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ASSESSMENT OF THE STATE OF POLLUTION OF THE MEDITERRANEAN SEA BY CADMIUM AND CADMIUM COMPOUNDS

In co-operation with:

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BACKGROUND

The Protocol for the Proctection of the Mediterranean Sea against Pollution from Land-based Sources (LBS Protocol) was adopted by the Conference of Plenipotentiaries of the Coastal States of the Mediterranean Region on 17 May 1980, in Athens, Greece. The Protocol has so far been ratified by 13 Contracting Parties to the Barcelona Convention and has entered into force on 17 June 1983.

Article 5 of the LBS protocol stipulates that:

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

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

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

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

Article 7 of the same Protocol stipulates that:

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

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

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

At their Fourth Ordinary meeting (Genoa, 9-13 September 1985), the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution and its related Protocols agreed that, with regard to the technical implementation of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based Sources, the Secretariat would propose an order of priority and a realistic time-table for the development of programmes and measures for at least two substances annually, including common emission standards and standards of use, required for the implementation of the Protocol, and that in preparing such a proposal, substances listed in Annex I to the Protocol should be accorded priority (UNEP/IG.56/5, III, F, 3).

A meeting of experts on the technical implementation of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based Sources (Athens, 9-13 December 1985) approved a workplan and time-table for the progressive implementation of the protocol (UNEP/WG.125/10, Annex VII), which included an assessment of the state of pollution of the Mediterranean sea by cadmium and cadmium compounds and proposed measures, as well as guidelines for the elimination of pollution from land-based sources, in terms of Article 5, by substances listed in Annex I to the Protocol (UNEP/WG.125/10, Annex V). The guidelines which were adopted by the Contracting Parties include the preparation of an ''assessment document'' on which the measures proposed to the Contracting Parties should be based. Such assessment documents should include inter alia chapters on:

- sources, point of entries and amounts of pollution from 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 compliance with the above and in conformity with the guidelines established, the Secretariat prepared document UNEP/WG.160/9 which was submitted to the Fifth Meeting of the Working Group for Scientific and Technical Cooperation for MED POL (Athens, 6-10 April 1987). The Group discussed the document and decided that it should be revised to incorporate information on industries producing cadmium containing discharges and on treatment methodologies. The present document is a revision of document WG.160/9 and includes the required additional information. The Scientific and Technical Committee is expected to consider the concluding summary and the proposed measures for eventual submission to the next meeting of the Contracting Parties.

1. INTRODUCTION

The present document presents a picture of the state of pollution of the Mediterranean sea by cadmium and cadmium compounds, outlines a scientific rationale for establishing control measures, and recommends measures to be adopted by the Contracting Parties.

Chapter I, which deals with the assessement of the state of pollution, provides information on the inputs in the Mediterranean sea, and describes the nature and distribution of the sources of such inputs. It also reviews the available data on levels in the various compartments of the marine environment (sea water, sediments, biota, etc.), with the emphasis on levels recorded in marine organisms. The chapter also provides information on the effects of cadmium on marine organisms and communities, as well as man.

Chapter II includes available information on existing national and international control measures for the prevention of pollution by cadmium. It also outlines the scientific rationale for the establishment of environmental quality criteria, and other control measures, including emission standards. As a consequence, certain measures are recommended to the Contracting Parties for adoption.

I. ASSESSMENT

2. GENERAL FACTS ON CADMIUM AND CADMIUM COMPOUNDS RELEVANT TO THE MARINE ENVIRONMENT AND HUMAN HEALTH

Cadmium, atomic weight 112.40, belongs to subgroup IIb of the Periodic Table together with zinc and mercury. Cadmium is a rare element and seldom occurs in pure minerals. In nature, it is usually associated with zinc. The cadmium salts of strong acids are easily soluble in water. At low pH cadmium compounds are more soluble than under basic conditions. CdO, $CdCO_3$, $Cd(OH)_2$, and CdS are relatively insoluble, while CdF_2, $CdCl_2$, $CdBr_2$, CdI_2, $Cd(NO_3)_2$ and $CdSO_4$ are relatively soluble; so are cadmium cyanides and cadmium amines. Cadmium forms complexes with halogens and ammonium hydroxide. In nature, the predominate oxidation state of cadmium is Cd^{++}. Cadmium released to the atmosphere is rapidly oxidized to CdO and removed by precipitation or direct dry fallout. In soils, cadmium is not very mobile. It is leached from soils into ground water and rivers. Industrial sources are zinc mining operations and cadmium plating. Municipal wastes can contain significant amounts of cadmium (sewage sludge and fallout from incinerators). In freshwater, cadmium is predominantly associated with colloidal and particulate matter and according to thermodynamic calculations the soluble species of cadmium are mainly free Cd^{++} ions together with small amounts of $CdCl_2$ and $CdSO_4$. Reaching seawater environments, cadmium is partially desorbed from particles and replaced by chelating substances. In the sea, thermodynamic calculations predict that 66% of the soluble cadmium is present as free Cd^{++}, 26% as $CdCO_3$, 5% as $Cd(OH)_2$, 1% as $CdCl_2$ and 1% as $CdSO_4$ (Whitefield et al., 1981). Anodic stripping voltammetry shows likewise that the electroactive species predominate. However, in coastal waters 15 - 20 % and in estuarian waters up to 85 % of the cadmium present is associated with particulate matter and is present as complexes (Phillips, 1980).

Cadmium has no known biological function and in marine biota it should be associated with natural complexes, metallothionein or other metal-binding proteins which are induced by the exposure to cadmium or already present in the marine organisms. Contrary to the reasonably well understood role of cadmium metallothionein in terrestrial mammals regarding toxic effects, the formation and role of the various cadmium binding proteins described in non-mammalian organisms is still largely unknown and may be quite different from that of the mammalian metallothionein (Petering and Fowler, 1986).

3. SOURCES AND INPUTS INTO THE MEDITERRANEAN

No systematic survey of cadmium sources has been carried out in the Mediterranean. Data on natural and anthropogenic sources have come to light only when higher than average cadmium concentrations were observed in sediments and biota.

General data cannot be divided into natural and anthropogenic sources. For example, Arnold et al. (1983) estimate the atmospheric fallout of cadmium to about 140 metric tons(MT) $year^{-1}$ per million km^2. This value refers both to natural and anthropogenic cadmium. The fact that cadmium together with copper, lead and zinc are contained in the smallest particles of the aerosol, suggests that they were injected at high temperatures into the atmosphere where they, in the processes of volatilisation and condensation, form very small particles.

An example of how a city can influence the fallout of heavy metals is illustrated in Naples. Palumbo and Iannibelli (1985) determined the fallout of cadmium in the surroundings of Naples and found near Capri, Ischia and Sorrento levels of 10 to 50 ng m^{-2} in a period of 30 days, but near the city of Naples the levels were more elevated: from 130 to 390 ng m^{-2} also in a 30-day period. Surveys around other cities will reveal a similar pattern.

Rivers too, carry cadmium both from natural and anthropogenic sources. Sedimentation processes will deposit heavy metals such as cadmium, along with terrigenous and biogenic material on the sea bottom. These sedimentation processes are very important in river deltas but also in areas receiving domestic sewage as well as industrial effluents and solid wastes.

French rivers in the Rhone basin had water concentrations ranging from 1 ug to 7 ug Cd l^{-1} (Agence du Bassin du Rhône, 1983). Sediment concentrations in the French rivers Tet, Agly, Aude, Orb and Herault also show considerable cadmium levels ranging from 1.9 to 4.1 ug l^{el} (Buscail et al., 1985). The cadmium concentrations in major Italian rivers cover a very narrow range from 0.03 to 0.08 ug Cd l^{-1}, the only exception being the heavily contaminated river Entella where 1.8 ug Cd l^{-1} was found (Brondi et al., 1986).

El-Rayis and Saad (1985) studied the cadmium concentrations in the Nile waters. In the surface water of 10 stations the authors found 0.39 ug (0.13-0.66) dissolved Cd l^{-1} and in the bottom water 0.42 (0.16-0.58) dissolved Cd l^{-1}. The overall average was 0.4 ug dissolved Cd l^{-1}. Assuming a discharge of 3.5 billion m^3 $year^{-1}$ the authors estimated that the Nile would introduce 4.6 tons $year^{-1}$.

Work done by Chesselet et al. (1979) and Buat-Menard et al. (1980) has indicated that heavy metal concentrations in suspended particulates in the open Mediterranean waters could not just be the result of riverine transport of elements solubilized by crystal weathering and particles of planktonic composition. These authors indicated atmospheric inputs as a significant source.

Exchange with the Atlantic ocean may have a certain importance. Statham et al. (1985) found a pronounced negative anomaly in the concentration of dissolved cadmium, associated with the presence of nutrient depleted Mediterranean water (section 4.2). They also found that the profile in the top layer of the Alboran Sea has a higher cadmium/phosphate ratio than that which is characteristic of the deeper profile and the Atlantic. The authors suggest that this is evidence for an input of cadmium to the surface waters of the Mediterranean. On the basis of their data Statham et al. (1985) estimate a net export of 2.6×10^{-6} mol Cd $year^{-1}$ into the Atlantic, which is almost identical with the value estimated by Spivack et al. (1983).

3.1 Natural sources

Cadmium is one of the rare elements in the earth's crust. The average concentration is about 0.1 mg Cd kg^{-1}. It is widely distributed and is found in shale and igneous rocks, coal, sandstones, limestone, lake and marine sediments, soils, etc.. Typical concentrations in various matrices are shown in Table I (GESAMP, 1984).

Table I

Cadmium concentrations (mg kg^{-1}) in various environmental matrixes (GESAMP, 1984)

Matrix	mean	range
igneous rocks	0.15	0.001 - 1.8
metamorphic rocks		0.04 - 1
sedimentary rocks		0.3 - 11
shales		up to 90
marine clays	0.4	
marine phosphorites		60 - 340
agricultural soil, unpolluted	<1	

Geologic weathering and erosion of the earth's crust release and transport cadmium like other trace metals into the marine environment mainly through rivers and surface runoff. Other natural sources include deep sea volcanism and the atmosphere.

Due to weathering, cadmium may be enriched by 2 to 3 times in sediments. Phosphates contain on the average 15 mg kg^{-1}. Localized and naturally high cadmium concentrations can be found near deposits of sulfide ores such as shalerite, phosphorite, hydrothermally-mineralized rocks and some black shale deposits such as in the U.K. and in California. In similar deposits in the Mediterranean, higher than average cadmium concentrations may also be found. A few very rare cadmium minerals are known, such as Greenockite (CdS), cadmoseite (CdSe), monteponite (CdO), and otavite ($CdCO_3$), but concentrations of commercial interest are found in the sulphide deposits of zinc, lead and copper. In all these deposits cadmium is present as a minor part of the zinc fraction. In general, the Zn/Cd ratio will be 200 to 1 (Stoeppler, 1984).

Natural sources are therefore regions with higher than average zinc, lead or copper concentrations e.g. near mining sites of these metals (Figure 1). Higher than average cadmium concentrations in sediments and biota can be expected in these areas and consequently in the rivers draining them and possibly also in the marine environment adjacent to them. An example is reported for the coastal Lagoon of Mar Menor (Portman) in Spain which is influenced by a lead-zinc mine. De Leon et al. (1985) report cadmium concentrations near the shore of about 9 mg Cd kg^{-1} DW. We can compare this to the cadmium levels from stations in other transects along the coast from Valencia to Cartagena which reach levels of 0.6 mg Cd kg^{-1} DW.

3.2 Anthropogenic sources

The main anthropogenic sources relate to ore mines, metallurgical industries and to the disposal of sewage sludges. Cadmium is also found in sewage (domestic and mixed) in high proportions relative to other trace metals but the reason for this irregularity is not clear. Table II shows the concentration of cadmium in sewage from some Mediterranean cities. The same table indicates the inputs of cadmium into the EEC environment as estimated by Hutton (1982).

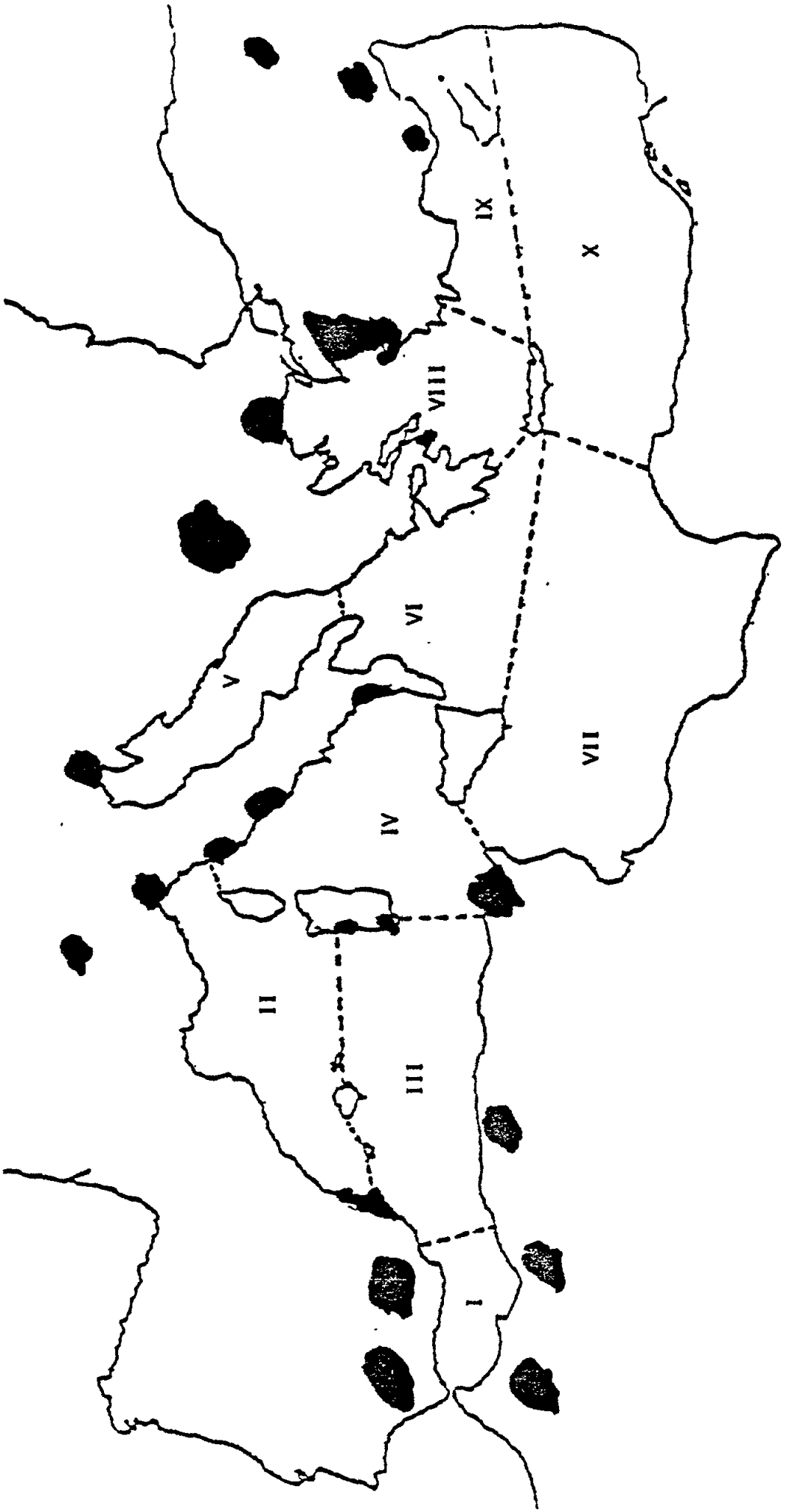

Figure 1. Mediterranean map showing mining areas of zinc, copper and lead and the MED POL regions.

Cadmium is a scarce and fairly expensive metal of low mechanical strength. Its yearly world production is about 18,000 tons. Mediterranean countries account for about 10% of this. Table III indicates the trend in the main uses of cadmium in percentages.

Table II

Summary of cadmium inputs (metric tons $year^{-1}$) to the environment of the European Economic Community from various activities (Hutton, 1982)

	air	land	water
Volcanic action	20	ND	ND
Non-ferrous metal production			
Zn + Cd	20	200	50
Cu	6	15	ND
Pb	7	40	20
Production of cadmium containing materials	3	90	108
Iron and steel production	34	349	ND
Fuel combustion			
coal and lignite	8	390	ND
oil and gas	0.5	14.5	-
Waste disposal	31	1434	ND
Sewage sludge disposal	2	130	33
Phosphate fertilizers	-	346	62
Total (estimate)	132	3009	273

ND: non detected

Cadmium concentrations (ug l^{-1}) in the sewage of some Mediterranean cities:

City	mean	range
Iskenderun	5	0.5 - 8
Mersin	2	ND - 24
Antalya		0.1 - 0.3
Marmaris	0.3	ND - 0.9
Valetta	0.25	

Table III

World trend in main uses of cadmium (Cadmium Association and Swedish Environment Protection Board, 1987)

Use	1965	1970	1977	1984
Electroplating	47	37	34	25
Pigments	25	25	25	22
Stabilizers	9	19	15	17
Batteries	7	8	15	27
Alloys	8	7	8	7
Others	4	4	3	2

Almost all cadmium is obtained as a by-product of zinc, copper and lead ore processing and refining. Therefore, industrial cadmium sources include the mining of cadmium-containing ore, primary metal production of cadmium, zinc, copper and lead, secondary metal production, iron and steel production and use of cadmium in industrial processes.

Potential sources of cadmium containing waste water are among others, the industries for metallurgical alloying, electroplating, manufacture of pigments and mine drainage.

All these processes resulting in cadmium containing discharges are described briefly here below.

Mining

Most sulphide ores are mined using underground mining methods. The ore is first broken, crushed and treated with water and reagents. The concentration process which follows involves flotation and gravity mechanisms. Water from the benefication processes are generally treated by line precipitation or by sedimentation basins. New and old mine tailings and wastes leach cadmium into the environment. The leaching rate is related to the acidity of the soil. Contamination is a long-lasting process that can probably go on for thousands of years if nothing is done. Oxidation leaching and metal leaching process from mine tailings are well known (Södermark, 1983). Future leaching can theoretically decrease by 90% if old depots are properly covered, sealed and screened off from air and water. An estimated cost would be ca. 15 ECU m^{-2}. Table IV indicates ore production figures for Cu, Zn and Pb in Mediterranean countries.

Primary metal production

When producing zinc, copper and lead, cadmium is obtained in the flue dusts in the exhaust system by the roasting process. Primary metal production involves the following processes; roasting (ca. 1,200°C), sintering and smelting. As the production mainly consists of thermal processes, cadmium emissions are to a large extent airborne.

Cadmium refining

The refining of cadmium collected from the flue gases in the exhaust system begins with a sulphuric acid leach plus the addition of an oxidizing agent. The cadmium is then distilled it the conventional horizontal retort (910°C) and condensed as metallic cadmium. Processes used for cadmium production are both pyro- and hydrometallurgical. Besides the commercial electrolytic cadmium, an impure blister cadmium of varying quality is produced. Refining is performed by distillation in vacuum at a temperature of 480°C. The completed product is in the shape of stalks, plates or pellets. The main producers of cadmium are USSR, Japan, USA, Canada, Germany and Belgium.

Secondary metal and non-ferrous metal production

Secondary metal production (based on scrap) involves the use of recovered cadmium containing materials.

Recovered cadmium is obtained by a pyrometallurgic purifying process and can consist of recovered Ni-Cd batteries and anodal residuals from electroplating scrap.

In copper production a primary feed is scrap (especially recycled automobile radiators) which may contain cadmium.

Iron and steel production

Cadmium from iron and steel production mainly comes from recycled cadmium containing scrap. Steelmaking by the electric arc steelmaking process (EAS) emits larger amounts of cadmium to air compared to the basic oxygen steelmaking (BOS) due to a higher scrap charge loading in the primer process.

The cadmium content of iron ore may differ substantially depending on the origin. Iron ore from the Lorraine region is reported to contain 10 ug g^{-1} while that used in the U.K., 0.4 ug g^{-1} (Hutton, 1982).

Cadmium emissions from iron and steelmaking are to a large extent airborne discharged in form of solid waste. By inadequate waste disposal, cadmium can be leached causing environmental contamination.

Electroplating

Cadmium is used in the protection of steels, iron, copper, brass and other alloys from corrosion.

Electroplating is mostly done in alkaline cyanide baths. The piece to be plated serves as the cathode and cadmium metal as the anode. In the electroplating industry cadmium can be efficiently substituted by zinc-coating (galvanizing), sometimes together with chrome- and nickel-plating. Cadmium is superior to other substitutes for certain environments e.g. in marine environments, in places where water is condensed, in the presence of alkalis, ammonia, acetic acid or steaming formalin.

Table IV

Ore production of zinc, lead and copper in Mediterranean countries (in thousand tonnes). Source: Samin

Country	Zn		Pb		Cu	
	1975	1984	1975	1984	1975	1984
Albania	-	-	-	-	9.8	15.0
Algeria	11.3	14.6	3.2	3.6	0.4	0.2
Cyprus	-	-	-	-	9.9	1.3
France	13.9	36.4	21.7	2.3	0.1	0.2
Greece	14.4	22.6	14.5	22.2	2.5	-
Italy	77.8	42.3	29.5	21.5	0.8	0.9
Morocco	18.8	11.9	69.9	100.6	-	21.8
Spain	84.2	228.0	57.5	95.6	51.6	63.5
Tunisia	6.0	6.7	10.8	4.1	-	-
Turkey	25.6	50.7	6.5	14.6	27.3	27.1
Yugoslavia	103.4	85.8	126.9	113.6	114.9	137.6
Total	355.4	499.0	340.5	378.1	217.3	267.6
Change %	+ 40.4%		+ 11.1%		+ 23.1%	

Of the cadmium purchased for electroplating/metal finishing purposes, only 90% is translocated to the products while 10% is lost in the plating process. High concentrations of cadmium have been reported in plating wastes. Cadmium can be removed from waste waters in the electroplating industry through various types of ion exchange and absorbing resins. Discharges from electroplating industries are either used for scrap steel or disposed in landfills.

Pigments

Cadmium pigments include pure cadmium sulphide, cadmium selenides and mixtures with other metals (e.g. Zn, Hg). Sulphides produce yellow colours and selenides maroon. Mixtures produce the entire scale from yellow, orange, red to maroon. Cadmium pigments are appreciated because of their brilliant colour tone, heat stability (up to 600°C) and good light, weather and alkali resistance.

Approximately 80% of all cadmium pigments are used within the plastic industry. Glass and ceramic glazers use about 10% and the remaining consists of artist's colours, enamels, printing ink etc.

When producing yellow pigments (cadmium sulphide/zinc sulphide) cadmium metal is taken into solution with a mineral acid, and a zinc salt added in quantity dependent on the final pigment shade required. The cadmium is then precipitated as cadmium sulphide, or as a cadmium zinc mixed sulphide, using sodium sulphide solution. In an alternative process, cadmium and zinc are precipitated from solution as the carbonate, which is then reacted with sodium sulphide solution to precipitate the required sulphide pigment; this process relies on the lower solubility product of the sulphide relative to the carbonate to produce a finer grained precipitate. Other colours are made in a similar way. An old process includes heating cadmium oxide with sulphur and calcination of the solid pigments (OECD, 1975).

The main use of cadmium pigment within the plastic industry, is for the production of high-volume plastics (polyethylene, polypropylene, polystyrene, ABS and PVC). In most cases it is possible to replace the cadmium without any deterioration. Approximately 15% of the cadmium pigment is used for engineering plastics (polyamide). These are more difficult to substitute due to higher processing temperature. Cadmium pigments are normally present in concentrations between 0.1 to 1.0% of the weight of the base polymer.

Stabilizers

Cadmium stabilizers are used to protect synthetic materials - almost exclusively polyvinylchloride (PVC) - from decomposing. It is used both in rigid and flexible PVC.

The production of stabilizers take place in a closed system. Cadmium oxide or hydroxide is dissolved in acid (e.g. stearic or lauric acid) and water from the reaction is removed.

Stabilizers can be in a liquid or in a solid form. The cadmium content of a finished PVC article is about 0.05% when liquid stabilizers are used, and 0.2% when solid stabilizers are used (Ernst, 1982).

Cadmium in stabilizers can, to a certain extent, be replaced by zinc, lead or tin. For certain flexible PVC products for outdoor use (PVC film; plastic windows in sails and boat covers) it has not yet been possible to replace cadmium completely without a substantial deterioration in quality. Other examples of products formed in rigid PVC are: plates, pipes, phonograph records and fittings. Flexible indoor products are: electrical cables, tubing, hoses, flooring, woodwork films and car upholstery.

Cadmium discharges from these products are not so large when they are produced; the problem occurs when these products are ultimately disposed of.

Nickel - cadmium batteries

The manufactures of Ni-Cd batteries are the largest industrial users of cadmium. Ni-Cd batteries use nickel oxide as cathode, cadmium as anode, and caustic potash as electrolyte.

There are two types of Ni-Cd batteries; pocket-plate cells and sealed cells (sintered plate). The cadmium amount in an average Ni-Cd accumulator (with pocket plate cells) is appr. 5%. Open Ni-Cd batteries are mainly used industrially and can be recycled. Cadmium in Ni-Cd batteries can be recovered either by dissolution in sulphuric acid followed by separation of the nickel and cadmium on the basis of their formation of amine complexes, or by melting the batteries with a reducing agent and distilling off the cadmium (OECD, 1975). Enclosed Ni-Cd batteries are used in photographic equipment, mini-computers, radio equipment etc.

Alloys

Cadmium in conjunction with other metals (nickel, copper, silver, zinc) has an improved mechanical and the resistance, and is thus used for bearing and blazing alloys. This application is important for aviation, defence and electronic equipment. Copper and cadmium produces a high temperature alloy which is sometimes used in automobile radiators (appr. 0.2% Cd).

Metals such as bismuth, lead and tin in combination with cadmium produce a low melting point alloy with application as safety plugs and fire alarms.

Cadmium-zinc alloys are used particularly for soldering aluminium.

In some crucial aviation and defence equipment cadmium substitution is yet difficult without loss of quality.

The manufacture of alloys is a source of cadmium discharge; recycling of the used products may also constitute a problem.

Miscellaneous

Cadmium is also used in the following industrial various processes:

- rubber industry uses cadmium oxide as an activator in the curing of rubber
- petroleum industry produces motor oils which contain cadmium
- chemical industry uses cadmium in production of golf course fungicides
- nuclear reactors have cadmium in the control rods.

Cadmium is also discharged in the manufacture of the following products: photocells, weston-cells, antiseptic material, insecticides, photographic films, flashlights (with magnesium), ceramics, television tubes, clock faces, fluorescent X-ray screens and washing detergents produced from raw phosphate.

Fertilizers

Cadmium in phosphate fertilizers come from the raw material, raw phosphate and apatite. The cadmium concentration in raw phosphate rock varies (5-300 ppm) depending on the origin.

The dispersion of cadmium in the terrestrial environment and subsequently into receiving waters via industrial fertilizers has proved to be considerable. Table V shows the contribution into farmland from different sources in Sweden.

Table V

Cadmium brought into farmland from different sources in Sweden.
(Swedish Environment Protection Board, 1987)

Source	Cadmium, kg/year	percent
Phosphate fertilizers	5.000	48
Stable fertilizers	800	8
Sewage sludge	500	5
Lime	100	1
Atmospheric fall out	4.000	38

The original method for making phosphoric acid is to treat phosphate rock with sulfuric acid, thereby precipitating calcium sulphate and releasing phosphoric acid. Nitrophosphates are produced by nitric acidulation of phosphate rock to produce a solution which could be ammoniated. In many instances phosphate rock must be pretreated in some way before it is used for phosphoric acid manufacture, in order to remove some of the impurities. Techniques vary depending on the type of rock, and can include washing, screening, flotation and calcination.

Figure 2 shows a schematic phosphatic fertilizer production.

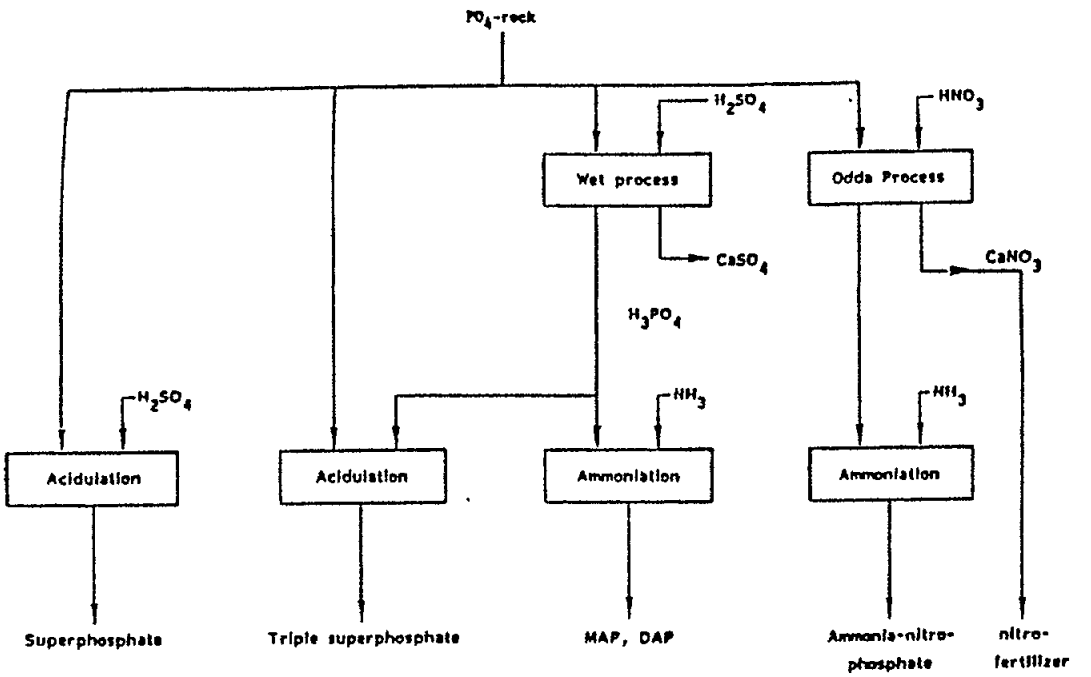

Figure 2. Schematic figure of phosphatic fertilizer production (From Deroutte and Porta, 1982). MAP = monoammonium phosphate, DAP = diammonium phosphate.

Fertilizer manufacturers can decrease the cadmium concentration in their product by choosing raw phosphate with low cadmium content.

Research for the improvement of the basic process used has led to various fertilizer manufacturing ways. Due to the process used, cadmium may be removed in different stages of the process. A Swedish company (SUPRA) has reached promising results from a pilot test plant, using the liquid-liquid extraction technique (see page 16) to remove cadmium from phosphoric acid. This control technique would only be feasible for nitrogen-phosphorus and nitrogen-phosphorus-potassium fertilizers.

Cadmium releases from the production of fertilizers are dependent on the process. Generally emissions to water are lower in the dry process alternatives. The major part of the cadmium from the phosphate mineral is expected to be in the final product ie the fertilizer also nitrogen-phosphorus and nitrogen-phosphorus-potassium.

Cadmium content in gypsum is appr. 5-10%. The major disposal route of the gypsum is dumping in coastal waters. Some is, however, recovered and utilized by the construction companies (Hutton, 1982).

3.3 Treatment technologies for cadmium containing waste water

The technology for the removal of cadmium from industrial waste waters is well established. The following factors are important chosing the method to be used: (a) concentration of cadmium in solution, (b) the presence of other heavy metals (c) the fact whether cadmium will be reused.

The principal technologies currently available are all based on physico-chemical methods such as:

Ion exchange;

Reverse osmosis, dialysis and electrodialysis;

Adsorption on activated carbon or other adsorbing materials;

Evaporation;

Electrolytic methods;

Miscellaneous methods such as freezing, ion flotation, liquid-liquid extraction and ultrafiltration.

Precipitation

Precipitation is a conventional water pollution control practice. Due to pH conditions these methods mainly apply to waste water treatment.

Precipitation of cadmium with sodium carbonate (soda ash) will give good levels of removal in a pH range of 9.5 to 10. Sulphide treatment particularly applies when cadmium is complexed with such agents as ammonia. Particulate matter carried in solution can be solubilized in dilute acid and then treated by one of these methods, or removed in settling ponds or thickeners and treated as a solids disposal problem.

Ion exchange resins

Ion exchange is an effective means of removing heavy metals from industrial streams. There are a variety of resins for specific applications with different metals. A number of resins which selectively remove cadmium ions from solutions containing a wide variety of other ions are reported in the literature.

Cadmium is quite frequently removed from waste waters from the electroplating industry by different types of ion exchange and adsorbing resins.

Recovering of cadmium from tailings using strongly acid cation resins has also been reported (Deroutte and Porta, 1982).

For ion exchange resins suitable for selective removal of cadmium compounds from photographic waste with low cadmium content (about 4 ppm) an adsorption efficiency between 85 and 97 percent has been reported (Deroutte and Porta, 1982).

Reverse osmosis and electrodialysis

Reverse osmosis is a treatment system utilizing semi-permeable membranes to produce a clear permeate and a concentrate containing the metal to be recovered. The concentrate which can retain all the residual metallic impurities can be further handled for disposal. The system operates at pressures up to 600 psi and has been utilized effectively in the plating industry.

Ion flotation

Ion flotation is one of the separation techniques which has been the object of research and development. It involves the combining of a surface-active reagent (collector) with a metallic ion to form a surface-active product. By bubbling an inert gas (usually air) through the solution using of a fine gas distributor, a larger air-solution interface is produced (Deroutte and Porta, 1982).

Adsorption on activated carbon

The use of activated carbon for the removal of cadmium ions from solutions has been referred to by a number of workers. Data published in the literature show adsorption capacities onto activated carbon in the order of 5 to 10 mg Cd g^{-1} of activated carbon for residual concentrations around 1 ppm, in the case of basic solutions, when using some of the best commercially available activated carbons (Deroutte and Porta, 1982).

Electrodeposition

Electrolytic metal removal from acid solutions has been practiced for several years mainly in copper processing plants. The conventional electrodeposition processes are quite ineffective for solutions characterized by low concentrations of the metallic ion to be removed.

Most electrochemical processes are limited by mass transfer rates and in recent years efforts have been made to develop reactors with greater mass transfer capabilities, for example the fluidized bed, the packed bed and other three-dimensional particulate reactors. Nevertheless, it seems that electro-recovery of metal impurities by three dimensional electrodes is technically attractive only in the concentration range of a few g l^{-1} down to some fifty ppm (Deroutte and Porta, 1982).

The development of a carbon fibre-based reactor by U.S.A. Reactors Limited in Canada using high surface area electrodes in the particular case of cyanide wastes from electroplating (EPA, 1981) appears successful. It has been found that the process can electro-oxidise and destroy cyanides and metal cyanide complexes more effectively than the existing standard alkali-chlorination process. Free cyanides and cyanide complexes of zinc, copper and cadmium can be completely destroyed, such that after treatment, cyanide can not be detected in the effluent. The heavy metals, including cadmium complexes, of various chelating agents can be electro-reduced, and cadmium is recovered in the cathode without involving the problems of sludge handling,

dewatering and disposal. The USA System recovers 99.6 percent of the cadmium dragged out of the plating bath (12 g Cd l^{-1}). The contribution of cadmium to the plant's final effluent from this source is 0.03 ppm (Yost, 1979).

Solvent extraction

Solvent or liquid-liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other one an organic solvent.

In certain cases the solute can be more or less completely transferred into the organic phase. An extractant is needed (Deroutte and Porta, 1982). This technique may be available for purifying phosphoric acid from cadmium.

Table VI indicates the results obtained using different methods of treatment of wastes containing cadmium, US EPA (1981).

Table VI

Summary of results obtained using different methods of cadmium removal from waste water (Source: US EPA, 1981)

Treatment process	Range of Removal %	Range of effluent conc. ug l^{-1}
Activated carbon adsorption		
- granular	76 - 95	<1.5-<40
- powdered	NM	<1.5-<10
Chemical oxidation		
- ozone	NM	<2 -250
Chemical precipitation with sedimentation		
- lime	0 ->99	ND - 80
- alum	38 - 88	12 - 47
- polymer/unspecified	0 - 99	5 -100
- $FeCl_3$	NM	<2
- sodium carbonate	67 ->99	<1 -<5
- sodium hydroxide	22 ->99	ND -930
- combined precipitants	11 ->99	ND -<80
Chemical precipitation with filtration	0 ->99	ND - 19
Chemical reduction	NM	BDL- <2
Coagulation and flocculation	99	BDL-<10
Filtration	0 ->99	ND - 97
Flotation	0 - 99*	BDL->72
Oil separation	>98	BDL-200
Reverse osmosis	0 - 60	<0.5-48
Sedimentation	0 ->99	BDL-200
Ultrafiltration	67 - 93	BDL-200
Activated sludge	0 - 99	BDL- 13
Lagoons		
- aerated		2

BDL= below detection limit; ND= not detected; NM= not meaningful.

4. LEVELS IN THE MEDITERRANEAN

4.1 Data quality and intercalibration

One of the major problems encountered in the determination of cadmium levels in air, sea water, sediment and biota is the uncertainty in the accuracy and precision of chemical measurements (quality control). Recognizing that insufficient analytical quality control may jeopardize the success of the MED POL projects, FAO/UNEP accepted the recommendation of the 1975 Expert Consultation to sponsor an analytical quality control programme (MED POL XI "Intercalibration of analytical techniques and common maintenance service") in collaboration with the IAEA's International Laboratory for Marine Radioactivity at Monaco (FAO/UNEP, 1975). This project prepared and distributed sediment samples and samples prepared from various marine organisms for intercalibration exercises (e.g. Fukai et al., 1978; IAEA, 1978; IAEA, 1985). Unfortunately there are no intercalibration standards which could be used for cadmium analysis at the low levels found in sea water, rainwater and air. This is regrettable since, due to the extremely low cadmium concentrations in sea water, rainwater and air, the uncertainty of the data available is very high.

Intercalibration has two important aspects: participation increases the confidence in the analytical data published and it also improves the analytical technique used, since very often errors in the analytical procedures can only be detected through participation in an intercalibration or a comparison with a certified standard. Topping (1983) describes the experience gained during several intercalibration exercises in the framework of the ICES monitoring programmes. The distribution of standard metal solutions revealed that some analysts used wrong working standards. Adjusting for these differences in standards, reduced the range of submitted means of the intercalibration samples. Comparing the range of means submitted by laboratories which had participated in the first three exercises showed a interlaboratory coefficient of variation (CV) of around 40% at a grand mean of 15.1 umol kg^{-1} DW. However, lower levels of cadmium in the third and fourth intercalibration increased the CV to 75 and 87%. The International Laboratory of Marine Radioactivity (Monaco) distributed four biological intercalibration samples in the framework of the MED POL programme. The CV in the different matrices ranged from 15 to 50% (Fukai et al., 1978; IAEA, 1978; IAEA, 1980). Intercalibration of a mussel homogenate showed that the means of 38 laboratories, some Mediterranean, ranged from 0.260 to 6.225 ug g^{-1} (IAEA, 1985). After excluding the outliers from a statistical point of view a mean of 1.32 ug g^{-1} DW was accepted as the value of the sample.

The results from these intercomparisons show that the data from different authors are not easily comparable since differences in the cadmium concentrations reported may be significant. The uncertainty increases with decreasing cadmium concentrations. This means that the uncertainty of the sea water concentrations, which are in the ng l^{-1} range, is much greater than that of the much higher levels (ug kg^{-1}) in sediments and biota. Nevertheless, large errors can also be committed by experienced laboratories on biological samples (Topping, 1983).

New analytical techniques with increasing sensitivity and specificity make it possible to measure trace elements in very low concentrations. Examining for example the sea water values one gets the impression that the older data are much higher (section 4.2). A greater awareness of the analytical limitations of certain methods and of sample contamination risks 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 older ones and that the lower trace element levels are necessarily the more accurate.

Unfortunately, despite the availabilty of the UNEP/IAEA intercalibration service and of the reference standards from other agencies, not all laboratories use these facilities. In reporting their data the authors must state their intercalibration results or give at least the identification number of the UNEP/IAEA exercise.

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

4.2 Air

Some data on cadmium in air from the Mediterranean are available. Over the sea the cadmium levels in air are much lower than over cities such as Marseille and Monaco (Table VII). Mean atmospheric concentrations over the Western Mediterranean are given as 0.45 ng Cd m^{-3} by Arnold *et al.* (1983) from data of the Etna 1980 cruise but those summarised by GESAMP (1989) for various cruises and two monitoring sites in Corsica range from 0.86 to 1.9 ng m^{-3}.

Over the sea, concentrations in non-Mediterranean areas ranged from 0.003 to 0.62 ng m^{-3}, with the most typical concentrations in the range of 0.01 to 0.2 ng m^{-3} (GESAMP, 1985).

Total atmospheric deposition for the Western Mediterranean is given by Arnold *et al.* (1983) as 140 MT $year^{-1}$ for one million km^2. GESAMP (1985) estimates total deposition to be 10-50 ng Cd cm^{-2} $year^{-1}$; for the North Atlantic 5 ng Cd cm^{-2} $year^{-1}$, for the Baltic Sea 13-20 ng Cd cm^{-2} $year^{-1}$ and for the North Sea 20-85 ng Cd cm^{-2} $year^{-1}$. A more recent estimate made by GESAMP (1989) for the deposition rate of Cd over the Western Mediterranean gives the value of 100 ng/cm^2/yr and the total deposition of Cd over the northwestern Mediterranean basin ($5x10^5$ km^2) was estimated as 500 t/yr which amounts to 19% of the total European cadmium emissions estimated by Pacyna *et al.* (1984).

GESAMP (1985) does not give any estimates for cadmium in precipitations in the Mediterranean basin. For the North Sea and the Baltic Sea the estimates range from 0.3 to 1.2 ug Cd l^{-1}. At Bermuda 0.006 ug Cd l^{-1} were determined and at Enewetak 0.004 ug Cd l^{-1}.

Very high concentrations were found on Mt. Etna (Buat-Menard and Arnold, 1978): about 90 ng Cd m^{-3} in the volcanic plume and 30,000 ng Cd m^{-3} above hot vents.

Table VII

Atmospheric concentrations of cadmium (ng m^{-3}) over the Mediterranean (GESAMP, 1985).

Region		n	mean	range	Reference
Tyrrhenian Sea	1979	9	0.4	0.07 - 1.6	Chester et al., 1984
Centr. + Tyrrh.	1980	19	2.1	0.2 - 6.0	Seghaier, 1984
	1982	16	0.9	0.2 - 2.4	Buat-Menard et al., unpl.
West. Mediterranean					
Phycemed 1	1981	13	1.4	0.1 - 5.5	Seghaier, 1984
Phycemed 2	1983	15	1.6	0.4 - 3.2	Buat-Menard et al., unpl.
Alboran Sea	1981	7	1.5	0.3 - 7	Seghaier, 1984
Marseille	1977-1979	200	5.9		Viala, et al., 1979
Monaco	1978	30	4.5		Seghaier, 1984

Over 90% of the total global emission of cadmium originates from point sources (smelters and metal processing plants, incinerators, etc.) (Nriagu, 1980). Assuming that 50% of the anthropogenic releases into the air are exported outside the area of origin and distributed uniformly throughout the Northern hemisphere and that the atmospheric residence time for cadmium aerosols is 10 days, in remote areas one can expect 0.04 ng Cd m^{-3} (Nriagu, 1980). In fact, airborne cadmium concentrations at remote locations range from 0.006 to about 0.4 ng m^{-3}. In rural areas, levels around 1 to 4 ng Cd m^{-3} have been measured. As is to be expected, in urban areas the cadmium concentration in air can increase markedly: ranges between 1 and 15 ng m^{-3}. Towns with large metal industries can have concentrations of several hundreds ng m^{-3}.

4.3 Sea water

Older data on cadmium in sea water must be considered with precaution, since in the majority of cases sampling was not given proper attention and pretreatment was not carried out under clean conditions. During the last ten years researchers have come to the conclusion that cadmium is found in oceanic waters in concentrations that are significantly lower than previously thought, but because no sea water standard exists, it is difficult to compare data given by different authors. Older data on cadmium concentrations in the open Mediterranean waters suggest a range from less than 0.05 up to 0.60 ug l^{-1} (UNEP, 1978).

It was also found that cadmium appears in well defined distributions in the world oceans. In his review of trace metals in sea water, Bruland (1983) classifies cadmium as a nutrient-type trace element. A nutrient-type distribution shows a depletion in the surface layer and enrichment due to resolubilization from biological debris at greater depth, showing a correlation with nutrient concentrations in the depth profiles. Similar nutrient-type distribution has also been found in the Alboran Sea and in the adjacent North Atlantic (Fig. 3). In the upper 500 m, the cadmium concentrations increase from about 0.002 ug Cd l^{-1} at the surface to about 0.02 ug Cd l^{-1} at 500 m depth. Also Boyle et al. (1984) report cadmium concentrations in the sea of Alboran to be 0.004 ug l^{-1} in surface waters with a maximum of of 0.012 ug l^{-1} at a depth of 500 m. On the other hand, Copin-Montegut et al. (1985) found no cadmium depletion in the 500-m layer in the Eastern basin of the Mediterranean and in the Sicilian channel the vertical cadmium concentrations ranged between 0.005 and 0.01 ug Cd l^{-1} (circa 50 to 100 pmol l^{-1}). Only in a station in the Strait of Gibraltar and a station in the near Atlantic the concentration in the surface layer down to about a 75 m depth remained within the range of 0.001 to 0.005 ug Cd l^{-1} while in the Atlantic station the concentration markedly increased to 0.01 ug Cd l^{-1}.

The increase in the Straight of Gibraltar station was not so big (Fig. 4). For comparison, Bruland et al. (1978) found a depletion starting at 0.015 ug Cd l^{-1} in the surface in a northeast Pacific station reaching about 0.1 ug l^{-1} at a depth of approximately 600 m remaining constant at this concentration down to a depth of 2500 m. Other examples are shown in Bruland (1983). The example for the North Atlantic shows that the deeper, almost constant vertical cadmium concentration in the Atlantic is about 5 times lower than the Northeast Pacific cadmium profile.

In Table VIII the more recent data on concentrations of cadmium in Mediterranean open waters are summarized. The analytical methods used by authors are also included since they can influence results. Monitoring data of Yugoslavia show for the years 1979 to 1985 surface cadmium concentrations for the North Adriatic determined with ASV at pH 2 as ranging from 1 to 74 ng l^{-1} and at pH 8 as ranging from 2 to 28 ng Cd l^{-1}.

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 sea water is rather difficult. Furthermore, analytical methods usually determine different fractions of the total heavy metal concentration. In comparing heavy metal data, at least the values for total, dissolved and particulate forms have to be considered and it would be better if the chemical species present could also be determined.

Huynh-Ngoc and Fukai (1979) have reported mean concentrations of dissolved cadmium in different Mediterranean regions that range from 0.04 to 0.15 ug l^{-1} and a Mediterranean open water average of 0.13 $\pm$ 0.02 ug l^{-1}. Laumond et al. (1983) however have reported much lower values for the Western Mediterranean (0.005 to 0.10 ug l^{-1}). In the Tyrrhenian Sea surface Cd concentrations range from 0.05 to 0.09 ug l^{-1} (Nurenberg, 1977). Also Kremling and Petersen (1981) report lower concentrations suggesting a Mediterranean open water average of 0.017 $\pm$ 0.007 ug Cd l^{-1}.

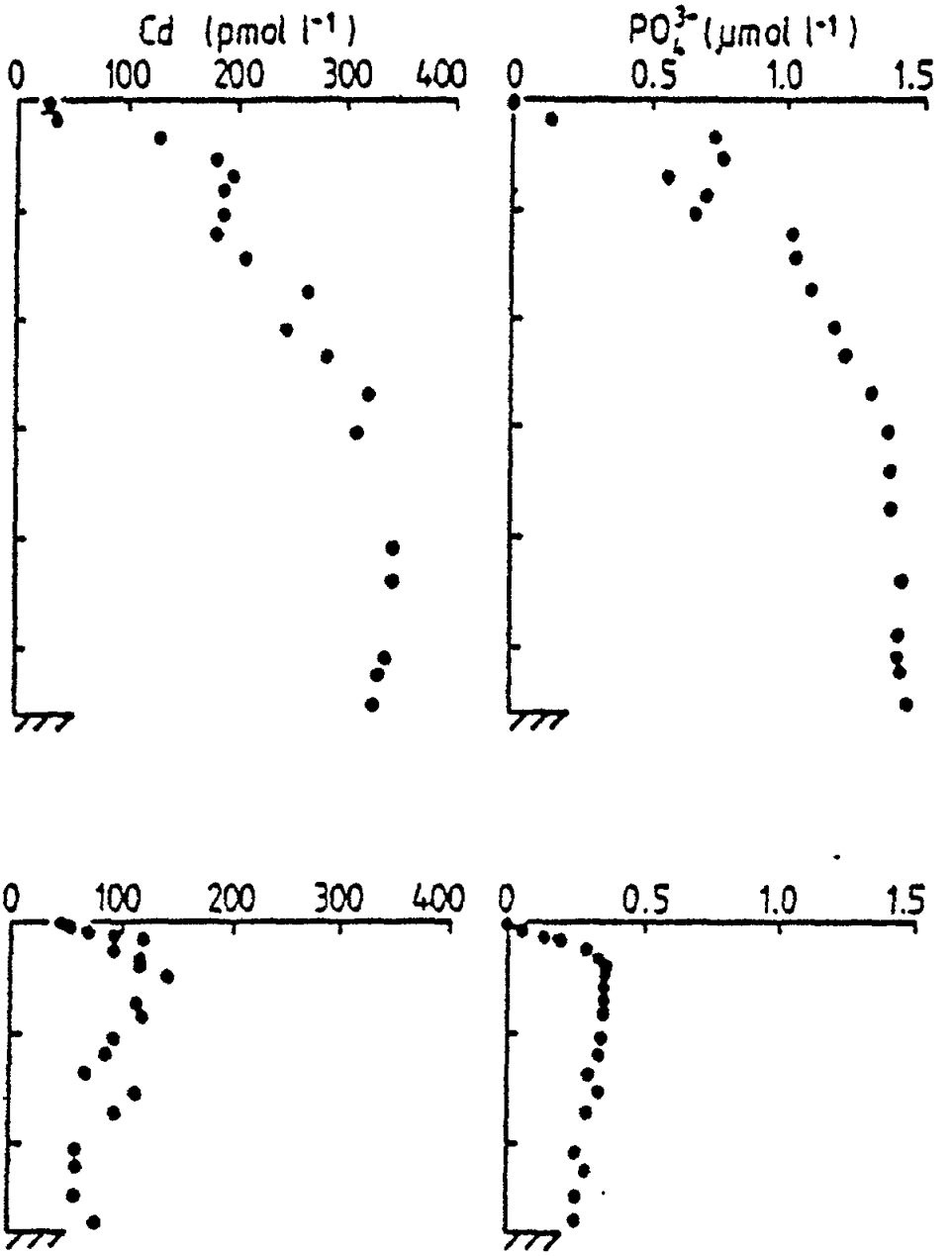

Figure 3. Vertical profiles of dissolved cadmium and reactive phosphate (Statham et al., 1985) (upper graphs refer to Atlantic stations; lower graphs to Mediterranean stations).

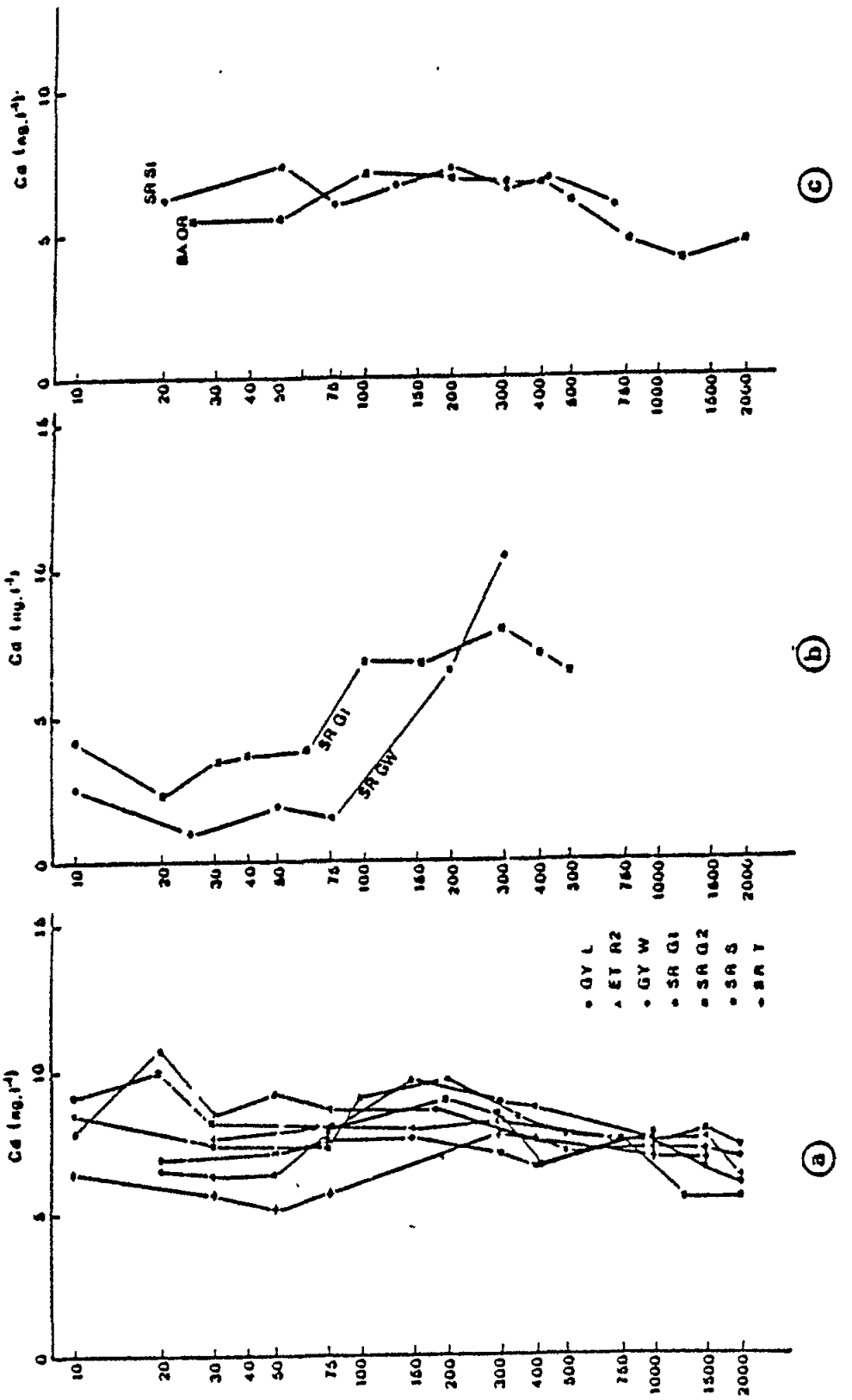

Figure 4. Vertical distribution of cadmium: (a) in the western basin, (b) in the Strait of Gibraltar (SRGI) and adjacent Atlantic (SRGW, ~ 30 km north-west off Tanger), (c) in the Sicilian Channel (SRSI) and 120 km south of Siracusa (BAOR) (Copin-Montegut et al., 1985).

Table VIII

Cadmium concentrations in open waters of the Mediterranean (ug l^{-1})

Region		Method	Cd	Reference
II		ASV	0.15	Huynh-Ngoc and Fukai, 1979
		ASV	0.11	Huynh-Ngoc and Fukai, 1979
IV		ASV	0.11	Huynh-Ngoc and Fukai, 1979
		ASV	0.05-0.09	Nurenberg, 1977
V	"ionic"	ASV	0.004	Branica et al., 1985
	"total"	ASV	0.007	Branica et al., 1985
VI-VII		ASV	0.15	Huynh-Ngoc and Fukai, 1979
VIII		ASV	0.07	Huynh-Ngoc and Fukai, 1979
X		ASV	0.04	Huynh-Ngoc and Fukai, 1979
Recent data				
I-II			0.004	Boyle et al., 1984
V	"ionic"	ASV	0.003	Branica et al., 1985 (Mohoroviccic cruise)
	"total"	ASV	0.015	Branica et al., 1985 (Mohoroviccic cruise)
	"ionic"	ASV	0.01	Branica et al., 1986 (open sea 1983-86)
	"total"	ASV	0.017	Branica et al., 1986 (open sea 1983-86)
IV-VI-VII			0.010	Boyle et al., 1984
II		Dowex/ Extraction/AAS	0.06	Frache et al., 1980,
II			0.008	Copin-Montegut et al., 1985
II		DPASV, dissol.	0.006 (0.0024-0.012)	Seritti et al., 1986
		part.	0.0012 (0.00054-0.009)	Seritti et al., 1986
III		ASV	0.005-0.010	Laumond et al., 1983
Mediterranean		Freon extraction AAS or ASVO	0.017±0.007	Kremling and Petersen, 1981

For regions see Figure 1

ICES (1980) has reported a range of 0.001 to 0.10 ug l^{-1} in oceanic waters. These values are very close to Mediterranean concentrations.

In coastal waters cadmium concentrations are reported to be as high as 1.4 ug l^{-1}, considerably increased compared to recent open Mediterranean values of 0.004 to 0.017 ug l^{-1} (Table IX). At present, without an intercalibration for cadmium it is difficult to decide whether these high concentrations are real or a result of contamination during sampling and analysis. However it seems that certain coastal areas of Spain and Italy have cadmium concentrations higher than those for the open-sea (see Table IX).

Table IX

Cadmium concentrations in Mediterranean coastal waters (ug l^{-1})

Region	Method	Cd	Reference
I			
-Quadalhorce river mouth, Malaga	AAS	0.14-0.27	Aviles et al., 1986
II			
-Coastal waters	ASV	0.01-0.8	Fukai and Huynh-Ngoc, 1976
-Ligurian Sea	Dowex A-1/AAS	0.03	Frache et al., 1980
-Var lagoon, France	APDC extraction/ AAS	0.9	Chabert and Vicente, 1981
-Italian estuaries	Filtration/ASV	0.004-0.029	Breder et al., 1981
-Lagoons, Spain	Freon Tf extraction/AAS	0.040-0.09	De Leon et al., 1983
-Ligurian coasts, Italy	Filtration/Dowex A-1/AAS		
	Dissolved	<0.002-1.4	Baffi et al., 1983; 1984
	Particulate	0.06	Baffi et al., 1983; 1984
IV			
-River Tiber mouth	AAS	0.1-0.6	Pettine et al., 1982
V			
-Adriatic Sea	NAA	1-36	Grancini et al., 1976
-Limski Canal	"ionic" ASV	0.003	Branica et al., 1985
	"total" ASV	0.015	Branica et al., 1985
-coastal 1983-86	"ionic" ASV	0.01	Branica et al., 1986
	"total" ASV	0.017	Branica et al., 1986
VI			
-Sicilian coasts	Dissolved	0.01-0.47	Alpha et al., 1982
	Particulate	0.02-0.13	Alpha et al., 1982
VIII			
-Saronikos Gulf, Greece	ASV	0.15-0.70	Huynh-Ngoc and Zafiropoulos, 1981
-Northern Greece	APDC-MIBK	0.16-0.52	Fytianos and Vasilikiotis, 1983
-Izmir Bay, Turkey	Extraction/AAS	0.01-0.03	Gücer and Yaramaz, 1980

For regions see Figure 1

Breder et al. (1981) have found small increases in cadmium concentrations when moving towards the mouth of several Italian estuaries. Background concentrations of 0.004 to 0.008 ug l^{-1} increased to 0.016-0.029 ug l^{-1} inside the estuaries. On the other hand, Fukai and Huynh-Ngoc (1976) while studying the cadmium concentrations in coastal and offshore waters in area II did not observe any significant differences except in areas with high anthropogenic inputs. In coastal and offshore waters of the Ligurian sea no systematic differences in cadmium concentrations have been found, although some stations close to input sources showed considerably higher concentrations (Frache et al., 1980, Baffi et al., 1983; 1984). Grancini et al. (1976) observed high cadmium concentrations in the Adriatic Sea. Their results need to be confirmed.

Aboul Dahab et al. (1985) report on the influence of the release of cadmium from an agriculture drain. The inshore concentrations for dissolved cadmium ranged from 160-190 ng l^{-1}, while that for colloidal cadmium was 17 ng l^{-1} and that of particulate cadmium 36 to 42 ng l^{-1}. Offshore concentrations gave the following pattern: 70-110 ng dissolved Cd l^{-1}, 16 ng colloidal Cd l^{-1} and 18-23 ng particulate Cd l^{-1}.

4.4 Sediments

Levels of cadmium in Mediterranean coastal sediments have been studied much more extensively than in open Mediterranean. The concentrations of cadmium in sediments will depend not only on pollution inputs but also on factors such as organic carbon content, mineralogical characteristics, grain size and sedimentation rates.

The analytical determination of heavy metals in sediments involves as a first step the solubilization of the sample. A wide variety of reagents, usually acids, are used by different investigators, ranging from total solubilization by $HF-HClO_4-HNO_3$ to simple extraction by dilute HCl. Some investigators analyzed the whole sediment sample, others a fraction of less than 200, 63 or 5.5 um. It is obvious that because of different methodologies used, data on cadmium in sediments are not easily comparable.

Distribution of heavy metal concentrations determined on the whole sediment is only a first approach to the identification of areas contaminated by industrial or urban activities. Donazzolo et al. (1984a and b) studying heavy metal concentrations in North Adriatic sediments found that these depend on sediment fine fraction composition, specific surface area and accumulation level in the less than 63 um fraction (pelite). They report that 74-86% of the total concentration of cadmium is bound in the pelite fraction. Another difficulty in comparing heavy metal concentration in sediments is defining what the natural background values are for a certain area. These natural background values will depend on factors such as grain size, organic carbon content and mineralogical characteristics.

Early publications have reported cadmium concentrations in Mediterranean marine sediments to range between 0.1 and 2.3 ug g^{-1} (UNEP, 1978). Data reported since 1978 are summarized in Table X. Minimum concentrations reported range from 0.1 to 10 ug g^{-1}. Donazzolo et al. (1984a) report a probable background cadmium concentration, as calculated from core samples, of 1.2 ug g^{-1}. Frignani and Giordani (1983) report concentrations of 0.5-2.5 ug g^{-1} in offshore sediments, whereas Voutsinou-Taliadouri (1983) a value of 0.4 ug g^{-1} for Aegean sea

sediments. A probable background cadmium concentration should be in the range of 0.1 to 2.5 ug g^{-1}. Recently, Whitehead et al. (1985) tried to estimate the cadmium background concentration. Their data base consisted of data from Donazzolo et al. (1984b) (samples leached with nitric acid) and Voutsinou-Taliadouri (1983) who found only levels 0.4 ug Cd g^{-1} DW. Whitehead et al. (1985) suggested a background concentration of 0.15 ug Cd g^{-1} DW of sediment.

The results of the Calypso cruise around the Mediterranean coastline give a mean of 0.13 ug Cd g^{-1} DW (range: 0.035 to 0.56 ug Cd g^{-1} DW) (Whitehead et al., 1985). On one occasion it was possible to compare the data from the Calypso cruise with those of Donazzolo et al. (1981). The 7 samples of Donazzolo et al. (1981) taken in 1981 around the sampling station of the Calypso in 1977 had cadmium concentrations about ten times higher than the sample of the Calypso cruise in 1977. The different pretreatment used could not be the cause of this large difference. From Donazzolo et al. (1984b) it is evident that higher cadmium concentrations are found in sediments located in front of the outflows of Venice.

In other cases where samples were taken from areas close to source inputs, industrial or urban, cadmium concentrations have been reported to range from 0.3 to 10 ug g^{-1}. Badie et al. (1983) contoured the cadmium concentrations round the mouth of the river Rhone (Figure 5). Similar distribution patterns, are to be expected from other river mouths and industrial outfalls. The various lagoons along the French coast of the Gulf of Lyon are also heavily polluted with cadmium (Table X). Voutsinou-Taliadouri (1983) and Voutsinou-Taliadouri and Varnavas (1986) found high levels near pollution sources and lower levels in unpolluted areas (Table X). From the data it is evident that the Axios river is the main source of cadmium. Very high concentrations (32-64 ug g^{-1}) have been reported in sediments of Spanish lagoons (De Leon et al., 1983), in Izmir Bay (Uysal and Tuncer, 1985) and in the harbour of Alexandria (Saad et al., 1981).

It is evident that cadmium concentrations in coastal sediments from areas receiving industrial effluents, solid wastes and domestic sewage, as well as in river deltas and estuaries are considerably higher than Mediterranean background values. The concentrations reported by researchers depend not only on the actual degree of heavy metal pollution in the area, but also on the extraction technique used, as well as on the proximity of stations to source inputs. Evidently in some cases the very high values reported are not representative of the whole areas studied.

4.5 Biota

Cadmium concentrations in an organism depend on environmental factors such as the concentration of cadmium in sea water, on its food-chain position and, in particular, on the chemical species of cadmium to which the organism is exposed (see section 5.2). Various biological species may have different cadmium concentrations. Futhermore different biological tissues of the same species can have different cadmium concentrations. This means that for a comparison of cadmium concentrations in biota from different locations the same tissue of the same biological species must be compared. In fact, Lafaurie et al. (1981) found that in Mullus barbatus the cadmium concentration in the muscle tissue ranged from non detected to about 40 ug Cd kg^{-1} DW, in the gonads from about 20 to 130 ug Cd kg^{-1} DW, in the kidney from 50 to 280 ug Cd kg^{-1} DW and in the liver from 500 to 1200 ug Cd kg^{-1} DW. The muscle has the lowest concentration and the liver the highest. The authors also found that the cadmium concentration varied during the year.

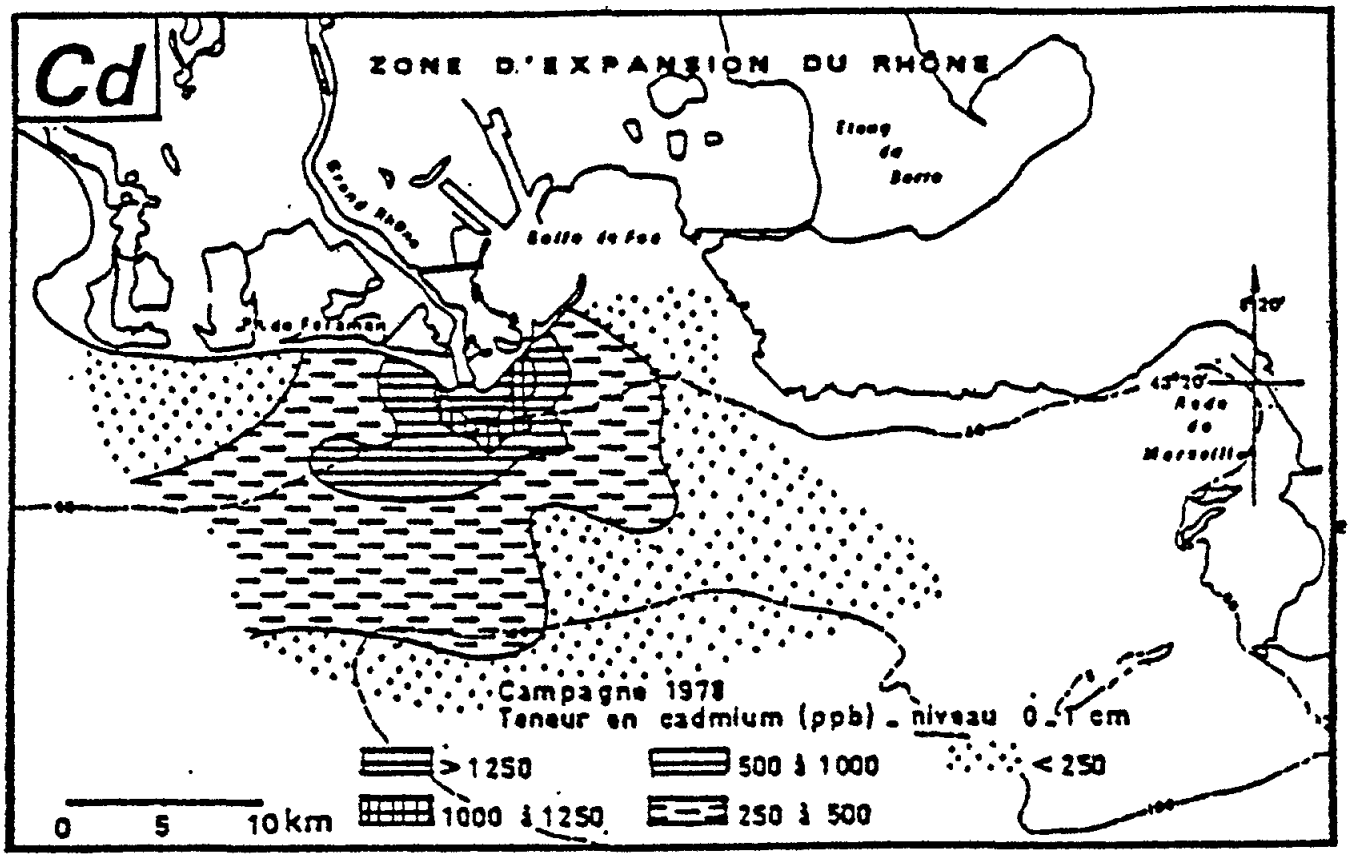

Figure 5. Horizontal cadmium distribution off the Rhone delta (Badie et al. 1983)

Table X

Cadmium concentrations in Mediterranean sediments (ug g^{-1} DW)

Region	Method	Cd conc.	Reference
II			
-Var lagoon, France	$HF-HClO_4-HNO_3$	3.7	Chabert and Vicente, 1981
-Coastal lagoon,	<63 um	10-32	De Leon et al., 1983
-Spanish coast	Conc. HNO_3	0.1-0.3	Peiro et al., 1983
-River Ebro Delta	HNO_3	0.12-0.37	Obiols et Peiro, 1981
-River Ebro Delta	HNO_3	0.04-2.1	Obiols et al., 1985
-Etang Salses-Leucate	<63 um	>5.5	Buscail et al., 1985
-Etang Bages-Sigean	<63 um	>6	Buscail et al., 1985
-Etang de Thau	<63 um	>4	Buscail et al., 1985
-River Rhone Delta	HNO_3-HClO_4	0.25-5	Added et al., 1981;
-River Rhone Delta		0.3->0.5	Span et al., 1985
-Marseille	<200um $HCl-HNO_3$	1.8-3	Arnoux et al., 1981
-Cannes	<63um HNO_3-H_3PO_4-HCl	1.8-7	Ringot, 1983

Table X (cont.)

Region	Method	Cd conc.	Reference
-Gulf of Nice	HNO_3-HCl	0.7-2.4	Flatau et al., 1983
-Italian Estuaries	HNO_3-HCl	0.21-0.55	Breder et al., 1981
	HNO_3	0.7-1.7	Frignani and Giordani, 1983
III			
-Portman	HNO_3-H-peroxide	up to 10.4	De Leon et al., 1985
-Castellon-Guardamar	"	ND-0.5	"
IV			
-Offshore sediments	HNO_3	0.5-2.5	Frignani and Giordani, 1983
V			
-River Po delta	HNO_3	0.16-1.7	Fascardi et al., 1984
-Gulf of Trieste		0.3-5.3	Majori et al., 1979
-Gulf of Venice	HNO_3	0.1-3.1	Angela et al., 1981
-Bay Mali Ston, Yugoslavia		0.1-0.2	Vukadin et al., 1985
-Northern Adriatic	-	0.05-5.6	Donazzolo et al., 1984a, 1984b
-Offshore sediments	HNO_3	0.80-1.2	Frignani and Giordani, 1983
VI			
-Patraikos Gulf, Greece	$HF-HNO_3$ $HClO_4$	-	Varnavas and Ferentinos, 1983
-Gulf of Catania	HNO_3	2.2-4.6	Castagna et al., 1982
-Offshore sediments	HNO_3	0.6-1.1	Frignani and Giordani, 1983
VIII			
-Thermaikos-Kavala, Greece	63um HNO_3	0.6-1.1	Fytianos and Vasilikiotis, 1983
-Thermaikos Gulf, Greece	45um HNO_3	0.40-2.5	Voutsinou-Taliadouri, 1983
Industry	0.55	(0.45-1.15)	Voutsinou-Taliadouri
Axios river (1983)	2.5	(0.45-8.5)	and Varnavas 1986
Axios river (1985)	3.7		
Aliakmon river	<0.4		
-Pagassitikos Gulf, Greece	45um HNO_3	<0.4	Voutsinou-Taliadouri and Varnavas 1986
-East Aegean offshore	45um HNO_3	0.4	Voutsinou-Taliadouri, 1983
-Izmir Bay	HCl-HNO_3	0.2-40	Uysal and Tuncer, 1985
-Guelbahce Bay	HCl-HNO_3	1.4-14	Uysal and Tuncer, 1985
X			
-Haifa Bay	<250um	<0.4-2.5	Krumholz and Fleischer, 1985
-Alexandria		2.8	El Sokkary, 1979
-Abu Kir Bay, Egypt	HNO_3	2	Saad et al., 1981
-Damietta estuary, Egypt	HNO_3	0.16-2	Saad and Fahmy, 1985
-Western Harbor, Alexandria	HNO_3-$HClO_4$	7-64	Saad et al., 1981
XIII			
-Black Sea,Nearshore	HNO_3	1.3-4.8	Pecheanu, 1983
Offshore		2.8	Pecheanu, 1983
Mediterranean		0.1-2.3	UNEP, 1978

Reviewing the cadmium concentrations in non-Mediterranean organisms of different trophic levels Bernhard and Andreae (1984) found that cadmium is one of the trace elements in which the concentration remains about constant or decreases slightly with the size of the specimen. The cadmium concentrations increase starting from plankton and reaching a maximum with crustaceans, and then decrease again in carnivorous fishes. For Mediterranean species few studies on the relation betwen size and cadmium concentration exist. Hornung and Oren (1981) report an inverse relationship between cadmium (and also copper, lead and zinc) concentrations in Donax trunculus and size of the specimens collected in Israel. Also Majori et al. (1979) reported that cadmium concentrations in Mytilus galloprovincialis are sometimes negatively correlated with size.

In order to assess risk in human seafood consumers the most important tissue to be analysed is the muscle tissue (fillet) in fishes and the edible parts in other seafood.

The largest uniform data base on cadmium-T concentrations in the Mediterranean was collected in the framework of the UNEP/FAO pilot project on baseline studies and monitoring of metals, particularly mercury and cadmium, in marine organisms (MED POL II) (MAP Tech.Rep.Ser. 2 and 9). The participants in this project were aware that certain criteria had to be established in order to make the survey efficient. First of all, all participants had to intercalibrate with the reference materials distributed by IAEA (see section 4.1). Since different species and specimens of the same species of different size cannot be compared and also different tissues of the same specimen may have different cadmium concentrations, the results of the monitoring exercise can only be comparable if the size range and the tissues to be analyzed were specified. Wide distribution in the Mediterranean of the species to be monitored and edible tissue were the characteristics for selecting the species to be monitored:

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

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

Since high mercury concentration had been reported for tuna and swordfish it was recommended to analyse specimens of the bluefin tuna (Thunnus thynnus) also for cadmium whenever available and regardless of size. The present assessment is mainly based on data reported by participating institutes as far as cadmium concentrations in marine organisms are concerned. The results of the intercalibration exercise were taken into consideration and certain data were excluded from the statistical analysis. It should be pointed out that average concentrations reported should not be interpreted as representative mean values for a given region, or the whole Mediterranean. Most samples of mussels were collected from coastal areas which may have received industrial effluents or domestic sewage and may, therefore, have higher cadmium concentrations than organisms living in the same area but not exposed to high local cadmium sea water concentrations. There is a considerable variability of concentrations reported. Standard deviations are sometimes higher than the respective arithmetic means.

4.5.1 Plankton

Only a few data have been published on cadmium in plankton. Fowler (1985) reporting on the various data obtained for mixed plankton caught with various plankton nets of different pore size (60 - 500 um) in cruises from 1975 and 1977 found in pelagic areas means ranging from 1.8 to 2.9 ug Cd g^{-1} DW and ranges of individual determinations from 0.4 to 4.6 ug Cd g^{-1} DW. In coastal areas the means ranged from 0.6 to 2.5 with a range of the individual concentrations from 0.3 to 11 ug Cd g^{-1} DW. Euphausids ranged from 0.4 to 0.66 ug Cd g^{-1} DW. Policarpov et al. (1979) determined in males of Anomalocera patersoni 1.4 ug Cd g^{-1} DW and in females 1.6 ug Cd g^{-1} DW.

Haerdstedt-Romeo and Laumond (1980) and Haerdstedt-Romeo (1982) found in off-shore plankton (pore size 200 um) sampled in the Liguro-Provencal Basin (n = 18) a mean of 1.7 ug Cd g^{-1} DW (range: 0.5-3.4 ug Cd g^{-1} DW) and in nearshore areas subject to pollution from sewage and other sources of pollution in the Bays of Nice and Cannes (n = 29) a mean of 2.4 ug Cd g^{-1} DW (range: 1-4.9 ug Cd g^{-1} DW).

4.5.2 Seaweeds

No data seem to be available on seaweeds since no species had to be monitored.

4.5.3 Crustaceans

Only a few data exist for crustaceans (Table XI). Bezard et al. (1985) analyzed the decapod Calocaris macandreae. The cadmium concentration in the abdomen varied from 210 to 490 ug Cd kg^{-1} FW. Uysal and Tuncer (1983) report two concentrations for Penaeus kerathurus: 180 and 210 ug Cd kg^{-1} FW. Capelli et al. (1983) found in Nephrops norvegicus a mean of 140 ug Cd kg^{-1} FW with a range from 90 to 200 ug Cd kg^{-1} FW.

Some samples from the ICES areas have considerably higher cadmium levels than Mediterranean crustaceans (Table XII).

Table XI

Cadmium concentrations in crustaceans (ug kg^{-1} FW) (UNEP/FAO, 1986)

	No. of samples	Mean	Stand. Deviat.
Nephrops norvegicus	61	50	39
Parapenaeus longirostris	27	46	55

Table XII

Cadmium (ug kg^{-1} FW) in crustacean species (whole body) from ICES areas (data from ICES 1974, 1977, 1980)

	Median of and range of means		Location and year
feed on invertebrates			
brown shrimp	640	<500-1000	North Sea, 1974
brown shrimp	100	20-280	North Sea, 1977
brown shrimp	60	<20-230	North Sea, 1980
"typical"	100		
deep sea prawn	300	<200-950	W. Greenland, 1977

4.5.4 Molluscs

Mytilus galloprovincialis was an obligatory species in the monitoring programme.

The concentrations in mussels are difficult to compare from samples taken in different seasons and locations because the concentrations can vary widely since the mussels were subject to local pollution influences. Fowler and Oregioni (1976) studying the variation of heavy metals, in Mytilus galloprovincialis reported maximum concentrations in spring samples. They suggest that this is probably a result of the reproductive state of the mussels but also of high particulate metal loads in the sea water caused by increased winter runoff. Majori et al. (1979) report significant variations of Cd concentrations in Mytilus galloprovincialis.

Cadmium concentrations in Mytilus galloprovincialis range from 5 to more than 2000 ug kg^{-1} FW (Tables XIII and XVI). From the regions studied, region VI has the lowest average (38 $\pm$ 6 ug kg^{-1}). Most values are below 250 ug kg^{-1} and the average over the regions for which data exist (excluding 5% of higher values) is 120 $\pm$ 80 ug kg^{-1}, but very high levels are reported from Monaco and the Yugoslavian coast south of Trieste. It is also probable that in other polluted areas high cadmium levels will also be found.

Furthermore Asso (1985) found high mean cadmium concentrations in the mussel Perna perna collected around Algiers ranging from 880 to 1800 ug Cd kg^{-1} DW or about 175 to 360 ug kg^{-1} FW. Earlier, Asso (1981) found concentration, ranging from 75 to 260 ug Cd kg^{-1} FW.

For comparison, in the North Sea, mean values reported for Mytilus edulis ranged from 5 - 1060 ug kg^{-1} (ICES, 1974, 1977a and b). In the ICES North Atlantic baseline study, values reported were between 90 and 330 ug kg^{-1} (ICES, 1980). In the Oslo Commission area (1983) cadmium concentrations in Mytilus edulis have been reported to range between 43 and 12600 ug Cd kg^{-1} FW with a mean of 1040 ug Cd kg^{-1} FW. These data show that in other non- Mediterranean areas high Cd concentrations in mussels have also been observed.

Table XIII

Cadmium concentrations in molluscs (ug kg^{-1} FW) (UNEP/FAO, 1986)

Region	No. of samples	Mean	Range Minimum	Maximum
Mytilus galloprovincialis:				
II	105	190	40	1060
V	72	160	25	475
VI	25	38	24	52
VIII	76	100	5	780
Donax trunculus:				
X	16	80 ± 26		
Mytilus galloprovincialis:				
All regions	265	120 ± 83		

For the location of regions see Fig. 1

4.5.5 Fish

Some seasonal variations of cadmium in the liver and gonads of Mullus barbatus appear to be related to the sexual physiology of this fish (Lafaurie et al., 1981). No such influence was evident for muscle tissue. Similarly, Uysal and Tuncer (1983) found small differences in the concentrations of cadmium in Mullus barbatus, Mullus surmuletus and Sardina pilchardus according to length and season. However, it is not clear whether the differences are statistically significant.

Average cadmium concentrations in Mullus barbatus and other fishes from the Mediterranean are summarized in Tables XIV and XV. In Mullus barbatus cadmium average regional values range from 17 to 50 ug kg^{-1} FW. In view of the considerable variability of data there seem to be no significant differences between regional means. The overall Mediterranean average (335 samples) is 46 ug kg^{-1} with a standard deviation of 67. Most data however are below 60 ug kg^{-1}.

Table XIV

Cadmium concentrations in Mullus barbatus (ug kg^{-1} FW) (UNEP/FAO, 1986)

Region	No. of samples	Mean	Range Minimum	Range Maximum
II	136	50	1.0	590
VI	50	26	5.0	52
VII	11	17	5.5	49
VIII	46	47	15	162
X	21	39	14	65

For location of the regions see Fig. 1

Cadmium concentrations in Thunnus thynnus were reported in samples from area II. The mean concentration was 38 ± 43 ug kg^{-1}. In Thunnus alalunga the mean of reported concentrations was 23 ± 6.5 ug kg^{-1}.

Average cadmium concentrations in other Mediterranean marine organisms are summarized in Tables XV and XVI. The highest mean was reported in Mullus surmuletus (140 ug kg^{-1}) which has a value more than twice that of other fishes. Surprisingly, it is much higher than the concentration in the closely related M. barbatus. Whether this difference is real and whether it is due to different food habits needs to be established. Furthermore, one tuna sample had a high cadmium level, but this level needs confirmation as well.

A comparison with another large data base from the ICES areas shows that the Mediterranean fishes have similar concentrations to those from the ICES areas (Table XVII).

4.5.6 Birds and marine mammals

High levels of cadmium were found in the liver and kidney of marine birds and marine mammals from non-Mediterranean areas (Bull et al., 1977, Falconer et al., 1983). Liver levels between 10 and 50 mg Cd kg^{-1} DW (2 to 10 mg Cd kg^{-1} FW) and kidney concentrations from 15 to 230 mg Cd kg^{-1} DW (3 to 40 mg Cd kg^{-1} FW) seem to be common in birds and these levels are thought to be predominantly of natural origin since Bull et al. (1977) found that marine insects living in remote locations likewise have high Cd levels (up to 200 mg Cd kg^{-1} DW).

4.6 Levels in ecosystems under the influence of anthropogenic sources

The influence on sea water and sediments of cadmium released through rivers and industries in lagoons has been discussed in section 4. There follow some examples where the pollution source has been identified.

Table XV

Average cadmium concentrations in Mediterranean marine organisms ug kg^{-1} FW (UNEP/FAO, 1986)

Species	No. of samples	Mean	Standard Deviation
Engraulis encrasicolus	81	34	25
Merluccius merluccius	27	63	34
Mugil auratus	10	47	85
Mullus barbatus	318	34	28
Mullus surmuletus	218	140	83
Thunnus alalunga	38	23	6.5
Thunnus thynnus	111	38	43

Table XVI

Recent data on cadmium concentrations (ug Cd kg^{-1} FW) in selected seafood species from the Mediterranean

Species	date	mean	S.D	location	reference
M. gallopr.	Aug. 1984	770	± 120*		Veglia & Vaissière, 1986
	Dec. 1984	730	± 150*		
	Apr. 1985	1900	± 230*		
	July 1985	710	± 360*		
	1983/1985	1160	± 650*	Koper St.5	Tusnik & Planinc, 1986
		1390	± 400*	Piran St.23	
		1310	± 310*	Piran St.27	
		1390	± 430*	Piran St.35	
	July/Nov 1985	70		Valencia/Cast.	Hernandez et al., 1986
	1985	170	± 160	Aegean	Uysal and Tuncer, 1985
Corbula gibba	1984/85	210	± 45		Nat. Co-ord. Yugoslavia, 1986
Alcyomium palmatum		200	± 30		
Haliclona		30	± 40		
Pecten jabobeus		1015	± 60		
Ostrea edulis		730	± 40		
Chlamys operculariз		1180	± 60		

Table XVI (cont.)

Species	date	mean	S.D	location	reference
Ostrea edulis		100			Nat. Co-ord. Tunisia, 1986
Mullus barbatus		140			
Pagellus erythrinus		115			
Trachurus trachurus		135			
Palaemon serratus	July/Nov 1985	70		Valencia/Cast.	Hernandez et al., 1986
	M	81			
	F	42.5			
S. pilchardus		46		Valencia/Cast.	Hernandez et al., 1986
	1985	120	± 90	Aegean	Uysal and Tuncer, 1985
M. barbatus	M	16.6		Valencia/Cast.	Hernandez et al., 1986
	F	17.9			
M. surmuletus	M	8.4		Valencia/Cast.	Hernandez et al., 1986
	F	18.8			
S. scomber	1985	130	± 110	Aegean	Uysal and Tuncer, 1985
T. thynnus	F	280		Valencia/Cast.	Hernandez et al., 1986

* dry weight

Table XVII

Cadmium (ug kg^{-1}FW) in some fish (muscle) species from ICES areas
(data from ICES 1974, 1977a, 1977b, 1980)

Median of and range of means		Location and year
Plankton feeder		
herring	<30	30-700 North Sea, 1974
herring	20	<20-20 North Atlantic, 1977
herring	20	ND-80 Irish coast, 1980
"typical"	20	
sardine	60	9-60 North Atlantic, 1977
sprat	75	60-90 Irish coast, 1980
capelin	<70	10-30 North Atlantic, 1977
feed on invertebrates		

Table XVII (cont.)

Median of and range of means			Location and year
cod	<30	20-500	North Sea, 1974
cod	10	<1-30	North Sea, 1977
cod	-	100-900	North Atlantic, 1977
cod	25	2-40	Irish coast, 1977
cod	40	27-53	NW-Atlantic, 1977
cod	6	6-7	NW-Atlantic, 1980
"typical"	20		
feed on crustaceans and fish			
hake	40	20-60	North Atlantic, 1977
haddock	40	ND-130	Irish coast, 1980
haddock	4		NW Atlantic, 1980
whiting	10	ND-150	Irish coast, 1977
Greenland halibut	<200		North Atlantic, 1977
plaice	350	<20-600	North Sea, 1974
plaice	4	3-4	North Atlantic, 1977
plaice	25	ND-80	Irish coast, 1980
"typical"	25		
sole	20	<10-50	North Atlantic, 1977

ND = non detected

De Leon et al. (1985) investigated the cadmium concentrations along the Spanish coast from Castellon to Cartagena. With the exception of Portman where a lead-zinc mine is polluting the coastal sediments, cadmium levels range from about 0.05 to 0.5 ug Cd g^{-1} DW. Near Portman and the adjacent Cartagena area the pollution from the mine is evident in the sediments; the station nearest to the coastline had 10.4 ug Cd g^{-1} DW and a near-shore station still had about 1.6 ug Cd g^{-1} DW. The examination of cadmium content in marine organisms from this coastal area shows that the cadmium concentrations in a benthic fish are not influenced by the cadmium pollution, but the cadmium concentrations in some of the molluscs follow the cadmium concentrations in the sediments (Table XVIII). The fact that cadmium concentration in M. barbatus was elevated near the major source of Portman may also be due to the fact that M. barbatus was caught much farther from the shore-line where the sediment concentration was highest.

The results from a non-Mediterranean area are interesting. Lobsters caught near a lead smelter were highly contaminated while at a distance of about 20 km from the release point the cadmium concentrations in lobsters return to background (Ray et al., 1981).

Table XVIII

Cadmium concentrations in sediments (ug g^{-1} DW) and in marine organisms (ug/kg^{-1} FW) along the Spanish coast from Castellon to Cartagena (data from De Leon et al., 1985)

Location	sediment range	M. gallopr. m.	M. gallopr. range	D. trunc. m.	D. trunc. range	M. barbatus m.	M. barbatus range
Castellon	0.5 - 0.4	67	38-100	8	5 - 11	5	1 - 13
Sagunta	ND - 0.16	-		12		7	1 - 14
Valencia	0.12- 0.5	86	53-120	22	6 - 41	5	3 - 8
Cullera	0.08- 0.12	61	35- 90	5		2	1 - 4
Alicante	0.17- 0.28	113	41-175			2	1 - 4
Guardamar	0.02- 0.55	100	70-130	6		6	2 - 11
Portman	0.02-10.4	940	930-950				
Cartagena	0.2 - 1.6	400	160-650			7	1 - 23

M = mean

The influence of the cadmium discharges of a tannery in the Gulf of Geras Mytilini, Greece (effluent concentration 0.7 ug Cd l^{-1}) had a notable effect on the body levels of several marine organisms. The mollusc Eledone moschata collected at a distance of about 2 km from the outfall had a concentration of six times (5.8 mg Cd kg^{-1} FW) higher than specimens collected at distances of more than 4 km from the outfall. Samples of the sea urchin P. lividus had cadmium concentrations, in the polluted area, about 3 times higher than specimens collected in unpolluted areas, but for other organisms the evidence was not so clear (Catsiki and Florou, 1985).

Voutsinou-Taliadouri and Satsmadjis (1982) investigated whether the discharge of sewage and other wastes had an influence on the body levels of cadmium in M. barbartus. Although considerable higher levels of chlorinated hydrocarbons were found in the fish the cadmium concentrations were only slightly higher than background.

5. ELEMENTS OF THE BIOGEOCHEMICAL CYCLE OF CADMIUM

5.1 Transformation of cadmium species

In sea water the inorganic cadmium species are mainly present as chloro-complexes (section 2). However, at least in coastal waters a large part of the cadmium may be associated with particulate matter. Organic matter which had chelated (humic and fulvic substances) cadmium in the freshwater

environment may release it in the estuaries following encounter with the sea water. In anaerobic sediments, cadmium occurs as cadmium carbonates and cadmium sulphides which are much less soluble. Cadmium discharged with organic wastes e.g. sewage sludge, is partly present as carbonates and sulphides and partly as complex organic combinations (GESAMP, 1984). In biota, cadmium is bound to various cadmium binding proteins some of them similar to metallothionein. In mammals, cadmium thionein is induced by cadmium and other trace metals. On the other hand, thionein is relatively easily biodegradable. As the cadmium thionein degradates, the cadmium released induces a new production of thionein and this leads to a steady state in the synthesis of new thionein and its degradation. Since cadmium thionein has a very high apparent stability constant, it competes successfully with cadmium bound to other ligands, with the result that most of the cadmium is bound to metallothionein and thus not toxic. At present, although many different cadmium binding proteins have been identified in non-mammalian marine organisms, not enough information is available to establish whether a similar mechanism works also in non-mammalian organisms (Petering and Fowler, 1986). More details can be obtained from the Proceedings of a recent conference on high affinity metal-binding proteins in non-mammalian species (Fowler, 1986).

5.2 Uptake and release of cadmium species by biota

The cadmium species to which the organisms are exposed has a great influence on the amount of cadmium taken up. There are several papers which show that it is the ionic species of cadmium which is taken up by the organisms. In fact, cadmium uptake by the diatom Phaeodactylum tricornutum is negligible when the cadmium is complexed with EDTA. Cadmium contaminated P. tricornutum cells lose nearly all previously accumulated cadmium when transferred into a medium containing 21 mM cystein (Cossa, 1976). Also in higher organisms a reduction of cadmium tissue levels was observed in the presence of chelating agents. For example, the cadmium uptake is decreased in the barnacle Semibalanus balanoides in the presence of humate, alginate and EDTA (Rainbow et al., 1980) and in the clam Macoma balthica in the presence of EDTA (McLeese and Ray, 1984). When the marine worm Nereis virens or the marine shrimp Pandalus montagui were exposed to cadmium and EDTA the cadmium levels were reduced by 40% and 20 % respectively (Ray et al., 1979). In the American oyster (Crassostrea virginica) cadmium complexed with EDTA, NTA or humic acid was accumulated by as much as 70 % less than inorganic cadmium present at the same concentration (Hung, 1982). Similar observations were made by Foster and Morel (1982) who found that EDTA (10 to 100 uM) reduced the cadmium toxicity to another diatom Thalassiosira weissflogii of otherwise toxic concentrations. However, it was not possible to reverse the cadmium toxicity only by increasing the EDTA concentration (to 100 uM); the iron concentration had to be increased as well. The authors suggest that the interaction between cadmium and iron does not occur in the medium but is due to a physiological interaction within the cell. Experimenting with the grass shrimp Palaemonetes pugio, Sunda et al. (1978) showed that the calculated free cadmium ion is responsible for the observed cadmium toxicity. Only George and Coombs (1977) found that chelating agents (EDTA, alginate, humus and pectin) would double the increase of cadmium uptake by mussels with respect to the uptake from unchelated cadmium (900 nM). However, further experiments have cast doubts on the enhancement of cadmium uptake in the presence of EDTA observed earlier, since the uptake of 115-$CdCl_2$ (the reference in this study) varied between experiments. This is thought to have been caused by the use of different ages of stock isotopes (George, pers. comm., 1984). Furthermore, unpublished experiments with isolated gills by the same author

showed that the rate of Cd-109 influx was very much lower when EDTA was present. These recent observations are now in accordance with other authors who found a decrease in the cadmium tissue levels in the presence of EDTA.

The foregoing discussion shows how important the chemical species is and how difficult it will be to extrapolate results obtained in laboratory experiments to field conditions, in which cadmium containing wastes have been released, because in most cases the cadmium in the waste will not be in ionic form but associated with particles and organic matter. For example, Fisher and Fround (1980) found that the uptake of cadmium added to natural sea water rich in dissolved organic matter was less than that present in sea water low in dissolved organic matter.

Plankton: Wolter et al. (1984) studied the uptake of cadmium by natural plankton. They found that the cadmium enrichment factor decreased with increasing exposure concentration up to 4 ug Cd l^{-1} and then remained constant. This means that up to 4 ug Cd l^{-1} the cadmium concentration in the plankton increases slower than the exposure concentrations, but at higher than 4 ug Cd l^{-1} the cadmium concentration increases proportionally to the external cadmium concentration. Since the carbon fixation rate decreases at 4 ug Cd l^{-1} to about 80 % of the controls, this experience seems to indicate that up to 4 ug Cd l^{-1} the plankton can control to some extent its internal concentration, but it cannot do the same at higher concentrations. Also Fisher et al. (1984) found that at concentrations higher than 10 ug Cd l^{-1} the degree of association of cadmium with the phytoplankton cells was directly proportional to the external exposure concentrations. Similar observations were made in culture experiments (Kayser and Sperling (1980).

Crustaceans: Crustaceans are also able to control the cadmium uptake at low concentrations. Shrimps and lobsters do not accumulate appreciable amounts from sea water at concentrations below 2 ug Cd l^{-1} (McLeese, 1980). Fowler and Benayoun (1974) using radioactive labelled sea water in studying the uptake and loss of cadmium by the benthic shrimp Lysmata seticaudata found that the concentration factor (organism/water) did not reach a steady state after 2 months of exposure and that the concentration factor based on radiotracer data was several times lower than the concentration factor of stable cadmium observed in specimens collected in the environment. This indicates that under natural conditions the shrimp obtained most of its cadmium through the food. The elimination rate was estimated as a biological half-time of about 380 days. Interesting are the results of a comparison of lobsters exposed near a lead smelter (Ray et al., 1981) with lobsters from an unpolluted site. In both sites the highest cadmium concentrations were found in the hepatopancreas, the green gland (an excretory organ). The hepatopancreas which constitutes only 5% of the total wet weight contained more than 90% of the total body burden. The cadmium concentration in the hepatopancreas of the lobsters from the exposed site was 15 to 20 times higher than the cadmium concentrations in the hepatopancreas of animals from the unpolluted site. On the other hand, Turnberg et al. (1977) did not observe any cadmium increase in the hepatopancreas of lobsters exposed in the laboratory to 3 and 6 ug Cd l^{-1} in water for 60 days. Probably the concentrations below 6 ug Cd l^{-1} allow the lobster to control its internal cadmium concentration when exposed only to the cadmium in water. In the natural environment, food presents an additional route of entry and hence higher exposure to cadmium.

Molluscs: Since the quantity of food available affects both the filtration rate and the food intake (e.g. Schulte, 1975), Poulsen et al. (1982) found that the uptake from water is linearly related to the cadmium concentration in the sea water until a concentration of 800 ug Cd l^{-1}. Borchardt (1983) studied the relative influence of cadmium uptake from water and food (unicellular algae) in Mytilus edulis with double labelled cadmium radioisotopes. Both the uptake from food and from sea water depended on the amount of food available. The cadmium uptake efficiency was high at low food supplies. Fed mussels had a 50% higher cadmium uptake than starved mussels (Jansen and Scholz, 1979). On the other hand Bryan (1980) observed low cadmium body burdens in mussels from areas with high primary production. Assimilation efficiency from food varied between 30 and 60% and from water between 10 to 20%. The half-time of elimination of cadmium taken up from food and from water varied from about 100 to 190 days (Borchardt, 1983). For M. galloprovincialis, Fowler and Benayoun (1974) observed an elimination rate of 300 to 1250 days. However, uptake from food under natural conditions was estimated by Borchardt (1983) at only 0.2 to 0.5% of the total water and food uptake.

Fish: Exposing marine organisms to high concentrations of heavy metals such as cadmium can easily result in artefacts as can be seen from Fig. 6. Comparing the body levels with the concentrations of exposure to cadmium showed that up to a certain concentration the interal body concentration of cadmium remains constant. At concentrations higher than about 1000 ug Cd l^{-1} the cadmium concentrations in the fish increase proportionally to the exposure concentration. Note that the LC-50s of various time periods are all in the "proportional range". Interestingly the LC-50s for less developed oysters and shrimps are at the level where the fish begins to lose control of its internal concentrations. At lower, more realistic concentrations, no appreciable amounts of cadmium were taken up in the muscle tissue of plaice and only the liver concentrations increased after an exposure of 70 days to 5 ug Cd l^{-1} (Von Westerhagen et al., 1978). Similar results were obtained by Pentreath (1977) on plaice and by von Westernhagen et al. (1980). Furthermore, Eisler (1974) found that exposing Fundulus heteroclitus (mummichog or killifish) to radioactive cadmium it was only in the viscera that the radioactivity increased with time. 90% of the whole body activity was lost during 180 days. However, in interpreting the loss data one must keep in mind that uptake from water only often results in a distribution pattern of the metal different from that observed in nature. Pentreath (1977) found that 4 days after feeding plaice with cadmium labelled Nereis about 5% of the radioactivity was associated with the gut walls and none could be detected in the internal organs. The half-time of the cadmium taken up was 100 to 200 days.

5.3 Biogeochemical cycle

Due to a lack of sufficient data, to the uncertainties of many concentrations reported and, most of all, to the lack of data on fluxes it is only possible to come up with a very general qualitative description of the biogeochemical cycles. Nriagu (1980) attempted the description of a global cycle of cadmium (Fig. 7). This figure may however give an idea about relative amounts in sinks and of the fluxes between compartments. The most important inputs come from rivers followed by atmosphere. Atmospheric deposition has been estimated at 140 MT per year per 1 million km^2 of the Western Mediterranean (section 3). Assuming a total world ocean surface of 360 million km^2 Nriagu estimated the atmospheric flux to the world oceans to

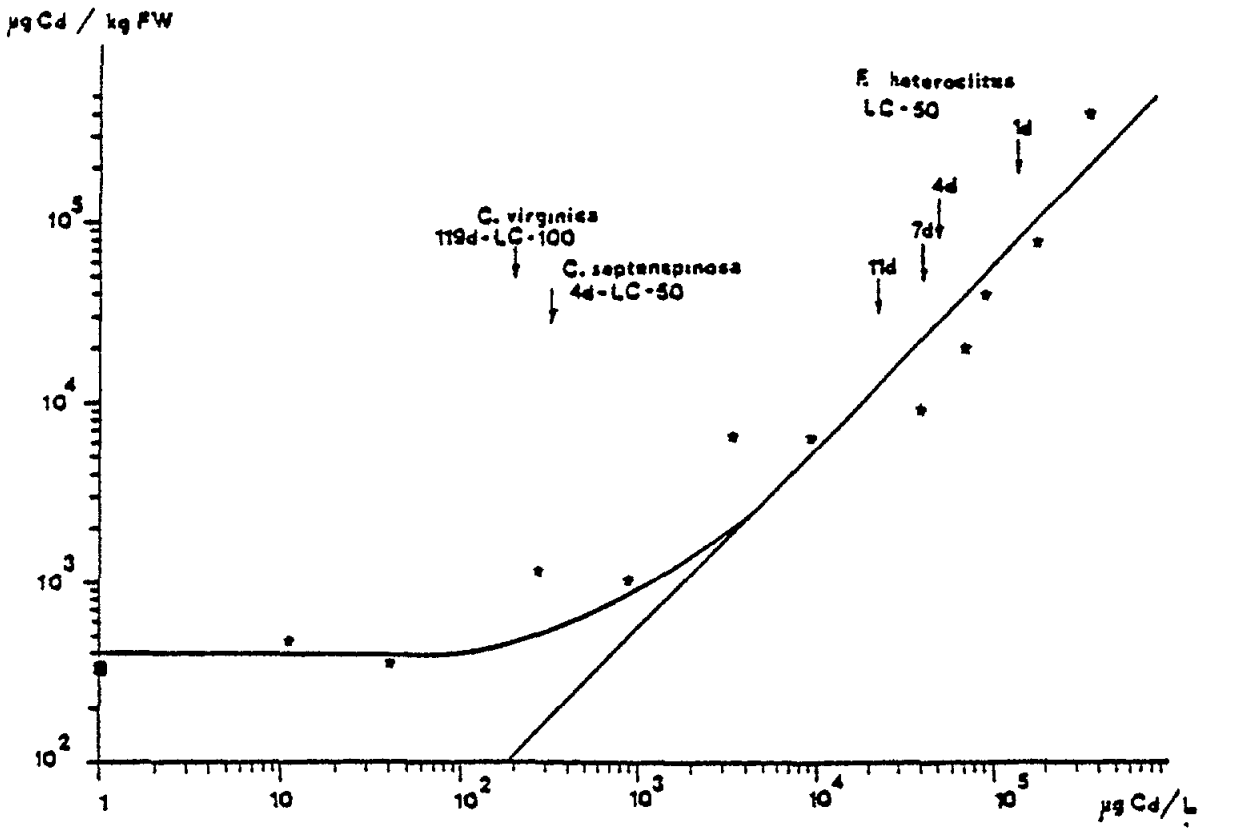

Figure 6. Comparison between cadmium concentration in sea water and in the fish Fundulus heteroclitus. Note: the arrows indicate various LC's for F. heteroclitus, Crassostrea virginica and Crangon septemspinosa (After Bernhard and Zattera (1975) with data from Eisler (1971) and Eisler et al. (1972).

be 2400 MT year^{-1} i.e. about 20 times smaller than the flux into the Western Mediterranean. This is possible since the Western Mediterranean is surrounded by many industries and large cities. General Mediterranean river inputs for cadmium are not available, but the zinc input into the Mediterranean is estimated at about 25000 MT year^{-1} (Helmer, 1977). Assuming that the zinc input is 200 times the cadmium input (section 3.1), this would give a river input of about 100 MT year^{-1} into the entire Mediterranean (including the Black Sea) for about 3 million km^2. From this very approximate estimate it seems that atmospheric input and river input are of the same magnitude. The river inputs are demonstrated in the higher cadmium concentrations observed, especially in the sediments of the river mouths. Other comparisons are difficult to make.

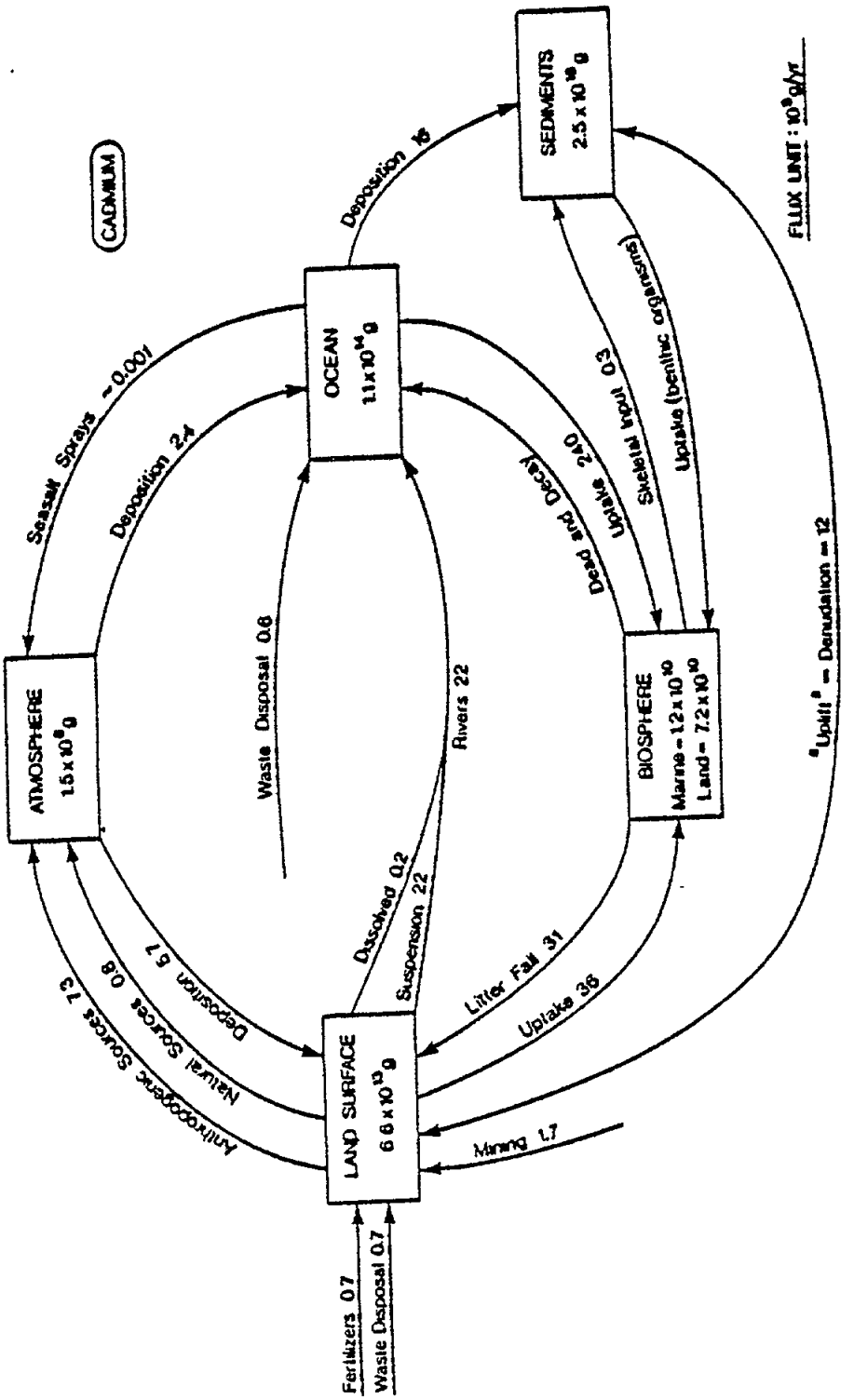

Figure 7. The global cycle of cadmium (Nriagu, 1980).

6. EFFECTS ON MARINE ORGANISMS

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

Evidence presented in section 5.2 shows that the uptake of cadmium in marine organisms depends both on the chemical species of cadmium and on the route of entry into the organism. Organisms which belong to the first trophic level, such as algae and aquatic plants, take up inorganic cadmium directly from the surrounding sea water. Since the first trophic level enriches cadmium by a concentration factor of about 5000 over the concentration in sea water, the uptake of higher trophic levels should occur primarily through the foodchain.

The majority of older data on the toxicity of cadmium deals with its acute toxicity. In order to produce meaningful water quality criteria an application factor was introduced in order to reduce the concentrations at which acute toxicity was observed to the so-called "minimum risk concentrations". In general an application factor of 0.01 was used, but the arbitrariness of this procedure is now recognized generally (Phillips, 1980). In fact, cadmium is slowly accumulated at low concentrations in sea water and therefore, only long-term chronic exposures can be used to estimate the

toxicity of this metal (see also discussion on exposure concentration versus body levels in section 5.2). This explains why only very high concentrations in the range of 10 to 50 mg Cd l^{-1} show any effect in short-term exposure experiments (Phillips, 1980). In fact, long-term effects are noted at less than one thousandth of this concentration in fish. However, even the results of sublethal exposures are often difficult to interpret and comparisons with body levels in bioassays and in organisms living in contaminated environments are needed in order to extrapolate laboratory results to actual situations.

6.1 Algae

The data in Table XIX show that algae have lower cadmium sensitivity than organisms belonging to higher trophic levels because their dominant entry route is from the surrounding water. In unicellular algae effects are observed at the level of 1 ug l^{-1}, but some can withstand concentrations as high as 25 ug Cd l^{-1} without apparent effects. Laboratory cultures can become Cd-tolerable. However, it should be noted that these are effects due to cadmium salts and that in the natural environment most of the cadmium is likely to be associated with organic ligands or particulate matter. As was seen from the discussion in section 5.2 there now exists well confirmed evidence that the ionic species is taken up and that it is the concentration of ionic cadmium that is important in establishing the toxic concentration. If only the total cadmium concentrations are determined, they can be considerably higher than the ionic effective concentrations.

6.2 Crustaceans

Crustaceans can withstand cadmium concentrations between 5 and 10 ug Cd l^{-1} (Table XIX). Different developmental stages can have different cadmium sensitivities. In the crab Eurypassopeus depressus the development up to the megalopa stage was not affected by concentrations of 10 ug Cd l^{-1}, but the following development was delayed and the mortality increased. Experimenting with cadmium additions to an enclosed mesocosm, Kuiper (1981) observed that the copepod population increased; this was due to a reduction in predation by ctenophores when exposed to 5 ug (ionic) Cd l^{-1}. When exposed to 50 ug Cd l^{-1} the number of copepods decreased.

6.3 Molluscs

The range of effective cadmium concentrations on molluscs is reported to be similar to those affecting crustaceans (Table XIX). Establier and Pascal (1983) found that 400 ug Cd l^{-1} were needed in order to reduce the hatching in the cuttlefish (Sepia officinalis). Mihnea and Munteanu (1986) fed Chlamydomonas grown in 0.5 ug Cd l^{-1} to mussels (M. galloprovincialis). They found that the mussels had accumulated 19 to 35% more cadmium than the controls. The highest concentration (1.9 ug Cd g^{-1} FW) was reached by mussels of 4.5 to 7 cm in length.

6.4 Fish

Various influences on development were noted at concentrations as low as 5 ug Cd l^{-1} (Table XIX). Mortality, as well as enzyme and fin regeneration inhibitions were noted at concentrations higher than 10 ug Cd l^{-1}.

Table XIX

Long-term effects of cadmium on marine biota

Conc. ug l^{-1}	species	effect	reference
	ALGAE		
1	Isochrysis galbana	growth inhibition	(1)
1.2	Prorocentrum micans	growth inhibition	(2)
2	Scrippsiella faeroense	no growth inhibition	(3)
5	Prorocentrum micans	growth inhibition	(4)
>10	Prorocentrum micans	increased vacuolation and number lysosomes	(5)
10	Scrippsiella faeroense	growth inhibition	(3)
10	4 phytoplankters	growth inhibition	(6)
25	4 diatoms	no growth inhibition	(7)
25	Skeletonema costatum	growth reduction *	(8)
	CRUSTACEANS		
4.8	Mysidopsis bahia (mysid)	no effect	(9)
5	Mysidopsis bahia	no effect	(10)
6.4	Mysidopsis bahia	reduced reproduction	(9)
10	Eurypassopens depressus (crab)	increased mortality	(11)
10	Mysidopsis bahia	reduced reproduction	(10)
	MOLLUSCS		
5	Crassostrea virginica (oyster)	larvae, delayed develop.	(12)
10	Crassostrea margarita (oyster)	larvae, reduced growth	(13)
5	Mytilus edulis (mussel)	no effect	(14)
10	Mytilus edulis	reduced growth	(14)
400	Sepia officinalis (cuttlefish)	50% reduced hatching	(15)
	FISH		
5	Baltic herring	larvae hatch earlier hatched smaller larvae	(16)
5	Pleuronectes platessa (plaice)	reduced feeding and growth rate	(17)
5	Platichthys flesus (flounder)	reduction in potassium and calcium level in blood	(18)
10	Fundulus heteroclitus (killfish)	inhibition of fin regeneration	(19)
50	Limanda limanda (dab)	30% mortality	(20)

* medium contains TRIS

(1) Li, 1980; (2) Kayser and Sperling, 1980; (3) Kayser, 1982; (4) Prevot, 1980; (5) Soyer and Prevot, 1981; (6) Fisher et al., 1984; (7) Fisher and Pround, 1980; (8) Berland et al., 1977; (9) Nimmo et al., 1978; (10) Gentile et al., 1982; (11) Mirkes et al., 1978; (12) Zaroogian and Morrison, 1981; (13) Watling, 1982; (14) Stromgren, 1982; (15) Establier and Pascual, 1983; (16) Ojaveer et al., 1980; (17) Von Westernhagen et al., 1978; (18) Larsson et al., 1981; (19) Weis and Weis, 1976; (20) Von Westernhagen et al., 1980

7. HUMAN EXPOSURE

7.1 Toxicokinetic properties and doses causing health effects

Humans are exposed to cadmium from ambient air, drinking water, tobacco and food. On an average, approximately 5% of ingested cadmium is absorbed, but people suffering from anaemia or those on a Ca-deficient or protein-deficient diet may absorb cadmium at a much higher rate. Cadmium is transported via blood to other parts of the body. In blood, cadmium is bound to metallothionein which is mainly present in the red blood cells. The cortex of the kidney is the critical organ (see below) and it has in general a cadmium concentration 25% higher than the average in the whole kidney. The kidney contains about 30% of the entire cadmium body burden. Another organ with high cadmium concentration is the liver. Following a long-term low-level exposure to cadmium, about 50% of the cadmium body burden is found in the kidney and the liver. In the muscle tissues only low concentrations of cadmium are detected. The placenta is an effective barrier against cadmium uptake by the foetus and hence at birth the total cadmium body burden is only about 1 ug. Due to the continuous uptake of cadmium and the long biological half-time, humans accumulate cadmium during their life time so that at 50 years the total body burden is 10 to 30 mg. The cortex of the kidney has at that time a concentration of about 15 to 50 mg Cd kg^{-1} FW. The biological half-time of cadmium in the kidney is about 20 years and that in the blood is about 2 to 3 months. The cadmium concentration in the blood of non-smokers is below 1 ug Cd l^{-1}, but it reaches several ug Cd l^{-1} in smokers. Excretion takes place via faeces and urine and comprises only 0.005 to 0.1% per day of the total body burden (GESAMP, 1984; Stoeppler, 1984).

The kidney cortex is the critical organ, i.e. the organ in which the first signs of adverse effects to chronic cadmium intoxication occur. One major sign of this effect is the increased urinary excretion of low molecular weight proteins, such as beta-microglobin and retinol-binding proteins. At the same time, the cadmium concentration in the urine increases markedly. In 1972 a Joint FAO/WHO Expert Committee had recommended a Provisional Tolerable Weekly Intake (PTWI) of 400 to 500 ug Cd per adult person (70 kg weight) (FAO/WHO, 1972). There is still a relative lack of information on epidiemological data and data on dose-response relationship due to intake of cadmium from various sources (WHO, 1976) which explains why WHO has not yet issued health criteria for cadmium. Using a one-compartment model and assuming a 5% absorption of cadmium from food over 50 years, with 30% of the cadmium distributed to the kidney and a release half-time of 20 years, the intake of about 200 to 400 ug Cd day^{-1} (a 1400 to 2800 ug Cd $week^{-1}$) is estimated by a WHO Task Group (1980) to reach the likely critical concentration in the kidney cortex of 200 ug Cd g^{-1} FW. Applying a safety factor of only 5, this would result in a tolerable intake of 40 to 80 ug Cd day^{-1} or 280 to 560 ug Cd $week^{-1}$. A "typical" limit of about 400 ug Cd per week is double the average intake (section 7.4). Recently, Piscator (1985) estimated that an intake of 20 to 130 ug Cd per week is needed for 0.1% of a population to exceed critical renal concentrations. The estimate made by Piscator is only twice the highest average intake observed in Sweden. Consequently Piscator considers the safety margin between average intake and tolerable intake as small.

In a marine context, it may be worthwhile noting that in New Zealand persons consuming large amounts of oysters leading to a daily intake of 200 to 500 ug Cd had disproportionally low blood cadmium levels (McKenzie et al., 1982). Since it has been shown that cadmium in these oysters is bound to metallothionein or similar proteins, this seems to indicate that cadmium bound to metallothionein is distributed differently from unbound cadmium or cadmium associated with other ligands and may not be as toxic as inorganic cadmium.

7.2 Seafood consumption patterns

Unlike the case of mercury, where the main source of intake by man is through the consumption of contaminated seafood, data on the total amount of seafood consumed by Mediterranean populations have a lesser significance, from the practical point of view, in the case of cadmium, as the main sources of intake are food of terrestrial origin and tobacco. An exception to this general statement could be made in the case of mussels and other species recorded as having relatively high levels of cadmium. Based on seafood supply data (considering landings, exports and imports), national averages and percentages of seafood of Mediterranean origin can be estimated (Table XX), but these data are insufficient for an estimate of the risk of cadmium intake, not only because they do not show the actual pattern of consumption at individual level but also because, with the exception of a few species, the concentrations of cadmium encountered are very similar to those in food of terrestrial origin.

Table XX

Estimated average national consumption of fish, fishery products and non-food uses for the years 1979-1981 in Mediterranean and other selected countries (data from FAO 1983 and UNEP/FAO/WHO 1983)

Country	weekly consumption in grams live weight per caput total	% of Mediterranean origin live weight	non-food uses in 1000 MT
Algeria	20	100	-
Cyprus	80	30	-
Egypt	45	10	-
France	230	4	2.4
Greece	155	60	-
Israel	160	8	-
Italy	120	55	3.4
Lebanon	55	25	-
Libya	75	30	-
Malta	200	20	-
Morocco	55	10	103
Spain	300	10	175
Syria	15	10	-
Tunisia	75	100	1.1
Turkey	60	10	101
Yugoslavia	30	45	0.1

World	115	-	19088
Faeroe Island	950	-	100
Iceland	855	-	810
Japan	800	-	1812
USA	155	-	1229
USSR	245	-	2237

Note: Consumption is estimated to be 50 % of the supply taking into consideration export and import. About 90% of the "non-food uses" is estimated to be fish meal.

In the case of cadmium therefore, it is the overall food consumption pattern (rather than that of seafood alone) combined with other habits (such as smoking) which add to the cadmium intake, which would assume significance.

7.3 Direct and indirect cadmium intake through seafood

Direct data in the form of measurements on the amount of cadmium ingested by non-occupationally exposed humans in Mediterranean countries have not been published. The uptake of cadmium through seafood is linked to the cadmium concentrations in the various edible species, and the amount of seafood consumed. In this context, data on the seafood consumption of critical groups in the Mediterranean are relatively sparse. The epidemiological studies conducted on sample populations identified as relatively heavy seafood consumers (Paccagnella et al., 1973; Nauen et al., 1980), were designed for calculation of mercury intake. Similarly, the dietary surveys being conducted in Greece, Italy and Yugoslavia as part of the WHO/FAO/UNEP methylmercury project afford some data on species consumed, but would be meaningless unless correlated to cadmium concentrations in these species.

Indirect uptake of cadmium by human populations can occur through the cadmium contained in fish meal which is used as an additive to farm animal fodder and produced in considerable amounts in certain countries (Table XX), but the amount of cadmium which is introduced through this route should be negligible because of the low cadmium concentration in the marine species used to prepare fish meal.

7.4 Cadmium intake through food of non-marine origin

Man is exposed to cadmium from ambient air, drinking water, tobacco and food. The major source of cadmium for non-occupationally exposed individuals is food to which must be added inhalation of cadmium from cigarette smoking (Stoeppler 1984; GESAMP, 1985). Food contributes from 80 to 90% of cadmium intake for the non-smoker.

Cadmium concentrations in foodstuffs from uncontaminated environments will vary from 1 to 50 ug kg^{-1} for meat, fish and fruit (Table XXI). However, cadmium concentration in the liver and kidney of adult animals ranges from 10 to 1000 ug Cd kg^{-1} with high concentrations reaching even 100 mg Cd kg^{-1} in horses' liver.

The average mean dietary intake of non-occupationally exposed smokers and non-smokers in developed countries (Belgium, New Zealand, Sweden, USA) range from 20 to 130 ug $week^{-1}$. In Japan the intakes are higher: 175 to 400 ug $week^{-1}$ (GESAMP, 1985). Estimates on the weekly intake vary widely from 40 to 660 ug Cd $week^{-1}$ $person^{-1}$. In his review on cadmium, Stoeppler (1984) considers about 140 ug cadmium per week per person as a typical intake. In areas where the general intake through food is low, smoking can be a significant source of cadmium (Fig. 8). Cigarettes contribute 0.1 to 0.2 ug per cigarette to the cadmium intake and in a heavy smoker may contribute an amount of cadmium equal to that taken in with food (Piscator, 1985). The intake from drinking water (< 0.02 ug Cd l^{-1}) with 7 to 15 ug $week^{-1}$ (Piscator, 1985) and from air (25 ng m^{-3}) is insignificant.

Table XXI

Typical cadmium concentrations in food according to recent analyses (Stoeppler, 1984, GESAMP, 1984)

Cd in ug kg^{-1} FW	items	comments
<=200	kidneys and liver of beef, pork and horse, mushrooms	Cd levels in adult animals and mushrooms up to 1 mg kg^{-1}
<= 40	wheat, wheat-bread rice, roots and leafy vegetables	Cd levels in rice vary widely, Cd levels in Japanese rice can be as high as 500 ug kg^{-1}
<= 20	Rye, rye-bread, beans, tomatoes, fruit, eggs freshwater fishes	freshwater fishes and fruit often up to 10 ug kg^{-1}
<= 5	flesh of poultry, pork, beef, marine fishes, wine, beer, fruit juices	
<= 1	milk and milk products, drinking water	Zinc-plated waterpipes can increase Cd levels in drinking water

Note: 0.1 to 0.2 ug Cd is inhaled by smoking one cigarette

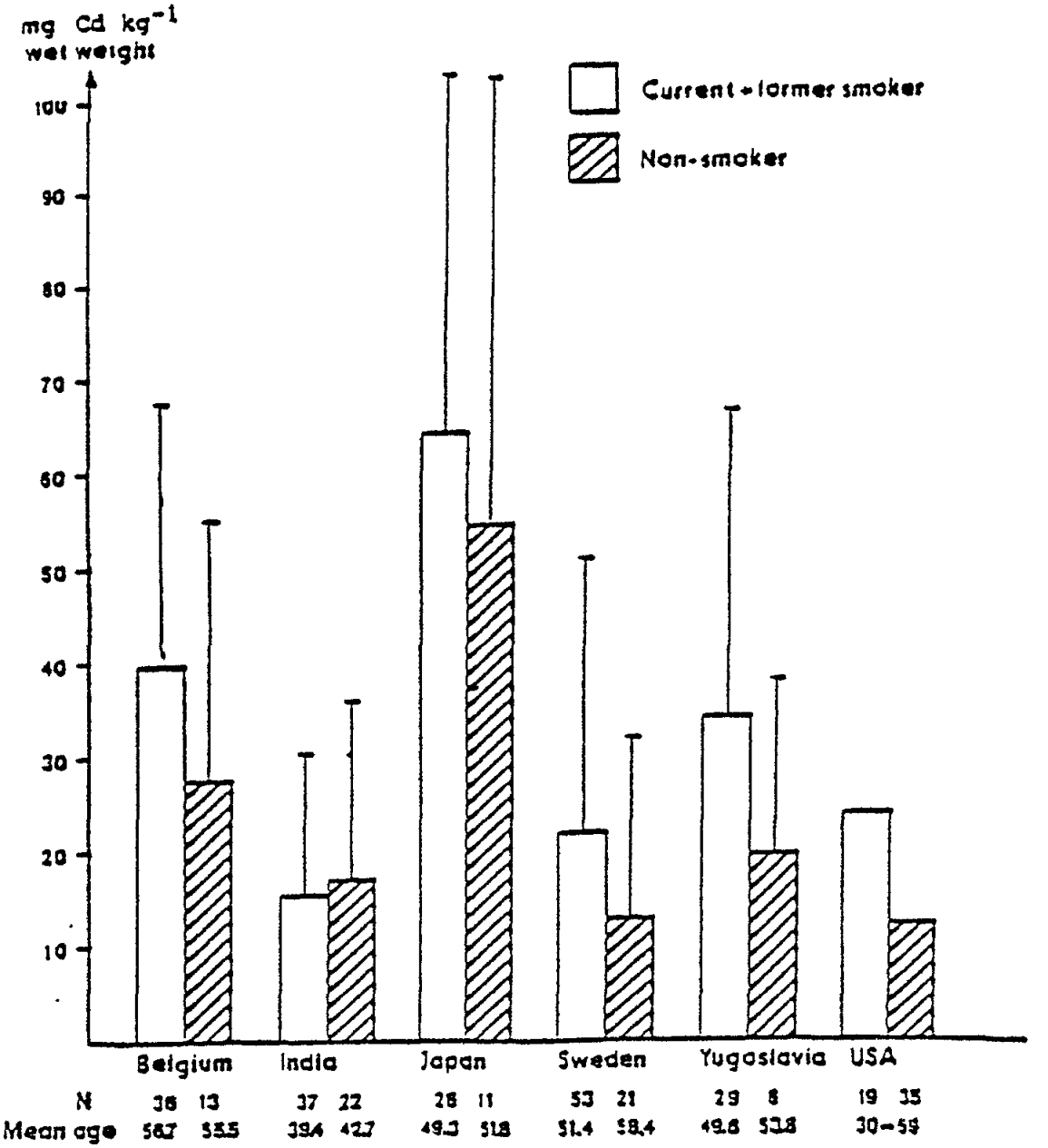

Figure 8. Concentration of Cd in the kidney cortex (geometric mean values with 1.28 times the geometric standard deviation indicated) in relation to smoking habits among the subjects (30-69 years of age) studied in Belgium, India, Japan, Yugoslavia. Number of smokers (including former smokers) and non-smokers, as well as mean age of subjects in each subgroup are indicated under the bars (GESAMP, 1984).

8. RISK ASSESSMENT OF CADMIUM

8.1 Risk to marine biota

Data given in the summaries by Taylor (1981) and IRPTC (1981) indicate that cadmium is not very toxic within short exposure periods, and the 96-h LC_{50}s for a wide range of species are usually in excess of 1 mg Cd l^{-1}. Similarly, chronic effects usually become apparent at concentrations greater than 50 ug Cd l^{-1} (GESAMP, 1984).

However, some species have been reported to be affected at cadmium concentrations less than 15 ug l^{-1} and usually after prolonged exposure under laboratory conditions. These data are included in Table XIX. Results from long-term bioassays show that marine algae are the most sensitive organisms in the marine environment. However, such results are difficult to interpret and comparisons with body levels in bioassays and in organisms living in contaminated environments are needed in order to extrapolate laboratory results to real environmental conditions.

Cadmium concentrations as high as 1.4 ug l^{-1} were reported for Mediterranean coastal waters (Table IX) but these samples were collected near Genova and cannot be representative of the area. Having in mind the values in Tables IX and XIX it can be considered that a value of 0.5 ug Cd l^{-1} should be safe for marine life.

8.2 Risk to humans

The Provisional Tolerable Weekly Intake (PTWI) of 400 to 500 ug cadmium per week per person proposed in 1972 is generally accepted by the international scientific community. Two US regulatory agencies have encouraged FAO and WHO to reassess the PTWI for adults, which they consider as highly conservative and to develop a PTWI for infants and children due to the cumulative nature of cadmium in the body, the greater absoprtion of cadmium by the young and the protracted period of time for the development of cadmium-induced renal damage. On the other hand, although some experts consider the PTWI too high (section 7.1) and suggest that a more conservative intake level would be slightly lower at about 300 ug Cd per week per person.

Table XXII shows the weekly intake of cadmium that could be reached by different combinations of fish consumption and cadmium concentration in different seafood species. The conclusions drawn from this table are that persons who are low seafood consumers (1 to 2 meals per week) would appear to run no risk of exceeding the PTWI, even considering that the main sources are not of marine origin, provided they do not eat the highly-contaminated species on a regular basis. For high seafood consumers the situation changes. Assuming a person consumes, over long-term periods, 14 meals of seafood per week, the seafood should not contain more than about 50 ug Cd kg^{-1} FW. This concentration is typical for the majority of the marine fishes from the Mediterranean, but is exceeded by mussels from polluted areas (see Tables XV and XVI). Persons habitually consuming large amounts of mussels from cadmium contaminated areas may easily exceed the PWTI, especially in view of the other important sources of intake. For example, smoking 20 cigarettes per day would contribute about 20 ug cadmium per week (Stoeppler, 1984). Thus a heavy smoker ($>$40 cigarettes day^{-1}) will obtain about the same amount of cadmium from smoking as the heavy seafood consumer from consumption of marine fish. In conclusion, terrestial food and cigarettes constitute a very important source of cadmium, but heavy seafood eaters, especially if they eat large amounts of mussels and are also heavy smokers can easily exceed the PWTI.

Table XXII

Estimate of effective human exposure to camdium from consumption of seafood

Cd level in seafoods ug Cd kg^{-1} FW	1 150	2 300	3 450	4 600	5 750	6 900	7 1050	14 2100	no. of meals g of seafood consumed
10	1.5	3.0	4.5	6	7.5	9	10.	21	
25	3.8	7.5	11.3	15	19	22.5	26	52.5	
50	7.5	15.0	22.5	30	37.5	45	52	105	
75	11.2	22.5	33.8	45	56	67.5	79	157.5	
100	15.0	30.0	45.	60	75	90	105	210	
125	18.8	37.5	56.2	75	90	112.5	131	262.5	
150	22.5	45.0	67.5	90	112.5	105	157.5	315	
200	30	60	90	120	150	180	110	420	
300	45	70	130	180	223	110	310	630	
500	75	150	225	300	375	450	525	1050	
750	112	225	338	450	562	675	788	1575	
1000	150	300	450	600	750	900	1050	2100	
1250	188	375	562	750	938	1125	1312	2625	
1500	225	450	675	900	1125	1050	1575	3150	

9. CONCLUSIONS ON THE CADMIUM ASSESSMENT

The analytical uncertainty of many measurements is great, especially in air and sea water but also in sediments, because reference materials and reference standards at the levels at which cadmium occurs in the marine environment are only available for biota and sediments.

Although many data have been collected, the different areas of the Mediterranean have been surveyed very unevenly. A few "typical" concentrations have been compiled in Table XXIII.

Air: the data available up to now are limited to the western Mediterranean. The data indicate that the cadmium levels of open sea areas are lower then overland. Near cities, due to anthropogenic air pollution, air has markedly higher cadmium concentrations than rural air.

Sea water: The lack of proper quality control of the sea-water measurements makes it very difficult to compare data from different authors. Some concentrations are very high and need confirmation. Some authors have observed a vertical "nutrient-type" distribution of cadmium, i.e. a depletion in the upper layer, but others found that the cadmium concentration remains about constant with depth. The cadmium concentration in coastal waters is not always higher than in open-sea areas, but in some polluted water extremely high cadmium concentrations have been determined. This needs to be confirmed.

Sediments: cadmium background concentration has been estimated at about 0.15 mg Cd kg^{-1} DW. Much higher concentrations have been found in lagoons polluted by industrial outfalls, at river mouths and near cities. Sediments can be a good pollution indicator, if the mineralogical composition of the sediment is also considered.

Biota: A considerable amount of data on seafood has been obtained for certain areas during the MED POL projects. For some areas, the data base available is still very limited. In general, the concentrations found in seafood from the Mediterranean are not different from those observed in the North-West Atlantic. Mussels, probably due to anthropogenic inputs, have the highest cadmium levels followed by crustaceans. This pattern is similar in the Mediterranean and the Atlantic. As in humans where the kidney is the critical organ, also in marine organisms, the excretory organs (hepatopancreas, kidneys etc.) have the highest cadmium concentrations.

Natural sources: Areas with higher than average cadmium concentrations (mining areas and their surroundings) should also influence the cadmium concentration in the biota living in the adjacent coastal areas. There is evidence from non-Mediterranean pelagic marine organisms that high cadmium body levels can be observed in organisms far remote from any anthropogenic pollution source.

Anthropogenic sources: The release of cadmium from industrial complexes shows that cadmium is highly enriched in sediments and cadmium concentrations in sediments may serve as indicators for cadmium pollution.

Effect on biota: The toxicity is only determined by adding cadmium salts to sea water. The toxicity of cadmium in food has not been tested. Since cadmium is most probably bound to metallothionein-like proteins in the food of marine organisms, its toxicity is difficult to assess. When in sea water, ionic cadmium is the effective toxic cadmium species. If complexing agents such as EDTA are present, the toxicity of cadmium is reduced since only ionic cadmium is effective. The lowest apparent concentration which caused an effect is given as approximately 1 ug ionic Cd l^{-1}. Marine algae are the most sensitive species tested. However 5 times higher concentrations are effective in interfering with reproduction and the embryonal development of species belonging to higher taxonomic groups. The influence of cadmium release on marine ecosystems cannot be evaluated due to lack of relevant data. Future studies on the effective toxic concentrations should be accompanied by data on the actual levels to which the organisms are exposed in the bioassay. The test organisms should not only be exposed to dissolved cadmium in water, but the intake routes through which food must be investigated. This means that the cadmium concentrations and the chemical species which are effective must be determined by chemical analysis of the sea water, in the food and in the body tissues of the organisms and in their target organs, because these data may be used to compare body levels observed in the laboratory with body levels of organisms living in polluted areas.

Risk to humans: Food is the main source of cadmium for humans who are non-occupationally exposed, and the intake from terrestrial food is generally much more important than that from seafood even for high seafood consumers. An important cadmium source is smoking. A heavy smoker (>40 cigarettes day^{-1}) will receive as much cadmium from cigarettes as a person eating 12 meals of marine fish a week. Obviously, heavy smokers and heavy seafood

Table XXIII

Some cadmium levels in the Mediterranean and in other selected areas which with the present state of knowledge may be considered typical.

Mediterranean:		
Air:	open sea	0.4 - 2 ng Cd m^{-3}
	cities	30 - 200 ng Cd m^{-3}
	total deposition	10 - 50 ng Cd cm^{-2} $year^{-1}$
Sea water:	open-sea	5 - 150 ng Cd l^{-1}
	coastal	up to 2000 ug Cd l^{-1}
Sediments:	background	0.15 ug Cd kg^{-1} DW
	polluted lagoon	up to 50 ug Cd kg^{-1} DW
Plankton:	open-sea	2000 ug Cd kg^{-1} DW (> 400 ug Cd kg^{-1} FW)
	coastal	10000 ug Cd kg^{-1} DW (>2000 ug Cd kg^{-1} FW)
Crustaceans:		50 ug Cd kg^{-1} FW
Molluscs:	Mytilus (coastal)	40-2000 ug Cd kg^{-1} FW
Fish:	Mullus barbatus	20-50 ug Ca kg^{-1} FW
	M. surmuletus	150 ug Cd kg^{-1} FW
Non-Mediterranean:		
Air:	open sea	0.02 - 2.5 ng Cd m^{-3}
	precipitation	0.004- 1.2 ng Cd l^{-1}
total deposition		
	open ocean	5 ng Cd cm^{-2} $year^{-1}$
	North Sea	20 - 85 ng Cd cm^{-2} $year^{-1}$
	Baltic Sea	13 - 20 ng Cd cm^{-2} $year^{-1}$
Sea water:	open sea	10 - 70 ng Cd l^{-1}
Crustaceans:	ICES area	20 -1000 ug Cd kg^{-1} FW
Molluscs:	Mytilus, ICES area	5 -1060 ug Cd kg^{-1} FW
Fish:	ICES area	20 - 60 ug Cd kg^{-1} FW
	Oslo Commission	1000 ug Cd kg^{-1} FW

eaters are specially exposed; another risk group comprises of persons having a preference for the kidneys and liver of farm animals. The Provisionally Tolerable Weekly Intake (PTWI) was estimated in 1972 by an FAO/WHO Expert Committee at 400 to 500 ug cadmium per person per week. Recent estimates suggest that these limits may be too high. In any case, the limits are close to the average intake of persons not exposed occupationally. There exists a scarcity of data on cadmium levels in humans and the influence of cadmium exposure on non-occupationally exposed persons and cadmium concentration in their diet. Since the average cadmium intake from mainly terrestrial food (and from cigarettes) is only slightly lower than the tolerable intake, every effort should be made to reduce the cadmium intake in general, including that through marine food. National surveys are urgently needed in order to identify persons who ingest high amounts of cadmium, mainly from terrestrial food but also from seafood and as a result, to enable appropriate action to be taken to safeguard their health (see section 7.4).

II. CONTROL MEASURES

10. EXISTING INTERNATIONAL AND NATIONAL CONTROLS AND MEASURES TO PREVENT CADMIUM POLLUTION

The information on existing national provisions in the Mediterranean has been received from the national focal points. The only international provisions covering also Mediterranean countries are those of the European Economic Community and appear in section 10.2.

10.1 Existing national provisions

Table XXIV summarizes the information provided by the MED POL national coordinators on maximum permissible levels of cadmium in seafood applying in the various countries. Table XXV lists the information received on water quality criteria and effluent standards in force.

Table XXIV

Maximum limits of permissible cadmium levels in seafood in Mediterranean countries

	Year of enactment	Maximum permissible concentration	Comments
Albania	*	*	
Algeria	*	*	
Cyprus	-	No	
European Community	-	No	
Egypt	*	*	
France	*	*	
Greece	*	*	
Israel			
Italy	*	2 mg kg^{-1}	indicative for cephalopods
Lebanon	*	*	
Libya	*	*	
Malta	-	No	
Monaco	*	*	

Table XXIV (cont.)

	Year of enactment	Maximum permissible concentration	Comments
Morocco	*	*	
Spain	*	*	
Syria	*	*	
Tunisia	*	*	
Turkey	-	No	
Yugoslavia	1983	0.1 mg Cd-T kg^{-1}	fresh fish
		1.0 mg Cd-T kg^{-1}	fresh tuna, shells and crabs
		0.15mg Cd-T kg^{-1}	canned fish
		1.5 mg Cd-T kg^{-1}	canned tuna, shells and crabs

* = no information available
- = not applicable
No= no criteria or standards

Table XXV

Water quality criteria and effluent standards in force in Mediterranean countries according to information received from the National Co-ordinators for MED-POL

	Year of enactment	Maximal Cd conc. in ug Cd l^{-1}		Remarks
		Water Quality Criteria	Effluent Standard	
Albania	*	*	*	
Algeria	*	*	*	
Cyprus	-	No	No	
Egypt	*	*	*	
France				the limits of the European Community apply
Greece				the limits of the European Community apply
Israel				
Italy			20	the limits of the European Community apply

Table XXV (cont.)

	Year of enactment	Maximal Cd conc. in ug Cd l^{-1} Water Quality Criteria	Effluent Standard	Remarks
Lebanon	*	*	*	
Libya	*	*	*	
Malta	*	No	10	
Monaco				the limits of the European Community apply
Morocco	*	*	*	
Spain				the limits of the European Community apply
Syria	*	*	*	
Tunisia	*	*	*	
Turkey	*	10 ug Cd l^{-1}	2000	Only set for discharges into sewage systems with complete treatment or discharge into deep waters
			100	Metal industry (ceramics and other raw materials production
			150	Raw material for dye production
			120	Petrochemical industry
			100	Miscellaneous industries
			600	Domestic wastewaters
Yugoslavia	1984	2 ug l^{-1}	No	For categories I to II
		5 ug l^{-1}	No	For categories III to IV of effluents

* = no information available
\- = not applicable
No = no criteria or standards

10.2 Existing international provisions

The European Economic Community has issued in 1983 a Council directive on limit values and quality objectives for cadmium discharges (83/513/EEC) in the framework of Directive 76/464/EEC which concerns pollution caused by certain dangerous substances discharged into the aquatic environment. Annexes I-IV of this directive appear in Table XXVI. In Annex I there are specific limit values for each type of industry which must be applied by the Member States unless they opt to employ the quality objectives of Annex II. The directive does not specify any limit values for industries manufacturing phosphoric acid and/or phosphatic fertilizers from phosphatic rock but this fact does not release the countries from their obligation to fix emission standards for these discharges.

Table XXVI

Annex I to IV of Council Directive 83/513/EEC of 26 September 1983 on limit values and quality objectives for cadmium discharges (O.J. L291 of 24/10/83)

Annex I

Limit values, time limits and verification frequencies and procedures for discharges of cadmium.

1. Limit values and time limits

Industrial sector (1)	Unit of measurement	Limit values which must be complied with as from	
		1.1.1986	1.1.1989(2)
1. Zinc mining, lead and zinc refining, cadmium metal and non-ferrous metal industry	Milligrams of cadmium per litre of discharge	0.3(3)	0.2(3)

(1) Limit values for industrial sectors not mentioned in this table will, if necessary, be fixed by the Council at a later stage. In the meantime the Member States will fix emission standards for cadmium discharges autonomously in accordance with Directive 76/464/EEC. Such standards must take into account the best technical means available and must not be less stringent than the most nearly comparable limit value in this Annex.

(2) On the basis of experience gained in implementing this Directive, the Commission will, pursuant to Article 5 (3), submit in due course to the Council proposals for fixing more restrictive limit values with a view to their coming into force by 1992.

(3) Monthly flow-weighted average concentration of total cadmium

Table XXVI (cont.)

Industrial sector (1)	Unit of measurement	Limit values which must be complied with as from	
		1.1.1986	1.1.1989(2)
2. Manufacture of cadmium compounds	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	0.5(4)	(5)
3. Manufacture of pigments	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	0.3(4)	(5)
4. Manufacture of stabilizers	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	0.5(4)	(5)
5. Manufacture of primary and secondary batteries	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	1.5(4)	(5)
6. Electroplating (6)	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	0.3(4)	(5)
7. Manufacture of phosphoric acid and/or phosphatic fertilizer from phosphatic rock(7)		-	-

(4) Monthly average

(5) It is impossible for the moment to fix limit values expressed as load. If need be, these values will be fixed by the Council in accordance with Article 5 (3) of this Directive. If the Council does not fix any limit values, the values expressed as load given in column "1.1.1986" will be kept.

Table XXVI (cont.)

(6) Member States may suspend application of the limit values until 1 January 1989 in the case of plants which discharge less than 10 kg of cadmium a year and in which the total volume of the electroplating tanks in less than 1.5 m^3, if technical or administrative considerations make such a step absolutely necessary.

(7) At present there are no economically feasible technical methods for systematically extracting cadmium from discharges arising from the producion of phosphoric acid and/or phosphatic fertilizers from phosphatic rock. No limit values have therefore been fixed for such discharges. The absence of such limit values does not release the Member States from their obligation under Directive 76/464/EEC to fix emission standards for these discharges.

2. Limit values expressed as concentrations which in principle must not be exceeded are given in the above table for the industrial sectors 2, 3, 4, 5 and 6. In no instance may limit values expressed as maximum concentrations be greater than those expressed as maximum quantities divided by water requirements per kilogram of cadmium handled. However, because the concentration of cadmium in effluents depends on the volume of water involved, which differs for different processes and plants, the limit values, expressed in terms of the quantity of cadmium discharged in relation to the quantity of cadmium handled, in the above table must be complied with in all cases.

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

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

This procedure must provide for the taking and analysis of samples and for measurement of the flow of the discharge and the quantity of cadmium handled.

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

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

However, a simplified monitoring procedure may be instituted in the case of industrial plants which do not discharge more than 10 kg of cadmium per annum. In the case of industrial electroplating plants, a simplified monitoring procedure may only be instituted if the total volume of the electroplating tanks is less than 1.5 m^3.

Table XXVI (cont.)

Annex II

Quality objectives

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

1. The following quality objectives (1), which will be measured sufficiently close to the point of discharge, are fixed, with the object of eliminating pollution within the meaning of Directive 76/464/EEC and pursuant to Article 2 of that Directive (2):

1.1. The total cadmium concentration in inland surface waters affected by discharges must not exceed 5 ug/litre.

1.2. The concentration of dissolved cadmium in estuary waters affected by discharges must not exceed 5 ug/litre.

1.3. The concentration of dissolved cadmium in territorial waters and in internal coastal waters other than estuary waters affected by discharges must not exceed 2.5 ug/litre.

1.4. In the case of waters used for the abstraction of drinking water, the cadmium content must conform to the requirements of Directive 75/440/EEC (3).

2. In addition to the above requirements, cadmium concentrations must be determined by the national network referred to in Article 5 and the results compared with the following concentrations (2):

2.1. In the case of inland surface waters, a total cadmium concentration of 1 ug/litre.

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(1) The cadmium concentrations indicated in 1.1, 1.2 and 1.3 are the minimum requiremts necessary to protect aquatic life.

(2) With the exception of quality objective 1.4, all concentrations relate to the arithmetic mean of the results obtained over one year.

(3) Directive 75/440/EEC concerns the quality required of surface water intended for the abstraction of drinking water in he Member States (OJ No L 194, 25.7.1975, p.26). It provides for a mandatory cadmium value of 5 ug/litre on the basis of 95% of the samples taken.

Table XXVI (cont.)

2.2. In the case of estuary waters, a dissolved cadmium concentration of 1 ug/litre.

2.3. In the case of territorial and internal coastal waters, other than estuary waters, a dissolved cadmium concentration of 0.5 ug/litre.

If these concentrations are not complied with at any one of the points on the national network, the reasons must be reported to the Commission.

3. The concentration of cadmium in sediments and/or shellfish, if possible of the species Mytilus edulis, must not increase significantly with time.

4. Where several quality objectives are supplied to waters in an area, the quality of the waters must be sufficient to comply with each of those objectives.

Annex III

Reference methods of measurement

1. The reference method of analysis used for determining the cadmium content of waters, sediments and shellfish is atomic absorption spectrophotometry after preservation and suitable treatment of the sample.

The limits of detection (1) must be such that the cadmium concentration can be measured to an accuracy (1) of ± 30% ad a precision (1) of ± 30% at the following concentrations:

- in the case of discharges, one-tenth of the maximum permitted concentration of cadmium specified in the authorization,
- in the case of surface water, 0.1 ug/litre or one-tenth of the cadmium concentration specified in the quality objective, whichever is the greater,
- in the case of shellfish, 0.1 mg/kg, wet weight,
- in the case of sediments, one-tenth of the cadmium concentration in the sample or 0.1 mg/kg, dry weight, with drying being carried out between 105 an 110 ^{o}C at constant weight, whichever value is the greater.

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

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

Table XXVI (cont.)

Annex IV

Monitoring procedure for quality objectives

1. For each authorization granted in pursuance of this Directive, the competent authority will specify the restrictions, monitoring procedure and time limits for ensuring compliance with the quality objective(s) concerned.

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

   - the points of discharge and the means of dispersal,

   - the area in which the quality objective is applied,

   - the location of sampling points,

   - the frequency of sampling,

   - the methods of sampling and measurement,

   - the results obtained.

3. Samples must be sufficiently representative of the quality of the aquatic environment in the area affected by the discharges, and the frequency of sampling must be sufficient to show any changes in the aquatic environment, taking into account, in particular, natural variations in the hydrological regime.

11. SCIENTIFIC RATIONALE FOR ESTABLISHING RESTRICTION AND CONTROL MEASURES

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

The enforcement of legal limits on the permissible concentration of any substance in seafood is normally practised when seafood constitutes the main source of human intake of such substance or, when this is not the case, such limit is usually combined with complementary limits on the permissible concentration of the 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 average amount consumed, with a built-in safety factor. It is not, and cannot feasibly be, designed to guarantee freedom from adverse health effects to those individuals or population-sectors, who consume amounts significantly exceeding calculated average values. Separate measures have to be taken with regard to these population-sectors.

In the case of cadmium (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 cadmium containing effluents in the vicinity. In this case, therefore, a limitation on the amount of camdium discharged into the marine environment will alleviate the general position, as long as the alternative means of disposal employed does not result in a proportionate increase in the concentration of cadmium in other sources of intake.

The only Mediterranean country which is reported to have a legal limit for cadmium in seafood is Yugoslavia (ranging from 0.1 to 1.5 mg cadmium kg^{-1} of seafood, depending on the type). Italy has an indicative limit of 2 mg kg^{-1} for cephalopods. Other Mediterranean countries may very well find it advisable to impose similar restrictions, particularly in the case of those species of seafood showing relatively high cadmium concentrations. However, such restrictions would be determined entirely by local circumstances, considering also the relative amounts taken in from other sources.

There is therefore a sound scientific basis for imposing an upper limit on cadmium 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 justifiable at national or local, rather than regional level. Even more important, it should be recognized that, with respect to intake from seafood cadmium presents a sectorial rather than a general hazard, necessitating the protection of specific individuals and population groups. The main measures taken, therefore, would by their very nature, have to be recommendatory rather than statutory.

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

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

In section 8.1 this value has been estimated to be 0.5 ug (as total Cd) l^{-1}.

Taking into account the dilution factor and the fact that jet diffusers are employed in effluent disposal, a maximum concentration of 0.2 mg Cd l^{-1} in such effluent can be tolerated.

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

Little experience on the release of cadmium from the cadmium handling industry has been reported, but it has been shown that lobsters caught near a lead smelter were highly contaminated while at a distance of about 20 km from the release point the cadmium concentrations in lobsters returned to background (section 4.5). Any additional cadmium releases into the same marine environment in a range of 10 km should be considered in the total amounts to be released per unit time.

No experience has been reported on changes in cadmium levels following the limitation of cadmium releases in to a previously cadmium-polluted marine ecosystem, although a reduction of cadmium levels in the environment should be expected. Monitoring the compliance with limitations on cadmium discharges by existing plants should result in a trend of decreasing cadmium concentrations in sediments and biota. Tentatively it is suggested that what should be achieved is a decrease to half the cadmium concentration in sediment and in biota every 5 years until levels are reached which do not exceed background levels by more than 50%.

Special attention should be paid to the food habits of those fishermen and their families who obtain all or large amounts of their seafood from heavily contaminated areas. A special survey to identify these consumers should be carried out in order to guarantee that they do not exceed the PTWI considerably. Limiting fishing activities in such areas could be considered until "safe" levels have been reached. In this regard, any action taken should be based on a calculation of cadmium intake from other sources, in order to ensure that any additional intake through seafood would not result in exceeding tolerable limits.

12. REQUIREMENTS FOR CONTROL AND FOR REDUCTION OF POLLUTION EFFECTS

12.1 Marine ecosystems

In order to achieve the water quality objective specified in section 11.2:

(a) an effluent concentration of 0.2 mg total cadmium l^{-1} would have to be set as a limit value.

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

(c) the cadmium concentration in sediments and resident biota in an area at a radius of 5 km from the outfall structures should not increase more than 50% above background levels which are to be determined before the waste discharges from the new plant begins. In the case of an existing plant, concentration of total cadmium in sediments and biota should decrease with a half-time of 5 years until levels less than 50% above background are reached. The background levels should be determined in an unpolluted, ecologically similar area.

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

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

- by monitoring the cadmium concentration in the sea water outside the mixing zone at monthly intervals to ensure concentrations below 0.5 ug Cd l^{-1}.

- by monitoring the cadmium concentrations in the sediments outside the mixing zone at monthly intervals. These concentrations must be less than 50% above background levels or decrease with a half-time of 5 years as specified in paragraph (c).

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

12.2 Human health

The overall criterion for the protecton of human health from excessive cadmium intake should be based on the Provisional Tolerable Weekly intake discussed in section 10.2, and should take all sources of intake of cadmium 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 section 12.1 above (which would contribute to amelioration of the position by reducing the overall amount of cadmium in the marine environment).

(a) the monitoring of species of seafood to determine their cadmium content;

(b) the identification of areas where the current concentrations of cadmium in edible species of seafood would pose a health problem, taking into account cadmium intake from other sources;

(c) the imposition of legal limits on the cadmium content of seafood in such areas, or any other restrictions considered appropriate under prevailing conditions, should the local situation so demand;

(d) the formulation and implementation of advisory and recommandatory 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 more general nature.

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