



REGIONAL SEAS

GESAMP:

***Cadmium, lead and tin
in the marine environment***

UNEP Regional Seas Reports and Studies No. 56

GESAMP Reports and Studies No. 22

Prepared in co-operation with



United Nations



FAO



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This document has also been issued by WHO in 1985 as GESAMP (IMO/FAO/UNESCO/WMO/WHO/IAEA/un Joint Group of Experts on the Scientific Aspects of Marine Pollution), Review of potentially harmful substances - cadmium, lead and tin. Reports and Studies, GESAMP, No. 22: 114 p.

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PREFACE

GESAMP, the Joint Group of Experts on the Scientific Aspects of Marine Pollution, was established in 1969 and is today co-sponsored by the International Maritime Organization (IMO), Food and Agriculture Organization of the United Nations (FAO), United Nations Educational, Scientific and Cultural Organization (UNESCO), World Meteorological Organization (WMO), World Health Organization (WHO), International Atomic Energy Agency (IAEA), United Nations and United Nations Environment Programme (UNEP). According to its present terms of reference, the functions of GESAMP are:

- to provide advice relating to the scientific aspects of marine pollution ^{1/}; and
- to prepare periodic reviews of the state of the Marine environment as regards marine pollution and to identify problem areas requiring special attention.

Since its beginning GESAMP involved a large number of experts as members of GESAMP or GESAMP Working Groups and produced, at the request of the sponsoring organizations, numerous reports ^{2/}.

This document reproduces the substantive part of the report of the GESAMP Working Group on Review of Harmful Substances, approved by the fourteenth session of GESAMP (Vienna, 26 - 30 March 1984).

The Working Group was chaired consecutively by Messrs B.H. Ketchum, A. Jernelöv, and L. Friberg. The following experts participated in the preparation of the report: Dr. B.G. Bennett, Prof. L. Friberg, Prof. A. Furtado Rahde, Prof. A. Jernelöv, Mr. R. Lloyd, Dr. L. Magos, Prof. S.P. Meyers, Dr. A. Oskarsson, Dr. P.M. Sivalingam, Prof. G. Tomassi, Dr. H. Galal-Gorchev, Dr. M. Gilbert, Dr. R. Helmer, Dr. J. Parizek, and Dr. G. Vettorazzi.

The Working Group was requested

- to prepare short and referenced reviews on selected substances which include an assessment of the following factors:
 - (a) the total amount of the particular substance(s) which reach(es) the marine environment (on a local, regional, and global scale) with particular attention being given to the relative importance of land-based sources;

^{1/} GESAMP defined marine pollution as "introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea-water, and reduction of amenities."

^{2/} V. Pravdic: GESAMP, The First Dozen Years. UNEP, 1981.

- (b) the fate (transport, distribution, and transformation) of the substance in the marine environment; and
 - (c) the effects of the substance on the marine environment and adjacent coastal areas, including direct and indirect effects on living resources, human health and amenities;
- to produce a scientific evaluation of the harmful effects of substances released into the marine environment on living resources, human health, aesthetics, and other legitimate uses of the marine environment and adjacent coastal areas.

The activities of the Working Group were organized by WHO, acting as the "lead agency". The Working Group was jointly sponsored by WHO, FAO, and UNEP.

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I. INTRODUCTION

1. Evaluation Mechanisms

From an examination of data profiles by UNEP's International Register of Potentially Toxic Chemicals (IRPTC), other data profiles, and available critical reviews of published data, significant papers were selected by the Working Group for thorough evaluation. These papers, together with recent and pertinent publications, then formed the basis of this review. It is recognized, however, that these papers provide only a partial coverage of the world literature. Information was lacking in several areas essential to an environmental hazard evaluation of cadmium, lead, and zinc, and these areas were identified in the review.

2. Working Procedures of the Group

The method and approaches applied by the Working Group were discussed and agreed upon at a planning session in Stockholm, 24-25 September, 1982. This was attended by the chairmen of GESAMP and of the Working Group, and by international agency representatives.

For each substance, selected experts prepared draft sections of the review. The reviews were then critically examined and revised by the Working Group members (Annex I). The final draft was submitted to GESAMP for consideration, comments, and adoption.

3. Quality of Data Base

3.1 Analytical quality control

Many studies conducted in the various countries aimed at evaluating normal and elevated levels of trace metals in different media. Unfortunately, most published reports lack quality assurance data, and valid comparisons cannot, therefore, be made. Furthermore, results from several inter-laboratory comparisons amplify the need for quality control. A review of such comparison studies, with particular emphasis on lead and cadmium in blood, has recently been published in connection with a UNEP/WHO Biological Monitoring Project on Assessment of Human Exposure to Lead and Cadmium through Biological Monitoring (Vahter, 1982). Various intercalibration exercises with those laboratories engaged in the determination of trace metals in commercially important marine organisms from the North Atlantic were also organized, since 1971, by ICES, the International Council for Exploration of the Sea (Topping, 1983). These reviews clearly show that errors may be large even in "experienced" laboratories. Since 1975, the IAEA's International Laboratory of Marine Radioactivity has also operated a large global analytical quality control programme for metals and chlorinated hydrocarbons in marine organisms and sediments. A similar programme has been run by the Intergovernmental Oceanographic Commission for Seawater Samples.

The introduction of sophisticated and increasingly sensitive analytical techniques has made it possible to measure trace substances in extremely low concentrations. Simultaneously, however, the risks of interference from competing factors has increased considerably. Although the awareness of the need for quality control has also increased during recent years, it is not possible to state, generally, that analyses carried out during the last 5-year period, for example, are always more reliable than earlier analyses.

Analytical problems may occur with any matrix to be examined. Particular problems arise, however, when analysing biological media or matrices which have very low trace metal concentrations (picograms/g). Schaule & Patterson (1980) showed that, for example, the lead concentrations in seawater samples have been overestimated by factors of up to 5000 and, that the lead concentrations reported for marine organisms are, with very few exceptions, several orders of magnitude higher than the actual concentrations present. These high concentrations are caused by the sample becoming contaminated during analysis. The importance of implementing rigid quality assurance programmes was amplified in 2 recent trace metal programmes sponsored by UNEP/WHO. One measured lead and cadmium in blood, and cadmium in kidneys (Vahter, 1982; Friberg & Vahter, 1983). The other measured trace metals in food (National Food Administration, 1982). In the

first programme, it was rare that a laboratory met the criteria for data acceptance throughout the training phase, and gross errors were often recorded. The food study noted that the results of current analytical quality control analyses allowed few conclusions to be drawn concerning the reliability of previously collected data. In addition to the various forms of analytical error, there is the possibility of contaminating biological samples, for example, by use of unsuitable sample collection vials and contaminated chemicals. Furthermore, errors due to adsorption and desorption on the walls of containers may cause inaccurate results.

The various sources of error which are possible make it necessary to exercise great caution when evaluating analytical data. In particular, it is more the exception than the rule that data on quality assurance are presented as part of published studies. Such caution has been exercised in the evaluation carried out by the Working Group, but there is still no guarantee that all the data used in this evaluation are completely valid. If rigid quality assurance criteria had been required, the analytical data available for use in the evaluation would have been extremely limited.

3.2 Ecotoxicological quality aspect

Experiments on marine organisms were carried out using many different procedures and techniques, and the usefulness of the results to the present review was critically examined. In particular, only a few experiments offered analytical confirmation of the concentrations and various forms of a substance that the subject was exposed to. There was little data on proven harmful effects resulting from chronic exposure. Therefore, extrapolations from the limited data base in order to predict whether environmental effects are likely to occur have to be treated with caution. In this respect, there is also a need for reliable analytical data on environmental concentrations for some species of the substances evaluated.

3.3 Quality of human toxicological data base

The quality and quantity of toxicological data show substantial variation from one marine pollutant to another. Ideally, the evaluation of the health hazard presented by a certain pollutant ought to be based on data which include a comprehensive dose-effect relationship. For a selected and preferably critical effect, a reliable dose-response curve should be provided. Equally important is an established correlation between the concentration of the toxic chemical (or one of its metabolites) in an index medium and the effects and responses. Some examples relevant to the substances selected by GESAMP are presented in the following paragraphs.

For one of the most widely studied metals, lead, the relationship between blood lead and the effect of lead on the synthesis of haemoglobin is well established, but the relationship between blood lead and the effect of lead at the lower end of exposure on the development of the Central Nervous System (CNS) in children is a question of controversy. The relationship between oral lead intake and blood lead concentration has not been investigated, and the lack of this information hinders the prediction of blood lead concentration from daily dietary intake and vice versa.

The corresponding correlation between blood cadmium and current exposure has been established. In a condition of changing exposure, however, blood cadmium may not correlate with the renal concentration of cadmium. However, the quality of data that predicts kidney accumulation of cadmium from dietary intake has recently become more reliable.

In many cases, the evaluation is dependent on experimental animal data, especially in experiments which aim to study those quantitative relationships which can be extrapolated to man. Unfortunately, in the cases of tin and particularly of organotins, even the animal data base is not sufficient for extrapolation, and dose-related human data are totally absent.

4. Dietary Intake Considerations

4.1 Basis for total dietary intake estimates

Accurate estimates of dietary intake of food contaminants are difficult to make for the general population because of the large variability in both environmental

contaminant levels and rates of consumption. It is possible, however, to estimate intake from measurements of the concentration of contaminants in specific foods and the amounts of food consumed. Alternatively, measurements may be made with composite samples of the total diet. This approach requires fewer measurements and may reflect actual intake more closely, but it has the disadvantage of disregarding the contribution of single foods to the total dietary intake of contaminants. The calculated dietary intake may be made for representative population exposures, or it may be made with special reference to critical groups, for example, children, pregnant women, high consumers, etc. From contributions of particular food items to the total dietary intake, it is useful to note the "critical" foods to which more attention should be given in surveillance programmes.

Comparisons between calculated dietary intake and tolerable intake limits may indicate safety levels, or the incidence of risk for the exposed population. Due to the large variations in food consumption patterns among countries and to the wide variations in food contaminant concentrations, mean dietary intakes should be calculated and evaluated at the national or even local level.

Finally, the total energy value and composition of the diet should be taken into account in an evaluation of potential risks for population groups. It has been demonstrated that not only total food intake but also components such as fat, calcium, iron, and zinc can influence a subject's susceptibility to toxicity of contaminants by modifying the degree of gastrointestinal absorption.

4.2 Seafood consumption patterns

Seafoods do not represent a significant component of the diet for much of the world's population. Marine foods consumed by man include many trophic levels. Seaweeds are eaten mainly in the Far East, but also in Europe, for example, as laverbread or agar. Phytoplankton and zooplankton are not themselves consumed, but their predators, such as oysters, mussels, clams, scallops, herring, and sardines are. However, krill is used for animal fodder. Higher trophic levels include the carnivorous gastropods, clams, cephalopods, crabs, and shrimp, and foremost, fish. The world (population 4150 million in 1977) average of fish and shellfish protein consumption is 3.8 g per person per day of a total of 68.8 g total protein per person per day (FAO, 1980a). These data can also be converted to and analysed in terms of the fresh weight of marine foods. The world's average daily consumption of 3.8 g protein corresponds to about 20 g edible fish and shellfish per day or 140 g edible tissue, which is equal to about one meal of fish and shellfish, per week. Aquatic plants and seaweeds make up only 4% of the world's harvest of marine and freshwater foods. Of the total catches of aquatic animals, 10% are caught in fresh water and the rest is marine. Seventy-seven percent of the world's landings are marine fish, 7% are molluscs, and 4% are crustaceans, with other marine animals contributing 1% or less. The northwest Pacific and northeast Atlantic are the most productive areas (FAO, 1980b).

From the Table on seafood consumption in selected countries (Table 1), it can be seen that the small populations on the islands mentioned eat relatively large amounts of marine foods. According to FAO's food balance sheets (1980a), the population (40 000 inhabitants) of the Faeroe Islands consumes, on the average, 38.6 g protein (equal to 193 g fresh weight of edible tissue) originating from marine foods. Assuming that 150 g of edible tissue constitutes one meal, this corresponds to more than one meal per day of seafood. The average Japanese intake is the highest among larger populations. By comparison, the average consumption of marine foods in Australia, the USA, and the USSR is small. However, certain individuals are reported to consume much greater amounts. Fisherman at sea, especially in less affluent regions, will consume exclusively marine foods. For example, about 800 g per day were consumed on fishing boats in southern Italy (Bernhard & Renzoni, 1977). Canadian Indians are believed to have an intake of up to 1300 g per day during the fishing season, while 800 - 1500 g per day were eaten by fishermen and their families at Minemata (Review: Piotrowski & Inskip, 1981). Average consumption levels have been estimated on a global basis to be 23 g per day per person, with 38 g per day as the value for Europe.

Attention must be paid to situations in which seafood consumption represents a significant part of the diet, or when the concentration of a particular contaminant in consumed seafoods from heavily-polluted areas is relatively high. This may, for

Table 1. Consumption of fish and seafood (g fresh weight) (living weight) and in percent of different types of marine food^a

	Population	Total marine protein	Seafood in fresh weight	% of different types of marine foods on protein basis		
Australia	13.8	3.4	17	68	24	
Bermuda	0.06	15.8	79	87	13	
Faeroe Islands	0.04	38.6	193	82	16	3
Iceland	0.1	19.2	96	83	13	
Japan	113.9	22.5	113	77	4	10
Maldives	0.14	37.1	186	100		
Portugal	8.8	10.2	51	87	2	3
USA	216.8	3.2	16	63	22	6
USSR	258.9	9.4	47	81		1
Vanuatu	0.1	23.2	116	99	2	
Yemen Republic	1.9	13.0	65	100		

^a From: Bernhard & Andreae (1983).

Note: The protein values (FAO, 1980a) have been converted into fresh weight, assuming that 100 g fresh weight contain 20 g protein.

example, be the case with mercury in certain species of fish, or that with cadmium in oysters. It has been calculated, for example, that, while the contribution of seafoods to the total dietary intake of cadmium and lead is only 6% for the general population in Italy, the percentage can increase up to 25% for cadmium and 40% for lead in fishermen living in the Italian coastal villages where fish consumption is about 10 times that of the average quantity of seafood consumed in the rest of Italy.

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II. CADMIUM

1. Cadmium in the Marine Environment

1.1 Reference documentation

The major reviews and reference works used were Aylett (1973) on the chemistry of cadmium, Frei & Hutzinger (1976) on analytical techniques, Webb (1979) on general chemistry and biology, WHO (1979) on environmental health criteria, Friberg et al. (1974) and Fleischer et al. (1974) on cadmium in the environment and its impact, and Simpson (1981) for a critical review of cadmium in the marine environment. On bioaccumulation, reviews by Alabaster (1978) and Coombs (1979) were consulted. The kinetics of uptake were reviewed by McLeese (1980), and George (1980) reviewed the pertinent literature on mussels.

Many other individual papers by research workers were consulted and are listed in the reference section.

1.2 General facts

Cadmium (Cd) (Greek Cadmean (earth), calamine) is in subgroup IIb, Zn, Cd, Hg of the transition series in the Periodic Table of Elements. It has atomic number 48 and atomic weight 112.40. Cadmium was first isolated and identified by F. Strohmeyer in 1817 from the zinc ore smithsonite (ZnCO_3). It has been released into the environment since the early days from the smelting of a variety of ores and the burning of wood and coal. Cadmium is among the rarer trace elements and is seldom found in pure minerals. It is extracted commercially from zinc ores, e.g., zincblende (ZnS), in which it occurs at 0.1 - 5.0%.

Cadmium is more mobile in non-polluted, undisturbed soils than, for example, lead. It is even more accessible and more mobile in cultivated soils under the many influences of soil chemistry (Page et al., 1981).

The predominant state of oxidation in nature is Cd^{2+} , which is a borderline Type (b) cation. In freshwater, cadmium is extensively associated with colloidal and particulate matter, and soluble speciation is confined to the free Cd^{2+} ion together with small amounts of CdCl_2 and CdSO_4 . In the sea, some 66% of cadmium is present as free Cd^{2+} together with CdCO_3 (26%), $\text{Cd}(\text{OH})_2$ (5%), CdCl_2 (1%), and CdSO_4 (1%) (Whitfield et al., 1981). In coastal and estuarine waters, a high proportion of cadmium is associated with particles and is present as complexes (Nriagu, 1980; MacKay, 1983).

1.3 Sources

Typical cadmium concentrations found in igneous rocks are $0.001 - 1.8 \mu\text{g g}^{-1}$ (mean, $0.15 \mu\text{g g}^{-1}$), in metamorphic rocks $0.04 - 1.0 \mu\text{g g}^{-1}$, in sedimentary rocks, $0.3 - 11 \mu\text{g g}^{-1}$, in shales, up to $90 \mu\text{g g}^{-1}$, in marine clays, $0.4 \mu\text{g g}^{-1}$, and in marine phosphorites, $60 - 340 \mu\text{g g}^{-1}$ (Page et al., 1981; Simpson, 1981). Agricultural soils from unpolluted areas usually contain less than $1 \mu\text{g g}^{-1}$. These data, derived from sundry original sources, reflect the extreme values that were found and may possibly include analytical discrepancies. Areas in which enhanced levels of cadmium are found are usually linked with the occurrence of zinc-rich ore bodies, zinc smelting, and other zinc-related manufacturing processes and metal plating operations. Localized and naturally high cadmium concentrations may be found near deposits of sulfide ores such as sphalerite, phosphorite, hydrothermally-mineralized rocks, and some black shale deposits such as in the United Kingdom and California, USA.

Smaller but important sources of cadmium are a by-product of copper refining and, to a lesser extent, lead processing. Natural emissions of cadmium to the atmosphere are associated with volcanic eruptions, such as that of Mount Etna (Buat-Menard & Arnold, 1978), and forest fires and windblown dusts (Simpson, 1981; Hutton, 1982). Similarly, cadmium is released into the atmosphere by power generation facilities which use fossil fuels, and by the burning of agricultural and municipal wastes, including dried sewage sludge (Hutton, 1982).

Cadmium in water comes from contaminated agricultural soils, mining wastes, mine waters, and the industrial use of cadmium. An important source is municipal sewage effluents and sludges, including those of domestic origin.

World production of cadmium metal was about 18 900 tonnes in 1979. The main producers are the USA, the USSR, Japan, and Canada, followed by Belgium and France.

The main anthropogenic sources relate to ore mines, metallurgical industries, and to the disposal of sewage sludges. Cadmium concentrations in the fumes of copper, lead, nickel, and zinc sulfide smelters can be relatively high due to the high volatility of the metal (Fleischer et al., 1974). Other major atmospheric inputs come from the combustion of fossil fuels in industries using coke and from the incineration of domestic refuse (Fleischer et al., 1974), as shown in Table 2. These atmospheric inputs have demonstrated effects on agricultural soils and products in the surrounding areas (Peterson & Alloway, 1979). In addition, cadmium may be introduced by urban and motorway dusts, cadmium-contaminated phosphorus-containing fertilizers, and sewage sludge applications on land.

Table 2. Summary of current cadmium inputs to the environment of the European Commission Countries (tonnes year⁻¹)^a

Source	Compartment		
	Air	Land	Water
Volcanic action	20	ND	ND
Non-ferrous metal production			
zinc and cadmium	20	200	50
copper	6	15	ND
lead	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
Totals	132	3009	273

^a From: Hutton (1982).

Cadmium is a scarce and fairly expensive metal of low mechanical strength. It is released slowly into the environment from widespread sources. Cadmium is mainly applied via electroplating or dipping to another metal as a thin film coating for protection against corrosion. It is also much used as a pigment in yellow or brown paints and cadmium metal is used in special alloys and solders. Seldom is it possible to recover the metal economically. Use of cadmium in alkaline Ni-Cd rechargeable batteries has potential environmental hazards in view of the amounts of nickel and cadmium involved in discarded used batteries. It is practical and economical, however, to collect worn-out batteries where fixed units are routinely serviced, for this enables about 30% of the cadmium to be re-cycled. World usage of cadmium is given in Table 3.

Table 3. World consumption of cadmium by main uses, 1965, 1970, and 1975^a

Use	1965		1970		1975	
	tonnes	%	tonnes	%	tonnes	%
Batteries	669	7	842	8	1102	14
Pigments	2463	25	2733	25	1980	25
Stabilizers	905	9	2089	19	1249	16
Plating	4518	47	4068	37	2614	33
Alloys	804	8	803	7	658	8
Others	333	4	382	4	300	4
Total	9692		10 917		7903	

^a Sources: S.A. Hiscock, Cadmium Association, 34 Berkeley Square, London.

There is a growing application of organocadmium compounds in the plastics industry. Alkyl-cadmiums are used as polymerizing catalysts in pvc manufacture. Cadmium laurate, stearate, palmitate, myristate, and others are used to reduce weathering effects on plastics. The rate of release of organocadmium complexes to the aquatic environment from these sources is likely to be low. However, the simpler methyl-cadmium (Me_2Cd) is decomposed rapidly in air and water.

The reasons why sewage (domestic and mixed) may contain high proportions of cadmium relative to other trace metals are not clear, nor is the reason why the cadmium content varies irregularly (Peterson & Alloway, 1979). The cadmium content of 189 samples from 150 wastewater treatment plants in the USA ranged from 3 to 3410 $\mu\text{g g}^{-1}$ dry weight sludge, with a strong positive correlation to the degree of industrialization in the area observed. The mean value was 16 $\mu\text{g g}^{-1}$ (Sommers, 1977). Förstner & van Lierde (1979) list values for Sweden, England, and Wales, and Michigan, USA in the lower part of this range, and the more recent ranges for England (Murray et al., 1980) are lower than the above average. The US Food and Drug Administration recommends, along with other restraints, an upper limit of 29 $\mu\text{g g}^{-1}$ for sewage sludge applied to agricultural land.

Relatively high levels of cadmium are found in dredged spoils. Data from dredging in US waters (Krenkel et al., 1976) range from 0.6 to 4.1 $\mu\text{g g}^{-1}$ dry weight (8 sites) with 17.6 $\mu\text{g g}^{-1}$ near Long Island Sound. Ranges were found in the Clyde and other Scottish estuaries for various harbour silts of 5.6 - 6.8 $\mu\text{g g}^{-1}$. Murray & Norton (1979) report many values in the range 0.2 - 8.2 $\mu\text{g g}^{-1}$. Using their data, they calculated an annual input of 17 tonnes cadmium for 1977 in the United Kingdom, on the basis that a total of 28×10^6 tonnes soil (14×10^6 tonnes dry solids) is dumped into the North Sea and Irish Sea from harbour and channel dredging in the country.

Studies on the transfer of the different forms of cadmium from freshwater to the sea are inconclusive. Certain estuaries are conservative in most trace metals (Bewers & Yeats, 1981). The daily inputs of cadmium to inshore waters of the North Sea from the Humber estuary (Table 4) have been assessed by Murray et al. (1980). The relative proportions and magnitudes of these inputs should be of general interest to other fairly heavily urbanized and industrialized estuary areas.

The estimated inputs to the environment of the European Community (Table 2) give a firm indication of emissions to the air and disposals to land but only an incomplete account of aquatic inputs. The generalized global anthropogenic input of cadmium to the ocean is calculated, on an even less firm basis, to be about 50% of the 9.25×10^3 tonnes year⁻¹ total quoted by Simpson (1981). Mohlenberg & Jensen (1980) give a detailed assessment of cadmium inputs to Danish marine areas.

Table 4. Comparison of cadmium inputs to the Humber Estuary^a

Rivers	15 kg day ⁻¹	40.4%
Sewage discharges	2 kg day ⁻¹	5.4%
Industrial discharges	8 kg day ⁻¹	21.5%
Sewage sludge dumping	0.3 kg day ⁻¹	0.8%
Industrial waste dumping	0	0%
Dredged spoil	6.8 kg day ⁻¹	18.3%
Atmospheric input	5 kg day ⁻¹	13.5%
Direct coastal discharges	0.05 kg day ⁻¹	0.1%
Total	37.15	100%

^a Extract from Table 5 of Murray et al. (1980).

1.4 Transport, transformation, and bioaccumulation

1.4.1 Transport

Cadmium enters the seas and oceans from the air mainly in particulate form and, to a lesser extent, dissolved in rain and snow. Wittmann (1979) quotes the enrichment of cadmium in atmospheric particulate matter relative to the earth's crust as 300 in north Atlantic westerly winds and 1900 in the urban air of the USA. In some remote areas, volcanic emissions may be the principal source of enrichment. The concentration of cadmium in samples of air, above the Atlantic Ocean between Iceland and the Bermudas, ranged from 0.003 to 0.62 ng m⁻³ (Duce et al., 1976). This concentration range is comparable with that of samples collected in rural areas of the USA (Fassett, 1980). Much higher levels of cadmium in air are observed in urban and industrialized areas, particularly near metal refining and processing plants. Airborne cadmium is a principal source of input to offshore and oceanic waters.

The transport of cadmium from freshwater to the sea occurs either in particulate or soluble form. The specific form depends on the state of the river, its mineralization and its sources of pollution, as well as on unidentified local factors. Quantification is difficult. The general range for cadmium content in clean rivers and lakes is about 0.1 - 1.2 µg litre⁻¹; in polluted industrial rivers in the United Kingdom, the USA, and in Europe, it is 1 - 36 µg litre⁻¹ (Coombs, 1979). Freshwaters respond to natural or anthropogenic exposure to metalliferous ores, soils, and sediments. Values of 1 - 9 µg litre⁻¹ were found for the Jintsu river in Japan which flows through the area where the Itai-itai disease occurred; 30 µg litre⁻¹ was found in the drainage streams of a nearby ore mine. In the United Kingdom, 3 - 95 µg litre⁻¹ was found in streams in North Wales, while 5 - 20 µg litre⁻¹ was found in areas in Cornwall affected by ore mining. Rivers are subjected to affected by cadmium inputs from raw and treated sewage, for example, the River Rhine has a range of 1 - 10 µg litre⁻¹ (Coombs, 1979).

River sediments generally reflect the neighbouring soils and mineral workings. High cadmium levels are invariably accompanied by high levels of other trace metals. As a result of these inputs, there are enhanced levels of cadmium in near-shore sediments and sea waters (see below).

1.4.2 Transformation

The transformation of inorganic forms of cadmium in sea water scarcely affects its solubility. Biomethylation appears to be a possibility when considering the properties

of the element, but this has not been demonstrated. Organic chelates, such as humates, are likely to liberate bound cadmium as the result of dilution and degradation in sea water. Cadmium is held in sewage sludge partly in combination with carbonates and sulfides, and partly in complex organic combinations. In the latter example, cadmium combines with the sulfur-rich fractions of organic matter of which there is great excess, for the inorganic and organic contributions are widely variable (Stover et al., 1976; Sommers et al., 1977). Since most biogenic cadmium-organic complexes, including metallothioneins, are fairly easily biodegradable (Coombs, personal communication, 1983), there is a ready release of cadmium into aerobic waters and sediments; under anaerobic conditions, insoluble cadmium carbonates and sulphides may persist in sediments.

1.4.3 Bioaccumulation

Simpson (1981) regards the processes of uptake (or absorption) by phytoplankton, followed with grazing by herbivores and the subsequent elimination of cadmium in faecal pellets, as a major contributory factor affecting cadmium distribution in the photic zone. Such a mechanism might also be the cause of elevated concentrations (up to $60 \mu\text{g g}^{-1}$) of cadmium in superficial sediments of the Walvis Bay, and might possibly explain the unusually high concentration, up to $600 \mu\text{g g}^{-1}$, for Red Sea sedimentary deposits in an anaerobic environment created by a massive bloom.

Many estimates are available for bioaccumulation in marine flora and fauna (Coombs, 1979). For many species, covering most phyla, accumulation factors are of the order of thousands. For some molluscs and some arthropods, they are tens of thousands, and for certain tissues (of which few, if any, are usually eaten by man), they are hundreds of thousands.

Aquatic organisms can be exposed to cadmium in the ambient water, in sediments, and in their diet. The bioavailability of cadmium and, consequently, its accumulation in tissues depends on a number of factors. Non-complexed cadmium added to a rapidly growing algal culture has slightly less effect on the growth rate than when added at the time of inoculation of the medium (Kayser & Sperling, 1980). In experiments with the American oyster, complexed cadmium was found to be less readily accumulated (Yen-Wan Hung, 1982); the lower concentration used, however, $40 - 60 \mu\text{g cadmium litre}^{-1}$, may also have contributed to this effect.

Ray et al. (1980) found that the rate of cadmium uptake by the polychaete Nereis virens, when exposed to contaminated sediments ($1 - 4 \text{ mg cadmium kg}^{-1}$), was the same as its uptake from solutions that contained the same cadmium concentrations ($30 - 100 \mu\text{g cadmium litre}^{-1}$) as that present in the water overlying the sediments. Further studies by Ray et al. (1981b) showed that little accumulation from cadmium-contaminated sediments occurred in Nereis virens, Macoma balthica, and Crangon septemspinosa. Similar studies showed that N. virens, Mercenaria mercenaria, and Palaemonetes pugio did not accumulate cadmium from contaminated sediments during a 100-day exposure period (Rubinstein et al., 1983). Hardy et al. (1981) exposed excised gills of the clam Protothaca staminea to contaminated sediments and interstitial water and concluded that "low level additions of cadmium to sea water are not likely to lead to significant bioaccumulation through the gills of suspension-feeding bivalves". Therefore, cadmium bound in contaminated sediments does not appear to be bioavailable to marine organisms. However, molluscan herbivores may accumulate cadmium from littoral algae, and this may be accumulated, in turn, by carnivores feeding on these organisms (Davies, 1981; Simpson, 1981).

Algae

Phytoplankton can accumulate significant concentrations of cadmium (Kremling et al., 1978; Kayser & Sperling, 1980), although decomposing cells rapidly release cadmium into the water. It is assumed that the metal is loosely bound to the cell's surface, and this process appears to be important in the biogeochemical cycling of cadmium in the marine system. Laminaria saccharina, in common with other seaweeds, can also accumulate significant concentrations (Markham et al., 1980).