicated that the two toxicants may interact antagonistically.

The WRC review (1984a) shows that fish are comparatively resistant to zinc, with LC_{50} values being >1 mg l^{-1}; some of the higher values may be eroneous because the solubility of zinc would have been exceeded. For copper (WRC, 1984b) embryos of two fish species were sensitive to concentrations >25 µg l^{-1}.

4.2.7 Summary

The data presented in the second section of this Chapter show that there is a considerable range of sensitivity to zinc and copper between the various groups of organisms tested. This variability will be due in part to the extent to which the organisms at different stages of their life cycles can detoxify these metals. But some of the variability may depend on the experimental conditions used, in particular the sources of the sea water and of the test organisms. The former may be important if the sea water contains organic matter that can form soluble complexes with copper; the latter may be important if the test organisms have been obtained from areas where the environmental concentrations of zinc or copper were elevated above background levels.

The lowest concentration at which zinc is reported to be toxic is >10 µg l^{-1} using the copepod Tisbe as the test organism. This value is close to the normal background concentrations of 1-5 µg l^{-1} found in offshore waters.

The lowest concentrations at which copper has been found to be toxic is 5 µg l^{-1} for reproduction in the isopod Idothea baltica and 10 µg l^{-1} for shell growth in the mussel Mytilus edulis. A value of 2 µg l^{-1} for the inhibition of filtration rate in mussels seems to be rather low and needs confirmation. As with zinc, these effect concentrations are very close to the levels found in Mediterranean offshore waters.

There appears to be a need for a further critical examination of the ecotoxicological and the environmental chemistry data to determine whether the small margin of safety between the two sets is real or the result of analytical errors or of inappropriate experimental procedures.

Several of these tests have been carried out and indicate that a number of organisms are particularly sensitive to copper and to a lesser extent zinc. In most acute toxicity tests on crustaceans the no effect level for copper was 10 µg l^{-1} whereas the lowest effect concentration recorded for zinc was 100 µg l^{-1}.

Harmful effects of zinc on mollusc larvae can occur at levels >40 µg l^{-1} whereas for copper this value was >5 µg l^{-1}. The latter coincides with the level where survival of crustacean juveniles were reduced by 60% at the 120 day of exposure. Zinc effects on the hatching stage of Artemia were detected at levels >15 µg $ZnCl_2$ l^{-1}.

Finally, based on filtration rates of Mytilus edulis for mussels exposed for 5 days to copper yielded an EC_{50} of 2 µg l^{-1}.

5. EFFECTS OF ZINC AND COPPER ON HUMAN HEALTH

5.1 Toxicity of zinc and copper to man

Seafood provides a major source of zinc and copper to man. Several species such as oysters have bioconcentration factors of many thousands both for copper and zinc, whereas common edible species such as mussels, shrimps and crabs have bioconcentration factors of several hundreds.

Further information on the concentrations of zinc and copper in the tissues of marine organisms found in the Mediterranean, including those from polluted areas, has been tabulated in Section 3.5.

Zinc toxicity on humans has been reviewed by IRPTC/UNEP (1978) and is summarised in Table 31.

NIOSH (1978) reported that the lowest lethal dose (LDLo) known for a human is 500 µg kg^{-1} bw/day. ITII (1975) has reported an LD50 of 630 µg kg^{-1} bw/day for the rat. The respiratory toxic low dose (TDLo) for zinc oxide is 600 µg m^{-3}. In this case the zinc oxide was inhaled and affected the pulmonary system.

Adverse effects of zinc include acute metal fume fever by the inhalation of fumes, throat irritation, coughing, dyspnea, muscle and joint pain (Lehmann, 1910), gastric irritation (Chrometzka, 1936), peptic ulcers and various liver effects (Guja, 1973).

There have been reports of human cases of zinc poisoning associated with the prolonged consumption of water from galvanised pipes. In two adults who drank water containing 40 mg l^{-1} of zinc, irritability, muscular stiffness and pain, loss of appetite and nausea were reported. There is no evidence that zinc in excess is carcinogenic, mutagenic, or teratogenic (NAS, 1977).

The only zinc salt on which several toxicity studies have been carried out is zinc chromate (reviewed by Berlin et al., 1989). Various forms of this compound could produce malignant or unspecified tumours at the site of application; it is DNA damaging, mutagenic in cultured mammalian cells and induces lung cancer. However, it is clear that it is the chromate and not the zinc that is responsible for the main toxic effects. Zinc is not found in the marine environment in this form.

Zinc has not been implicated in any human disease derived from the eating of seafood (Osterberg and Keckes, 1977). The low toxicity of zinc and efficient homeostatic control mechanisms make chronic zinc toxicity from drinking water and dietary sources an unlikely hazard in man (WHO, 1984).

Copper is widely distributed in foods. Intake of excessively large doses by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver could occur. Application of copper salts to the skin is corrosive and may lead to papulovesicular eczema (WHO, 1984). However, copper poisoning of dietary origin is rare in man and higher mammals owing to the powerful emetic action of copper (WHO, 1984).

5.2 Relationship between the uptake of zinc and copper from seafood and the ADI for man

Daily doses of 150 mg of zinc interfere with copper and iron metabolism, because zinc is a metabolic antagonist of both these metals. However, where dietary intakes of copper and iron are adequate, there is

Table 31

Effect of zinc on man and other mammals (from IRPTC/UNEP, 1978).

description of organism	exposure			retention tissue/percen/time	clearance rate percent/time	metabolite name/amount hazard	citation (as reported)
	route	concent.	duration of exposure				
human (patients)	intravenous	100µCi	single dose	liver/3.8%/174 days	-	-	Siegel et al., 1961 (FIRL, 1978 p.55)
human (patients)	intravenous	100µCi	single dose	% dose/g wet tissue: liver:0.061/1 day, 0.015/71 days kidney:0.040/1 day, 0.004/71 days spleen:0.012/1 day 0.0002/71 days lung:0.004/1 day 0.001/71 days intestine:0.004/1 day, stomach:0.01/1 day, skeletal muscle: 0.001/1 day, 0.002/71 days pancreas: 0.011/1 day, 0.001/71 days adrenal:0.009/1 day, 0.002/71 days prostate:0.002/1 day, 0.003/71 days	- - -	-	Spencer et al., 1965 (FIRL, 1978 p.57)
human	oral	0.6-1.0µCi	-	50%/154 days (29-48 years old)	-	-	Richmond et al., 1962 (FIRL, 1978 p.57)
human	intravenous	-	-	18%/30 days in faeces, 1%/30 days in urine	-	-	Prasad, 1966 (FIRL, 1978, p.57)
human	oral	-	-	19-76% days in faeces 0.7-2.1%/15 days in urine	-	-	Prasad, 1966 (FIRL, 1978, p.57)

little problem even with high zinc doses. Zinc is also a metabolic antagonist of cadmium. High zinc intakes may therefore, be expected to afford some protection against the toxic effects of cadmium exposure from the environment (Underwood, 1977). There is no official acceptable daily intake for zinc. In the case of drinking water, WHO recommends a guideline value of 5.0 mg l^{-1} which, however, is based primarily on aesthetic and organoleptic considerations, rather than health hazards as such (WHO, 1984).

In the case of copper, the position is similar in that there is no official acceptable daily intake. The guideline value for drinking water is 1.0 mg l^{-1}, mainly to prevent interference with intended domestic uses of water, rather than in connection with health hazards (WHO, 1984).

Both zinc and copper are classified as inorganic dietary constituents of potential health significance (WHO, 1984). In the case of the Mediterranean, seafood consumption may be said to present no general hazard, although problems could result from heavy consumption of seafood from highly polluted areas, particularly where intake from other sources is also higher than average.

6. CONTROL MEASURES AND RECOMMENDATIONS CONCERNING COPPER AND ZINC

6.1 The existing provisions within the Barcelona Convention

The Contracting Parties to the Convection for the Protection of the Mediterranean Sea Against Pollution (1976) undertook an obligation to take all appropriate measures to prevent, abate and combat pollution of the Mediterranean Sea area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources within their territories (Article 8).

In order to implement the above obligation, the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources (LBS Protocol) was adopted in 1980 and came into force in 1983.

The Protocol lays down (Article 6) that the Contracting Parties shall strictly limit pollution from land-based sources in the Protocol area by substances or sources listed in Annex II ("Grey list of substances") to the Protocol and that to this end, they shall elaborate and implement, jointly or individually, as appropriate, suitable programmes and measures.

Zinc and copper are included in Annex II which is a list of substances which are less harmful than those of Annex I. These metals were so classified because it is widely believed that they affect only relatively restricted coastal marine areas.

Their discharges are subject to special authorization (permit) by the Contracting Parties to the Barcelona Convection (National Authorities and the EC) according to the provisions of Annex III to the protocol.

The process for granting the permit for discharges containing zinc and copper should take into account in every case a number of factors under the following heading:

a) The characteristics of the metals.
b) Their ecotoxicological properties (persistence, toxicity, bioaccumulation, biotransformation, catalytic activity, etc).
c) The characteristics of the mode of discharge and of the recipient body of marine water.
d) The available waste water treatment and/or alternative technologies.
e) The potential disturbances caused to marine ecosystems and/or the seawater uses.

In addition, the Protocol lays down (Article 7) that the Contracting Parties shall progressively formulate and adopt, in cooperation with competent international organizations, common guidelines and, as appropriate, standards or criteria on specific requirements concerning the quantities of the substances listed in Annexes I and II discharged, their concentration in effluents and methods of discharging them.

The timetable of activities for the progressive implementation of the Protocol approved by the Fifth Ordinary Meeting of the Contracting Parties (Athens, September 1987) envisages that by 1995 common measures will be adopted for all substances listed in Annexes I and II to the Protocol.

The protocol for the prevention of pollution of the Mediterranean by dumping from ships and aircrafts includes in its Annex II para 1(i) zinc and copper. According to this Article the dumping of wastes and matter containing these metals requires "special care".

Annex III provides for the factors to be considered in establishing criteria governing the issue of permits for the dumping of matter containing zinc and copper at sea according to Article 7 of the protocol. These refer to the characteristics and the composition of the matter including its ecotoxicological properties, characteristics of the dumping site and method of disposal as well as potential effects on amenities, the marine life, various uses of the sea and the available alternative land-based methods of treatment, elimination, disposal etc.

6.2 National regulations

It was not possible to identify any systematic review of the existing national provisions at Mediterranean level governing the levels of zinc and copper in marine waters or permissible discharges to the sea. Several countries seem to have regulations at national regional or local level whereas the E.C. has also issued directives dealing indirectly with these two metals among many other parameters.

Croatia, France, Greece, Italy, the Libyan Arab Republic, Spain, Tunisia and Turkey seem to have pieces of legislation dealing with zinc and/or copper. It is most probable that other countries have similar provisions too but they were not available for this review.

More specifically:

(a) Croatia allows a maximum permissible concentration of 5.0 mg l^{-1} for zinc, and 0.1 mg l^{-1} for copper for water used or intended to be used as drinking water, and 0.01 mg l^{-1} for copper and 0.1 mg l^{-1} for zinc for fresh water used or intended to be used for aquaculture, watering of animals or public bathing area. Maximum permissible concentration for copper and zinc in coastal marine waters used or intended for use for mariculture and public bathing are 0.005 mg l^{-1} and 0.05 mg l^{-1}, respectively.

(b) Greece has issued in the late 70's and the beginning of 80's emission standards for liquid industrial effluents discharged into six of the most important semi-enclosed gulfs and bays of the country namely Saronikos, N. and S. Euvoikos, the Gulf of Geras, Patraikos-Korinthiakos, Pagassitikos and Thermaikos, as well as for industrial discharges received by the sewage networks.

The relevant number of the legislative act (usually a Common Prefectural Decision) and the corresponding values are given in the following Table 32. However, since the implementation of the E.C. directive (see section 6.3) in the late 80's this legislation has become rather inactive.

Table 32

Permitted effluent copper and zinc levels set in Greek legislation.

NAME	LEGISL. ACT	Cu (mg l^{-1})	Zn (mg l^{-1})
Saronikos	CPD 17823	1.5	1
N.S. Euvoikos	CPD 19640	1.5	7
Gulf of Geras (Lesvos)	Y 1052	0.1	0.5
Pagassitikos	CPD 119731	(30) ?	-
Patraikos and Korinthiakos	E2/11300	15	1
Thermaikos		30	-
Sewers (waste treat.)	CPC 1791	1	20
Directly discharged	82/656	0.2	0.5

The different order of magnitude of the standards probably reflects the degree of treatment considered as necessary to protect the various recipient waters.

(c) Italy has recommended limits for industrial and urban effluents of 1.0 mg l^{-1} of zinc discharged into public sewers, and 0.5 mg l^{-1} as zinc discharged into surface waters.

(d) The Libyan Arab Republic has proposed standards of 1.0 mg l^{-1} of zinc for effluents discharged into surface water reservoirs, for direct use in agriculture, discharged into aquifers used for public water supply and for effluents discharged into urban sewage systems.

(e) We have no information about the existing provisions in France, Spain, Tunisia and Turkey.

6.3 The E.C. and other provisions

The legislation introduced by the European Communities is particularly important for the management and environmental strategies of the Mediterranean because the E.C. regulations are binding for all its Member States and in fact this legislation prevails over the national ones in cases of discrepancies. Six of the signatories to the Barcelona Convection, (the EC and five countries: France, Greece, Italy, Spain and indirectly also Monaco) are bound by the relevant E.C. legislation:

a) The E.C. as a Contracting Party to the Barcelona Convention has signed and ratified in 1977 the Convention as well as the related protocols with Council decision 77/585/EEC of 25 July 1977 (OJ L 240/19 Sept. 77).

b) According to the Council framework Directive 76/464/EEC of 4.5.1976 (OJ L 129/18.5.76) concerning pollution from certain dangerous substances discharged into the Community marine environment, the Member States take the necessary measures to eliminate pollution due to substances appearing in List I (or Black List) of the Annex to the Directive and to reduce pollution due to substances appearing in List II (or Grey List) of the Annex which also includes zinc and copper.

c) Council Directive 79/923/EEC of 30.10.1979 (OJ L 281/10.11.79) concerning the required quality of shellfish waters aims at protecting and improving the quality of both the coastal waters and of brackish waters designated by the Member States as requiring protection or improvement for shellfish to live and grow in them.

   According to the Annex, monitoring is required at least every six months for both metals to be determined in the water and in the flesh of the shellfish, employing AAS. According to the Directive the concentrations should not exceed levels that affect the shellfish or their larvae. The possibility of synergistic effects of copper and zinc with the other metals listed (Ag, As, Cd, Cr, Hg, Ni and Pb) should be considered. No specific standards are set but the 100% of samples examined should fulfil the above mentioned provisions.

d) Council Directive 80/68/EEC of 17.12.1979 (OJ L 20/26.1.80), concerning the protection of underground waters from pollution by certain dangerous substances, lays down controls for the discharge of zinc and copper in the underground waters of the European Community. The Directive classifies zinc and copper in List II substances "the discharges of which should be reduced as much as possible" (Article 3b).

   Article 5.1 requires that for an underground discharge an impact assessment and a permit are necessary. Article 10 requires that detailed instructions, and the maximum acceptable discharge, is specified by the Authorities in every case.

e) Council Directives 80/778/EEC of 15.7.1980 (OJ L 229/30.8.80) on the quality of drinking water and 75/440/EEC of 16.6.1975 (OJ L 194/25.7.75) on the quality of surface waters destined for the production of drinking water in the Member States set both compulsory and target values for the concentrations of copper and zinc in:

- drinking water, with a "guide" value of 100 µg l^{-1} for each one of them, and

- surface waters used for the production of drinking water, where the compulsory and guide values respectively for the two metals are: for Cu: 0.05 mg l^{-1} and 0.02 mg l^{-1}, and for Zn: 3 mg l^{-1} and 0.5 mg l^{-1}.

The Ministerial meeting of the Oslo and Paris Commissions adopted PARCOM Recommendation 92/4 at their Paris meeting (21-22 September 1992) which deals with the reduction of emissions from the electroplating industry. It is recommended that treatment should be provided for the effluents from this industry so that the concentrations of the following metals do not exceed the following levels.

Metal	Concentration (mg l^{-1})
Chromium (total)	0.5
Chromium (VI)	0.1
Copper	0.5
Lead	0.5
Nickel	0.5
Silver	0.1
Tin	2.0
Zinc	0.5*

* only in justified cases a maximum zinc concentration of 2 mg l^{-1} may be allowed

At the same meeting the ministers adopted PARCOM Recommendation 92/3 concerning the limitation of pollution from new secondary steel production and rolling mills. It is recommended that waste water flow from pickling and plating should be reduced as far as possible. The maximum concentration of metals in effluent water in unfiltered samples should be:

Metal	Concentration (mg l^{-1})
Nickel	1
Chromium (total)	1
Chromium (VI)	0.1
Zinc	2
Cadmium	0.2

6.4 Scientific rationale for establishing control and restriction measures for copper and zinc

6.4.1 Environmental protection

In order to reduce the level of a pollutant in sea water to a concentration that is not harmful to marine organisms and ecosystems, it is necessary to limit the release of pollutants into the marine environment both in quantity per unit time discharged and as concentration of the pollutant in the liquid effluent or in sludges. This requires that the concentration in the marine environment (environmental quality criteria) must be below a concentration which will not cause significant harm (minimum risk concentration). From the review of the data presented in the previous chapters it became apparent that levels as low as 10 $\mu g\ l^{-1}$ for zinc and 5 $\mu g\ l^{-1}$ for copper could be harmful to sensitive marine organisms.

These values are close to the marine environmental standards proposed by the UK Water Research Centre (WRC) based on a more comprehensive and critical review of the literature which were 40 $\mu g\ l^{-1}$ for zinc and 5 $\mu g\ l^{-1}$ for copper, both as total metal and in the dissolved form. If a more stringent standard of 10 $\mu g\ l^{-1}$ is adopted for zinc, then both standards are close to the higher concentrations of these metals found in "unpolluted" Mediterranean waters of 3 $\mu g\ l^{-1}$ zinc and 0.2 $\mu g\ l^{-1}$ copper.

To some extent, this apparent small difference between natural and incipient harmful concentrations may be due to unadapted organisms being suddenly exposed to these higher concentrations in laboratory conditions; organisms living in higher concentrations of zinc and copper may develop some resistance and this acclimation may continue if the concentrations are raised a little further by anthropogenic inputs.

In the case of copper, a further complicating factor is that some of the soluble copper, particularly in inshore areas receiving organic inputs, will be in the form of less toxic organo-metal complexes. This factor will also reduce the toxicity of any ionic copper discharged to such areas. For these reasons, the UK WRC state that marine communities may be unaffected in areas where the proposed standard is exceeded because of a) adaptation of the organisms, and b) the formation of soluble cupro-organic complexes.

Assuming that effluents discharged to marine waters through jet diffusers obtain an immediate dilution of 100-fold, the concentration of zinc in such wastes should not exceed 1 $mg\ l^{-1}$ and for copper 0.5 $mg\ l^{-1}$. This report has shown that for wastes discharged from the metal industries, these standards can be obtained by existing treatment processes. Also, existing standards set for zinc and copper in effluents in some countries are close to these values.

In areas where a lesser dilution is obtained immediately after discharge (e.g. a high volume of waste being discharged to a semi-enclosed area), a mixing zone will be formed within which the environmental standard will be exceeded. Monitoring of the size of this zone can be carried out by chemical analysis of the water, by observing the status of the biological community, and by measuring trends of metal concentration in the biota, in transects away from the discharge point. However, because of all the variable factors mentioned in this Report, interpretation of such data may be difficult and this must be taken into account before surveys are carried out.

So far, only the dissolved forms of zinc and copper have been considered. Less attention has been given to the discharge of the metals incorporated into organic and inorganic particulate matter. While it is certain that some of this metal will subsequently become bioavailable, the extent to which this will occur in the water column and in different types of sediment is uncertain. It may be for these reasons that there are no international standards for the permitted concentrations of zinc and copper in solid wastes discharged to sea. Controls tend to be exercised in terms of total load of metal discharged to specific areas. Known local discharges of heavily contaminated solids should be examined in detail and in the context of all the relevant physical, chemical and biological features of the surrounding environment. If the discharge of such solid wastes to the Mediterranean area is perceived to be a general problem, then consideration will have to be given to the derivation of appropriate limiting concentrations for the metals and to the administrative procedures required for enforcement and control.

The control of these liquid and solid discharges will, as shown in earlier Chapters, only partially reduce the total anthropogenic load of copper and zinc entering the Mediterranean. However, it will reduce the extent of high concentrations found in polluted estuaries and coastal waters.

6.4.2 Human health protection

The enforcement of legal limits on the permissible concentrations of a substance in seafood in normally practised when seafood constitutes major source of human intake of such substance or, when this is not the case, such a limit is usually combined with complementary limits on the permissible concentrations of substance in other sources. Such limits are, for obvious reasons, intended to protect the general public, and are based on a combination of the toxicity of the substance (as expressed by a recognized acceptable intake value) and the amount consumed, with a built-in safety factor. Usually it is not designed to guarantee absence of any adverse health effects to individuals or population groups, who consume amounts significantly exceeding calculated average values although the use of an adequately high safety factor is expected to cover the majority of this cases. For rare local cases or habits of individuals of selected groups of high risk, separate measures have to be taken.

In the case of zinc and copper (a) the main source of human intake is not seafood, and (b) relatively high levels are found mainly in a few species of seafood, which are not normally consumed in gross amounts. Such relatively high levels are, more often than not, associated with the discharge of zinc and copper containing effluents in the vicinity. In this case, therefore, a limitation of the amount of the metals discharged into the marine environment will alleviate the general position, as long as the alternative means of disposal employed does not result directly or indirectly in a proportionate increase in the concentration of these metals in the mean intake.

No Mediterranean country is reported to have a legal limit for copper or zinc in seafood. Some countries may find it advisable, particularly in view of the observed trend towards an increasing fish consumption in the Mediterranean especially from intensive marine aquaculture, to impose some restrictions, particularly in the case of those species of seafood with relatively high copper and zinc concentrations, or high concentration potentials. However, such restrictions would be determined entirely by local circumstances and consider the relative intakes from other sources.

A scientific justification exists for imposing an upper limit on zinc and copper concentrations in those seafood species, the uncontrolled intake of which, (either alone or in combination with that from terrestrial sources), would present a general hazard to human health (particularly when control of exposure to non-seafood sources is not feasible). Such imposition would be more justifiable at national or local, rather than regional level. Even more important is that the intake of zinc and copper from seafood presents a sectorial rather than a general hazard, requiring regular zinc and copper monitoring of sites designated for fish and shellfish aquaculture in parallel with the protection of specific individuals and population groups. The main measures taken, therefore, would have to be by their very nature recommendatory rather than statutory.

In Chapter 2 the information on the release of copper and zinc from relevant industries as well as from effluents and sludges has been reviewed. It has also been reported that oysters and mussels polluted by copper (e.g. in Schereningen, Netherlands, where some heavily copper contaminated "green" oysters were produced) have found their way to the markets of Europe and the USA. The copper concentrations in the edible part of polluted oysters from Japan (Nebeoka) were found to be 320-687 mg kg^{-1} wet weight; unaffected oysters of the same region did not exceeded 40-99 mg kg^{-1}. We do not know, however, of any similar case of such polluted oysters being found in the Mediterranean, but a special short-term survey, to monitor commercial species as they reach the fishmarkets, could be very useful for Mediterranean consumers.

Special attention should be paid to the food habits of those communities and fishermen who obtain large amounts of their seafood from heavily contaminated areas. Limits on aquaculture and fishing activities in such polluted areas could be set until "safe" levels have been reached. In this regard, any action taken should be based on a calculation of copper and zinc intake from other sources, in order to ensure that any additional intake through seafood would not result in exceeding tolerable limits.

7. CONCLUDING RECOMMENDATIONS

7.1 Marine ecosystems

For the protection of marine life in the Mediterranean, it is proposed that

(a) the concentration of total dissolved zinc in sea water should not exceed 10 µg l^{-1},

(b) the concentration of total dissolved copper in sea water should not exceed 5 µg l^{-1}.

It is recognised that in waters with a high dissolved organic carbon content, copper may form less toxic cupro-organic complexes and in exceptional cases the proposed standard may be relaxed where this occurs.

It is also recognised that sensitive marine biota may not be harmed in areas where these proposed standards are slightly exceeded, if such organisms can become adapted to the higher concentrations. In the same way, the proposed standards may be relaxed in those areas where the natural or historic concentrations of zinc or copper already approach these values.

In order to achieve this water quality objective in the vicinity of pipeline discharges to coastal waters,

(a) an effluent concentration of 1.0 mg l^{-1} for total dissolved zinc and 0.5 mg l^{-1} for total dissolved copper would have to be set as limit values.

(b) the discharge of the outfall would have to be placed and its configuration adapted in such a way as to guarantee a minimum dilution of at least a hundred-fold in the mixing zone adjacent to the outfall.

(c) the effectiveness of the control measures should be checked by monitoring the concentration of the effluent; the limit values established in paragraph (a) should not be exceeded by the arithmetic mean of determinations obtained over a year with a monthly frequency. The monthly sample must be representative of the discharge during a 24 hour period.

Further consideration needs to be given to the discharge of zinc and copper as suspended particulates and in solid wastes, if there is a perceived need to reduce the total load of these metals discharged to the Mediterranean. It must be recognised that coastal pipeline discharges of these metals form only a small proportion of the total load entering the Mediterranean. If there is a need to reduce the offshore concentrations of zinc and copper, then stricter controls will need to be placed on discharges to freshwater and to the atmosphere from which the greater load arises. To some extent, the need for such controls will depend on a further critical examination of the actual concentrations of these metals in Mediterranean sea water and their physico-chemical state, and of the conditions of the experiments that demonstrated an apparent extreme sensitivity of certain marine organisms.

7.2 Human health

The overall criterion for the protection of human health from excessive copper and zinc intake should take all sources of intake of zinc and copper into account. Ideally, this problem should be tackled globally, with seafood as one of its components. In so far as seafood alone is concerned, however, the following measures would be necessary (in addition to the measures described in above) to contribute to an amelioration of the position by reducing the overall amount of zinc and copper in the marine environment:

(a) the monitoring of marketed species of seafood to determine their usual copper and zinc content;

(b) the identification of areas where the current concentrations of copper and zinc in edible species of seafood might pose a health problem, taking into account metal intake from other sources;

(c) the imposition of legal limits on the copper and zinc content of seafood in such areas (or any other restrictions considered appropriate under prevailing conditions) should the local situation so demand, including prohibition of aquaculture and fishing activities in such areas;

(d) the formulation and implementation of advisory and recommendatory measures to regulate the type and amount of seafood consumed by high-risk groups, if it is considered that such groups are not sufficiently protected by local measures of a general nature.

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