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Reviews

Editorial remarks. Since World War II we have witnessed a marked increase in the industrial and agricultural use of cadmium, and the question as to what eventually becomes of this element once it is released into the 'mainstreams' of our civilization is being posed with increasing urgency. Man has seen to it that the amount of cadmium present in our immediate environment is rising significantly above all natural levels. Waste incinerators and furnaces are the primary sources of airborne cadmium pollutants. Phosphate-containing fertilizers are contaminating agro-ecosystems with cadmium. Other cadmium sources are refuse dumps and sewage sludges. High concentrations of cadmium are found in our waters and are collecting in sedimentation. One measuring station in the Lower Rhine area has reported that 200-500 tons of cadmium are carried by the river yearly. One percent of this amount is of natural origin; civilization supplies the remaining 99%. Given the complexity of the problem, it is clear that only an interdisciplinary, pragmatic approach can - and must begin to - define the dangers which the proliferation of cadmium pollution holds for man and his environment. - We wish to thank our coordinator, Prof. O. Ravera (of the Euratom, Ispra), for guiding to fruition this review which, we hope, will set forth part of the scientific foundation needed for developing effective environmental protection policies.

H. M.

Cadmium - a complex environmental problem

Preface

The object of this review was to concentrate within a single journal some selected articles concerning important aspects of the cadmium pollution problem.
The initial difficulty in undertaking studies in new fields such as this one often lies in the complexity and the scattered character of the literature. We have therefore invited scientists who have made significant contributions in the area of cadmium research to summarize the advances made, to date, in their specific fields of competence. It is our hope that this compilation of information will allow experts in other disciplines to gain a clearer view of the present state of knowledge in the cadmium problem.
The articles have been organized into two parts for back-to-back issues of Experientia. Part I which is presented here concerns the distribution of cadmium in natural environments, the effects produced by this metal on organisms and the cadmium contamination in agriculture and zootechnology. The removal of cadmium from wastewaters and the cadmium content in sludges, as well as the effects of cadmium on man are the subjects of Part II which will appear in the February issue.
A salute is due to each author for his valuable collaboration as well as to his scientific achievement. The efforts of these authors are contributing to our better understanding of the dangers of cadmium contamination.

O. Ravera

Cadmium in freshwater ecosystems

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Introduction

From an ecotoxicological point of view any substance which substantially modifies population and community characteristics must be considered dangerous. It is evident that a toxic substance may influence the biota if its concentration in the environment is over a certain level. Indeed, some heavy metals, dangerous at high concentrations, are essential to the biota at low concentrations. Unfortunately, it is often difficult to establish this level. Legislation concerning environmental protection is based on these concepts and maximum permissible concentrations are established essentially on the conclusions drawn from short-term experiments carried out under standard conditions. On the other hand, difficulties arising when results from different authors are compared and the great unreliability of extrapolating conclusions from laboratory studies to natural environment are well known.
From these considerations it is clear that the ecotoxicological study of a metal must take into account the fate of the metal from its source to its uptake by organisms and its effects on individuals, populations and communities.
In addition, indirect effects of the metal on the physical environment, such as variations in pH-value and oxygen concentration in water resulting from toxic effects of the metal on photosynthesis must also be considered. The influence of the physical-chemical characteristics of the ecosystem on the metal species (i.e. its physicochemical form) and the influence of biological activity on the metal form and availability, are other important topics of research.
This paper will illustrate these aspects as they are related to the problem of cadmium pollution in freshwater.

Sources and loading

In the lithosphere cadmium is present as the sulphide ore, greenockite (CdS), and it is associated with zinc ores, which are the only sources industrially exploited[42]. The natural cadmium input to the biosphere derives from volcanic activity, exudates from vegetation, forest fires, wind blown dust and leaching of rocks. During recent decades phosphate fertilizers[54], incinerator waste, coal and oil combustion, and most significantly mining and industrial usage of cadmium, have resulted in an important increase of cadmium in the environment. Consequently, cadmium pollution is very hazardous but usually of local importance.
Because in recent years several cases of cadmium poisoning have been reported (for example, Itai-Itai disease)[102] and experimental results confirm its high toxicity, cadmium is considered (together with mercury) by national and international legislations to be the most toxic of metals. Consequently, the maximum permissible concentrations of cadmium in freshwater bodies are always low. For example, the US Department of Health, Education and Welfare established that cadmium concentration in drinking water does not exceed 10 ppb[55]. The Dutch Federation of Water Boards proposed in 1973 that industrial effluents discharged into surface waters should not contain more than 0.1 mg Cd/l[37]. Cadmium concentrations lower than 0.3 mg Cd/l were considered non toxic for waters not used by salmonids and with an alkalinity higher than 80 ppm by New York State legislation[37]. According to the US Envrionmental Protection Agency (EPA), the total amount of cadmium discharged per day through industrial effluents into water courses should not be greater than 5.88 kg into water courses, 4.9 kg into lakes and 39.2 kg into estuaries. In addi-

tion, the mean cadmium concentration in an effluent flowing into freshwaters must be lower than 40 ppb, if its flow rate is lower than $\frac{1}{10}$ that of the water body into which it is discharged[37]. In Swiss running waters the legally tolerated cadmium concentrations must not exceed $4.5 \cdot 10^{-8}$ mol/l[34].

Cadmium concentration in the physical environment

In the lithosphere the mean cadmium concentration is 0.2 ppm but with wide variations depending on the rock type. In sea waters cadmium concentrations are commonly low: for example, North et al.[74] reported a mean value of 0.11 ppb, Brooks[16] 0.02 ppb and Taylor[93] 0.1 ppb. Cadmium concentration in freshwaters shows large variations, but the highest values are the effect of industrial wastes. Cadmium concentration in industrial effluents may vary from 0 to 1000 mg/l, whereas that in municipal waste waters is commonly lower than 10 µg/l. The following examples will give an idea of the levels of cadmium found in freshwater. These are normally close to the sensitivity limits of the analytical methods in common use.

Taylor[93] measured in the River Tees, one of the major English rivers discharging into the North Sea, a mean cadmium concentration of 1 ppb in the soluble form, corresponding to a total concentration of 1.2 ppb. Cadmium concentration in the water of this river, highly polluted by industrial wastes, was lower than 1.5 ppb in the soluble form[93] measured in the River Rhine.

Cadmium concentration in the water of Lake Balaton (Hungary), slightly contaminated by industrial wastes, in particular by heavy metals, seems in comparison to be too high as Müller[69] reported values ranging from 0.42 to 0.24 ppm for total cadmium and from 0.57 to 0.32 ppm associated with clay fraction < 2 µm. In addition, values measured for the water of its tributary, the River Zala, of 0.37 ppm for total cadmium and 0.73 ppm for cadmium in particulate form, also seem to be high. Gächter[33] reported low cadmium concentrations in the water of two Swiss lakes, Lake Alpnach and Lake Luzern, where values varied from 0.01 to $0.04 \cdot 10^{-8}$ mol/l.

Baudo et al.[7] found a mean annual concentration of less than 1 ppb Cd for the water of Lake Mezzola (Northern Italy); concentrations of the same order of

in contact with sediments in the central zone of the basin had a cadmium concentration higher (2.3 ppb) than that in the littoral zone (0.7 ppb)[6]. Cadmium from rainfall amounted to 1.2 ppb in 1976 and 0.3 ppb in 1977; this difference was due to meteorological variations from one year to another. It is notable that in the Lake Mezzola region no significant difference in cadmium concentration has been noted between water bodies lying in non-polluted and those in polluted areas. De Bernardi et al.[27] found cadmium concentrations lower than 1 ppb in the water of 19 small Lombardian lakes (Northern Italy). The distribution of cadmium (and other metals) in water sediments and biota of Lake Maggiore (Northern Italy) has been studied by Muntau[70]; Baudo et al.[8], Locht and Muntau[60] and Gommes and Muntau[38,39]. Cadmium concentration in the tributaries on the east coast of Lake Maggiore varied from 0.32 ppb to 1.32 ppb and in those on the west coast from 0.32 to 2.10 ppb. The mean value in lake water near the east coast was 0.33 ppb and near the west coast 0.30 ppb. The concentration in the water of the lake outflow (Ticino River) reached 0.21 ppb. Seasonal variations of cadmium concentration, from 0.16 ppb to 2.57 ppb, in pelagic lake waters were very large[39]. According to Baudo et al.[8] in the epilimnetic water from different areas of Lake Maggiore, mean cadmium concentrations varied from 0.1 to 1.2 ppb, whereas the seasonal variations for the whole lake ranged from 0.1 to 0.2 ppb. Muntau[70] estimated that the annual load from the tributaries of the southern area of Lake Maggiore was 1.48 t soluble cadmium plus 4.7 t particulate cadmium. The same author using two different models, calculated that the total input of cadmium for this lake ranged from 7.2 t/year to 9.0 t/year. As a consequence, the amount of cadmium accumulated annually resulted in the range from 5.1 to 6.9 t per year. Cadmium uptake from fall-out was not very important, 56 kg/year derived from wet fall-out and only 5 kg from dry fall-out.

An important source of cadmium for Lake Maggiore is the natural load from rocks in its watershed, although the contribution from industry also seems to be of importance (Muntau, unpublished data). For example, cadmium concentrations up to 4.1 ppm measured in the sediments of a small tributary of Lake Maggiore (River Bardello) were due to the industrial wastes discharged into it[60]. Industrial activities probably caused the increase of cadmium concentration in the sediments of the southern area of this lake from 0.63 ppm in 1963 to 3.13 ppm in 1975. In a bay of Lake Maggiore (Pallanza), into which the River Toce flows, cadmium concentration increased from 0.62 ppm in 1963 to 1.96 ppm in 1975[60].

There is evidence that high values are associated with the fine sediments as cadmium concentration in the sediment increased from the mouth of the River Toce towards the Borromeo Isles, where finest mud is located. There are further examples indicating that the highest concentrations were not necessarily measured in the vicinity of the cadmium point source, but in the settling zone of the finest mud and organic material. For example Houba and Remacle[46] found very high concentrations in the sediments of the River Vesdre (Belgium), in an area 2-5 km from a factory that was the source of cadmium pollution. Dall'Aglio[25] analyzed the heavy metal content of water samples from 23 Italian rivers from August to September 1979; cadmium concentrations varied from 0.030 ppb to 0.085 ppb, except for a small river (Entella) which attained 1.8 ppb. In the sediments of Lake Biwa (Japan) Kobayashi et al.[56] found a mean concentration of 0.44 ppm, a value very similar to that of Lake Maggiore measured on sediments collected in 1963[60].

A mean cadmium concentration of 1.1 ppb in the interstitial water from littoral sediments of Lake Mezzola was identical to that from pelagic sediments[7]. In some polluted rivers the cadmium concentration found in the sediments is very high; for example in the Weser estuary a mean concentration of 2.4 mg/kg has been reported[20] and in the River Rhine 9.9 mg/kg dry wt[90]. The highest cadmium concentration in freshwater sediments was measured by Houba and Remacle[46] in the River Vesdre, a small tributary of the Meuse River, where the value reached a maximum of 195 mg Cd/kg sediment and the mean was 86 mg. The point source of this pollution seems to be a smelting works producing metal sheets and located at the confluence of the River Vesdre and the Magne brooks. At the time of the study the factory was no longer active, but in the preceeding years it had discharged daily 100 m^3 of waste water rich in cadmium and zinc into the river.

Concentration in the biota

Cadmium accumulation in aquatic plants and animals has been reported by several authors. A linear correlation between initial cadmium concentration in the growth medium and cadmium concentration in Cd-resistant and Cd-sensitive strains of bacteria has been established. Resistance to high cadmium concentration resulted from the ability of certain strains to immobilize greater amounts of cadmium than their more sensitive counterparts[85].

Gommes and Muntau[39] analyzed the concentration of cadmium in 17 species of macrophytes from Lage Maggiore and found values ranging from 0.20 to 9.60 ppm dry weight with an average of 0.33 for *Nymphaea* (the species with the lowest accumulation capacity) and 3.93 for *Ceratophyllum* (the species with the highest accumulation capacity). Reiniger[84] observed in algae from an experimental field an increase in cadmium concentration from 4.4 µg/g dry wt (if they were living on contaminated sediment with 2 µg Cd/g) to 132 µg/g (if cadmium concentration in the sediment was 24 µg/g). The same author found in three species of aquatic plants *(Elatine hexandra, Althenia filiformis* and *Monita rivularis),* growing in a flooded rice field contaminated with cadmium, far higher concentrations of the metal in the plant tissues than was calculated for leaves and roots of the rice plants.

Gommes and Muntau[38] have measured far higher concentrations of cadmium (15.70 ppm) in soft tissue of *Unio mancus* (bivalve) from Lake Maggiore than in that (0.75 ppm) of *Viviparus ater* (Gastropod) living in the same environment. The high concentration in *Unio* is very similar to that (15.0 ppm) measured in a marine bivalve *(Ostrea)*; this high accumulation is probably due to the filterfeeding activity of these bivalves. Cadmium uptake by *Mytilus edulis* (marine bivalve) was studied by Carpene and George[21] using an isolated gill preparation. From this study the following conclusions may be drawn: a) cadmium uptake increased with time; b) temperature, dissolved oxygen, Zn, Cu, Hg, Pb and Fe seem to have no effect on cadmium uptake; c) cadmium was apparently taken in by diffusion and accumulation and d) cadmium accumulation was facilitated by intracellular binding and sequestration. More difficult to explain are the different concentrations of cadmium found in the shells of *Unio* (1.80 ppm) and *Viviparus* (0.15 ppm) by Gommes and Muntau[38]. It may be that periphyton, which absorbs great amounts of heavy metals, was more abundant on the shell of *Unio* than on that of *Viviparus. Dreissena polymorpha* (bivalve) lives in brackish and freshwater attached to solid surfaces (stones, walls, etc.). Consequently, *Dreissena* may take up cadmium from water and suspended particles but not from sediments, whereas sedimented matter may be an additional source of cadium for other bivalves living in the sediments (e.g. *Unio, Anodonta*).

Marquenie[63] used *Dreissena* for an active biological monitoring programme transferring individuals from unpolluted to polluted areas. From the results obtained it was evident that the cadmium concentration in the soft tissues of *Dreissena* was related to cadmium concentration in the soluble form and not to the particulate form suspended in the water. Consequently, there is evidence that particulate cadmium is less available to the mollusc than the soluble form.

Cadmium accumulation in net plankton is very high, compared with the concentration in lake water. But, because of the comparatively small biomass of plankton, only a small quantity of cadmium present in a unit of water is accumulated by the plankters. Price and Knight[76] reported 15 ppm Cd (dry weight) for the plankton of Lake Washington, and Baccini[4] found a mean value of 5.6 ppm for that of Lake Luzern and Lake Alpnach. Baudo et al.[8] reported values ranging from 6.5 to 39 ppm dry weight for net plankton from Lake Maggiore (mesh size of 126 µm) and values from 6.4 to 16 ppm dry weight for plankton collected with a 76-µm meshed net. Large variations in concentrations have been noted in relation to season. For plankton of Lake Mergozzo, the same authors obtained values of 7.1 ppm for a 126-µm net and 8.3 for a 76-µm net. In the same paper concentration factor values were reported of between 6900 and 12,000 for Lake Maggiore and from 4500 to 5200 for Lake Mergozzo. These values are not ‘real concentration factors’ but ‘observed concentration factors’ as they are dependent upon environmental and biological factors existing at the time of plankton sampling.

Lucas et al.[62] calculated that the median concentration in different species of fish from the American Great Lakes was 94 µg Cd/kg wet weight for the total fish and 400 µg for its liver. Uthe and Bligh[95] calculated that the mean cadmium concentration in several species of fish from different Canadian freshwater bodies was 50 µg/kg wet weight. The authors do not agree on the relationship between the level of industrial pollution in water and cadmium concentration in fish. For example, analyses on several species of fish collected from 49 freshwater bodies (New York State) showed that the most part of the samples had a cadmium concentration of about 20 µg/kg wet weight or lower, and that values higher than 100 µg occurred only occasionally in samples collected from areas polluted by ore deposits containing cadmium[61]. Havre et al.[41] reported that cadmium concentration in fish living in a Norwegian fjord, polluted by a zinc factory was higher than in fish from the open sea, but not dramatically so. Cadmium concentration varied with the species and the higher values were associated with benthonic feeders. Jaakkola et al.[50], measuring the cadmium concentration in muscle of *Exos lucius* (pike) from polluted and unpolluted water bodies, found a mean value of 3 µg/kg wet weight for the clean waters and concentrations from 4 to 13 µg/kg wet weight for the polluted environments. Havre et al.[41] found that the cadmium concentrations in fish liver ranged from 80 to 2506 µg/kg wet weight and from 3 to 32 µg/kg wet weight for muscle. The mean ratio between the concentrations in liver and that in muscle was about 42, but no significant correlation between the two concentrations was observed. Other authors (e.g. Mount and Stephan[68] and Calamari and Marchetti[19]) found cadmium in greater concentrations in liver, kidney and gills than in muscle and bones of fish. Using *Lepomis gibbosus* which had been exposed to 40 ppb cadmium for 1 month, Merlini et al.[66] found 7 times more cadmium in the liver and 500 times more in the kidney of those treated than in those of the control experiment. Other authors observed that cadmium was preferentially accumulated in both the liver and kidney of bass and blue gills[22].

Calamari and Marchetti[19] observed that, having attained equilibrium between its tissue and that of its environment, *Salmo gairdneri* lost all its accumulated cadmium after 80 days exposure to unpolluted waters. The same authors found that the biological half-life of cadmium varied for different organs obtaining values, for example, of 70 days for gills and 50 days for liver and kidney. The time needed for attaining the equilibrium between cadmium concentrations in fish and that in water, varied with the species. For example, for *Lepomis macrochirus* the time needed varied from 30 to 60 days[68] and for *Micropterus salmonides* it was about 60 days[22].

Kumada et al.[58] reported that in *Leuciscus leuciscus* cadmium intake was principally via food uptake, but, in general, information on the direct uptake of cadmium from water by fish in comparison to that via food is very scarce. The importance of each pathway is difficult to evaluate as it is dependent on several factors; for example, quality and quantity of food ingested and the physico-chemical form of cadmium in the water.

Effects on the organisms

The high toxicity of cadmium has been established by several authors for different species of aquatic organisms[1, 3, 58, 81, 98]. Informations is rather poor on the effect produced by cadmium in bacteria and algae.

Remacle and Houba[85] compared the effects of cadmium in strains of saprophytic bacteria both resistant and sensitive to cadmium. The most resistant strain belonged to a gram negative genus *(Pseudomonas)* and resistance seemed to be associated with the plasmids. A concentration of 8 ppm cadmium in the medium abolished the growth of the sensitive strain, whereas 300 ppm had no influence on the growth of the resistant strain. Devanos et al.[28] isolated microorganisms, mainly bacteria, from different polluted environments, and with resistance to cadmium concentrations ranging from 1 to 500 ppm. Of these micro-organisms 94% were resistant to one or more antibiotics and 91% possessed multiple drug resistance. The authors postulated an extrachromosomal linkage of cadmium and antibiotic resistance in the isolated micro-organisms. Zwarum[103] reported that *Escherichia coli* was very tolerant to cadmium, and Bitton and Freihofer[12] studied the protective role of extracellular polysaccharides on the toxicity of copper and cadmium in *Klebsiella aerogenes.*

Population growth of *Euglena gracilis* was reduced in proportion to cadmium concentration in the culture medium; for example, 5 ppm prolonged the duplication time from 16–17 h to 30 h (Albergoni and Piccinni[2]). The same authors observed a significant reduction in motility, but no malformation in *Euglena* cells exposed to cadmium (5 ppm).

Concentration of cadmium from 50 to 500 ppb significantly reduced the growth of *Scenedesmus quadricauda*[17]. A reduction in growth of the same alga was obtained by Klass et al.[55] with 6.1 ppb. Growth inhibition in *Selenastrum capricornutum* was obtained at a cadmium concentration of 50 ppb in a culture with low carbonate content[5]. Cadmium had an inhibitory effect on the growth of a diatom *(Navicula pelliculosa)* at concentrations ranging from 14 to 140 ppm[59] and on that of a green alga (*Scenedesmus* sp.) at 0.1 ppm[14].

In the literature data on the effects produced by cadmium on macrophytes are scarce. Stanley[92] used *Myriophyllum spicatum* to determine the cadmium concentrations which produced a 50% reduction in growth of various organs. The following data were obtained: 7.4 ppm for root weight, 20 ppm for root length, 14.6 ppm for shoot weight and 809 ppm for shoot length. From these values it seems that the growth in length was less sensitive to cadmium than growth in weight. Hutchinson and Czyrska[48] found that the growth of *Lemna valvidiana* was inhibited by 25% and 80% by cadmium concentrations of 10 ppb and 50 ppb, respectively. The same concentrations produced growth inhibition of 50% and 90% respectively in *Salvinia natans.* The same authors[49] observed in both these species that the toxic effects produced by cadmium (10 ppb and 30 ppb) were enhanced if 50 ppb and 80 ppb of zinc were present in the medium. It is noteworthy that these concentrations of zinc alone stimulated the growth of these macrophytes.

More information is available on some species of animals. For example, information on the genus *Daphnia* is relatively abundant. Alabaster and Lloyd[1] stated that some freshwater invertebrates, such as *Daphnia magna,* were very sensitive to cadmium and there is evidence that the young are generally more sensitive than the adult. Baudouin and Scoppa[9] found an LC-50 (48 h)* of 65 ppb cadmium for *Daphnia hyalina* and 3800 ppb for *Cyclops sp.* Cebejszek and Stasiak[23] calculated an LC-50 (48 h) of 68 ppb cadmium for newborn *Daphnia magna;* Anderson[3] observed that the exposure of *Daphnia magna* to 2.6 ppb cadmium produced immobilization after 64 h. The 21-day and 48-h LC-50 values for *Daphnia magna* were calculated as 5 ppb and 65 ppb respectively by Biesinger and Christensen[11]. They found furthermore that cadmium at concentrations as low as 0.17 ppb may influence the reproduction of *Daphnia.* Bellavere and Gorbi[10] measured cadmium toxicity to *Daphnia magna* by the index IC-50, which corresponds to the metal concentration causing the immobility of 50% of the organisms tested in a prefixed time. Using *Daphnia,* kept in water with a hardness of 100 mg/l, they recorded an IC-50 (24 h) of 120 ppb and for water with a hardness of 200 mg/l a value of 160 ppb. When compared with data reported by other authors for the same species, these values seem to be very high, but we must remember that in this experiment the exposure time was particularly short. Increasing the exposure time would probably produce immobility even at concentrations far lower than those used by the authors. However, it is clear that the sensitivity of *Daphnia* decreased with increasing hardness. This relationship is more evident from experiments regarding the influence of cadmium on *Tubifex tubifex* mortality carried out by Brkovic-Popovic and Popovic[15]. LC-50 (48 h) values varied from 2.8 ppb cadmium to 720 ppb cadmium in water with a total hardness (expressed as carbonate) ranging from 0.1 mg/l to 261 mg/l.

The most evident anatomical effects of 3–4 days exposure to cadmium at concentrations lower than 100 ppb on *Biomphalaria glabrata* were the displacement of secreting cells of the epatopancreas and the degeneration of male cells, particularly those at the first stage of maturation[96]. Bellavere and Gorbi[10] determined that *Biomphalaria glabrata* was less resistant to cadmium than *Brachidanio rerio* (cyprinid fish), having an LC-50 of 4.80 ppm cadmium at 24 h and 0.30 ppm at 96 h as compared with LC-50 values for *Brachidanio rerio* of 21.08 ppm and 4.35 ppm, respectively. Decrease in LC value with exposure time demonstrates the limited value of results obtained from experiments of short duration.

Thorp and Lake[94] calculated that the LC-50 (4 days) of the mayfly larva *(Athalophebia australis)* was 0.84 ppm cadmium, and Warnick and Bell[99] found a higher value of 32 ppm cadmium for the stonefly *Acroneura lycorias.*

A wealth of information on the effects of cadmium on fish has been collected by Alabaster and Lloyd[1]. According to these authors many sublethal effects of cadmium in fish are caused by the modification of ionic balance induced by this metal. Examples are degeneration of muscle, lesions in the spinal cord, convulsion, tetanic and neuromuscular disturbances. The range of lethal concentrations for fish is very large: from 10 to 100,000 ppb cadmium. These authors[1] attributed this to inconsistency in length of exposure to cadmium, the species, the behavioral aspects of the fish and the slope of the concentration response curve. Salmonids seem to be the least resistant fish to cadmium, whereas cyprinids are the least sensitive. For example, 50% of the alevins of rainbow trout died after an exposure of 2 days at 150 ppb cadmium and 33% at 25 ppb[19] and an LC-50 (48 h) of 3000 ppb was calculated for trout by Jung[51], whereas for *Cyprinus carpio* (common carp) the LC-50 (4 days) was 240 ppb[83]. Kumada et al.[57] observed neither higher mortality nor growth reduction in rainbow trout exposed to 5 ppb cadmium for more than 30 weeks.

Certain developmental stages of *Xenopus laevis* (Amphibia) cannot tolerate cadmium concentrations higher than 2 ppm, but may survive concentrations lower than 1.5 ppm. The most evident embryonic anatomical alterations occurred at the epidermis, encephalon, eyes, pronephros and somites[96].

An experiment carried out by Merlini[67] showed that pumpkinseed sunfish *(Lepomis gibbosus)* exposed for 2 weeks at 40 ppb cadmium (as sulphate) contained less vitamin B_{12} in the liver than the control fish. These, however, had lower concentrations of this vitamin B_{12} in the gall-bladder, intestine and gills than the treated fish. Since vitamin B_{12} is eliminated through the intestine, it is probable that cadmium accelerated this process by stimulating the biliary excretion of vitamin into the intestine and its elimination through gill epithelium. Merlini et al.[66] drew the following conclusions from the experiments carried out on the effects produced by cadmium on the Zn-65 uptake by *Lepomis gibbosus*: a) Zn-65 concentration in fish exposed for 31 days to 40 ppb cadmium was ¼ that of the control fish; b) the percentage loss was similar in the control and treated fish; c) the control fish had higher cadmium concentrations in interrenals (2.85 μg/g wet weight), bone (1.48 μg/g wet weight) and brain (1.06 μg/g wet weight); d) contaminated fish had small cadmium concentrations in eye, brain, fin, scale and skin, one tenth that in the gonads, gills and bone and one hundredth of that in the heart, spleen and kidney. From these results it is evident that cadmium influenced zinc uptake, but not its elimination. Some organs (i.e. heart, spleen and kidney) concentrated a large amount of cadmium in treated fish but not in the control fish. As a consequence, it was clear that the distribution pattern of this element in fish exposed to cadmium was different from that in fish living in unpolluted waters.

The protective effect of selenium against cadmium in rats and mice is well known and there is information on the protective effect of cadmium against selenium in chickens[43,44]. We have found only one paper (by Van Puymbroeck et al.[97]) on the antagonism between selenium and cadmium in the freshwater snail *Lymnaea stagnalis.* These authors found that the effects of cadmium were reduced to about 50% in the presence of sublethal amounts of selenium. In addition, sublethal concentrations of cadmium protected *Lymnaea*

* LC-50 (lethal concentration 50%) is the concentration of any toxic substance reducing by mortality the number of tested individuals to 50% in a prefixed time.

against high concentrations of selenite (3 ppm Se) and selenate (15 ppm Se). For aquatic invertebrates, the biochemical mechanisms involved in this antagonism are unknown, but for mammals it seems that proteins (thiol groups) play a fundamental role in the Cd/Se interaction.

Effects at population and community level

Most of the information on the effects of cadmium in aquatic biota concerns short term experiments carried out in the laboratory. This information is insufficient to determine the real damage to individuals and populations and for the assessment of an acceptable unharmful metal concentration in the environment (e.g. Sprague[91], Nobbs and Pearce[71], Ravera[80], Hoppenheit[45]). On the other hand, there is much uncertainty about the real effects of a pollutant when it is observed in the field because toxic substances are generally present as mixtures in water bodies[78]. Long-term studies on laboratory populations concerning the life span of the tested species produce more useful and interesting results than experiments on acute toxicity.

Experiments carried out by Hoppenheit[45] on the effects of cadmium at population level in 20 successive generations of *Tisbe holothuriae* (coastal and brackish water copepod) give a clear example of the value of long-term population studies in ecotoxicology. The most important results produced from the research were: a) concentrations of 148 ppb and 222 ppb delayed by 8 weeks the decrease of the population density found in the control but, at the end of the experiment, the mean population density of the contaminated populations was similar to that of the control ones. According to the author this was probably due to the adaptation of the contaminated population within 20 generations; b) significant differences in density were observed between populations exposed to 148 and to 222 ppb; c) variability within treated populations was larger than that of the control populations and d) reduction in density of populations exposed to cadmium did not result in an increase in the number of nauplii, as, generally, occurred in control populations. In conclusion, *Tisbe holothuriae* tolerated relatively high concentrations of cadmium, compared with other freshwater and marine crustaceans (e.g. Andersen[3], Eisler[29]).

Marshall[64] carried out experiments on populations of *Daphnia galeata mendotae*, kept for 22 weeks with contaminating concentrations of 2 ppb cadmium and higher. He observed a significant reduction in population density and biomass and an increase in average brood size, and the ratios between number of ovigerous females and total number of females, and between the number of eggs and total number of females. The same author noted that 1 ppb cadmium dramatically increased embryo mortality.

A long-term experiment on the effects of cadmium on laboratory populations of a tropical freshwater snail *(Biomphalaria glabrata)* was carried out by Ravera et al.[81]. All adults were killed after 6 and 3 h by 2 and 4 ppm cadmium, respectively. Survival time for 50% (ST-50) of the tested snails was 15 h at 1 ppm concentration, 31 h at 0.5 ppm and 63 h at 0.1 ppm. Eggs were deposited by adults kept at 0.1 and 0.5 ppm, but their number was about ¼ that of the control. Although the eggs produced by contaminated adults were transferred to clean water, all the embryos died at 'morula' stage. No embryo completed its development when eggs from untreated adults were exposed to 3 cadmium concentrations: 0.1, 0.5 and 1.0 ppm. In this experiment the viability of the control was about 90%. A comparison of the sensitivity of the embryo and adult on the basis of ST-50, showed the embryo to be more resistant to cadmium, but this difference decreased with increasing cadmium concentration and at 1.0 ppm both ST-50 values were similar.

Ricci and Pozzoli[86] studied the chronic effects of cadmium ($CdCl_2$) and zinc ($ZnCl_2$) on the life span and reproduction of a Bdelloid rotifer *(Phylodina roseola)*. The rotifers were exposed to a series of cadmium concentrations ranging from 10 ppb to 10,000 ppb. This species seems to be exceptionally resistant to cadmium as, even at the highest concentrations, egg hatchability and life span were not significantly different from those of the control. In addition, neither cadmium nor zinc seemed to influence the age at which the rotifer attained reproductive maturity.

Premazzi et al.[75] studied the effects of cadmium and 5 other metals (Cu, Ni, Hg, Zn and Pb) on *Selenastrum minutum*. The culture medium was a very dilute solution of macro- and microelements with no chelating substances. From the results obtained for cadmium the following conclusions may be drawn: a) cadmium concentrations lower than 10 ppb had no effect at population level, concentrations between 60 and 200 ppb abolished algal reproduction and concentrations higher than 200 ppb killed all cells; b) concentrations between 15 ppb and 20 ppb caused a reproductive depression during the first 4–6 days, after which a population increase was evident. This increase probably followed a decrease of cadmium concentration in the solution, due to adsorption onto free surfaces (e.g. cells, wall of the container); Cd, Hg and Cu were the most toxic of the 6 metals; d) NTA addition to the medium had no effect on the toxicity of cadmium, whereas EDTA and humic acids strongly reduced the effects of this metal; e) at 4–5 ppb cadmium cell-size began to increase; this increase always occurred during the period of reproductive depression (at 15–20 ppb). It is probable that cadmium reduced or abolished reproduction by autospores indirectly causing an increase in cell-size; f) the hypothesis postulated in e) is supported by the cell-size decrease observed when cells were transferred from a solution with an algostatic concentration of the metal to a medium without cadmium; g) it is interesting to note that an increase in cell-size in association with a depression of reproduction was also observed in cultures contaminated by the other metals, and h) the high sensitivity of *Selenastrum* to cadmium in these experiments if compared with those of other authors, may be due to the low nutrient concentration of our medium and to the absence of chelating substances (e.g. EDTA).

Davies[26] noted that the presence of mercury in cultures caused cell division to be uncoupled from growth so that abnormally large cells were produced and he proposed that the action of mercury was to inhibiit intracellular production of methionine and amino acid associated with normal cell division.

An interesting hypothesis has been proposed by Foster and Morel[32] in order to understand the mechanism of cadmium toxicity on a marine diatom. They measured a 3-day delay between inoculation and the development of toxic effects in *Thalassiosira weissflogii.* Therefore it seems that toxic effects occurred only after cadmium had reached a certain concentration in the cell. This hypothesis was also supported by the shape of the uptake curve showing an accelerating accumulation of cadmium with time. A similar curve has been reported by Cain et al.[18] for *Scenedesmus obliquus,* but uptake curves from Break and Jenesen[13] for marine diatoms and Sakaguchi et al.[88] for freshwater green algae showed a rapid initial cadmium uptake, suggesting injury of the cell membrane. According to Foster and Morel[32] the rapid recovery of *Thalassiosira,* following the lowering of cadmium concentration in the medium, is explicable by the hypothesis that population growth cannot be inhibited if the metal concentration within the cell has not reached a given value. This suggests that one or more functions of the algal cell were blocked and the absence of these functions was not immediately lethal. As a consequence, the algae were able to recover soon after their cadmium load was reduced. In addition, EDTA did not produce a massive cadmium release from the cell, but presented further uptake. At sublethal cadmium concentration in the medium, the cells were balanced between inhibition and growth, a state that can be maintained for a long time without permanent damage.

Interesting results on the direct and indirect effects produced by pollutants at community level have been obtained by means of 'enclosure' techniques ('micrò-ecosystems'). This method has 3 main advantages: a) the community is sampled over a relatively long period of time; b) several populations belonging to at least 2 trophic levels are available in naturally occurring proportions and c) replicated enclosed populations can be tested in semi-natural conditions. By this method the effects produced by one or more pollutants on a natural community may be predicted with greater ease than from field observations and more realistically than from laboratory experiments. On the other hand, the disadvantages of this technique derive from the 'enclosure' itself, which prevents water renewal and horizontal water transport in the enclosed column. In addition, the inner wall of the 'enclosure' offers a relatively large free surface for the attachment of periphyton and the adsorption of various substances (for example metals).

In spite of this the method represents a useful compromise between laboratory experiments and field observation and a series of experiments using 'enclosures' has been carried out to evaluate the effects of cadmium in planktonic community and water quality[52]. To this end 8 'enclosures' were anchored in the shallow and eutrophic Lake Comabbio (Lombardy, Northern Italy) at 3 m depth. The water columns in 4 enclosures were maintained in contact with lake sediments (open series), while those in the remaining 4 were isolated from the sediment by PVC bases (closed series). Two enclosures were kept as controls. At the beginning of the experiment $CdCl_2$ was added to 3 enclosures of each series to produce initial concentrations of 10, 50 and 100 ppb cadmium. The duration of the experiment was 11 days (September 30–October 11, 1979) and the mean sampling interval was 2 days.

The results obtained were as follows. Dissolved oxygen (DO) and pH decreased progressively in all contaminated 'enclosures', but this decrease was more evident in those with higher initial concentrations of cadmium. In the 'open' contaminated enclosures the DO decrease was greater than in the corresponding 'closed' enclosures. As the experiment progressed cadmium concentration in the water of the contaminated enclosures decreased until it reached values similar to those of the controls (less than 5 ppb) at the end of the experiment, at which time the following cadmium concentrations were measured in the sediments: 0.80 µg/g dry weight in the control; 1.00 µg in the 10 ppb enclosure; 1.18 µg in the 50 ppb enclosure and 3.50 µg in the 100 ppb enclosure. At the beginning of the experiment an increase in phytoplankton biomass in both controls and 10 ppb enclosures was observed, but was absent from the enclosures with higher initial cadmium concentrations in which phytoplankton biomasses decreased to 20% of the initial values. Chlorophyll concentration followed a similar pattern to phytoplankton. In the contaminated 'enclosures' phytoplankton biomass decreased while orthophosphate and ammonia concentrations incrased. Diatoms were more resistant to cadmium than Cyanophyta and Pyrrophyta. During the experiment Cladocerans increased in both controls. This effect was noticeable but less marked in the 'enclosures' contaminated by 10 ppb, whilst in those with 50 ppb the population declined dramatically. Concentrations of 10 and 50 ppb had no apparent effect on Copepods, whereas 100 ppb reduced Copepod population density and eliminated the Cladocerans. Rotifers numbers also dropped in contaminated 'enclosures'.

To evaluate the influence of cadmium on various important demographic parameters (i.e. mortality, fecundity, fertility and embryo viability) of *Physa acuta* (Gastropoda, Pulmonata) population, a series of experiments was carried out partly in semi-natural conditions (enclosure) and partly in the laboratory (Ravera, Giannoni and Agostini; in press). The 'enclosure' were established in Lake Comabbio from which the material to be tested was collected. Initial cadmium ($CdCl_2$) concentrations ranged from 125 ppb to 1000 ppb and experiments were carried out in different periods of the year from June to October. All the concentrations tested produced toxic effects and a significant increase of mortality was measured even at the lowest concentrations. For example, at the end of the August experiment (20th day), 125 ppb caused a mortality 55% higher than that of the control. From the results obtained it is evident that adult mortality, calculated for each experiment, increased with cadmium concentration, but a given cadmium concentration produced different mortalities in different seasons. For example, the ST-50 value for the lot exposed to 250 ppb was 23.2 days in October, 11.2 in June and only 5.8 days in August. As variations in temperature could explain these differences, a series of laboratory experiments was carried out at 3 temperatures: 15 °C, 20 °C and 25 °C. Cadmium concentrations used were 250 ppb, 500 ppb, 750 ppb and 1000 ppb. From the results obtained it was evident that at constant temperature mortality increased with cadmium concentration, but the influence of temperature upon mortality increased with decreasing cadmium concentration. Although most of the higher ST-50 values came from experiments at 15 °C and few from the 25 °C experiments, for the same cadmium concentrations the relationship between ST-50 values and temperature was not clear. It seems that temperature may influence cadmium toxicity towards *Physa* but that other factors may also be involved. As the physiological condition of adult *Physa* varies with the time of year, it is likely that its resistance to cadmium (and probably to other pollutants) also varies with the season[77].

All eggs produced during the experiment were collected and counted. Samples of egg-capsules were chosen at random from each experiment and kept in the laboratory until the end of their development under conditions of temperature and cadmium concentration identical to those of the 'enclosures' from which they were collected, enabling fertility and embryo viability to be measured in addition to the mortality and fecundity data already measured in semi-natural conditions. Fecundity was strongly reduced even by the lowest cadmium concentration (125 ppb) and this reduction increased with concentration and also with time, increasing from the beginning to the end of each experiment. Fertility and embryo viability were completely abolished in all the contaminated 'enclosures', with one exception, the 125 ppb enclosure, where there was a viability value of 2.85%. Fertility of another freshwater snail *(Biomphalaria glabrata)* was abolished by 100 ppb of cadmium[79]. From these results there is evidence that *Physa* as well as *Biomphalaria* populations, living in an environment contaminated by a concentration even as low as about 100 ppb cadmium, are unlikely to survive.

Cadmium speciation

The chloride, sulphate and nitrate of cadmium are soluble compounds, whereas carbonate and hydroxide are not. In soft waters with low pH, cadmium in ionic form seems to be more abundant than in complexed forms[36] but the ionic form is readily adsorbed onto free surfaces[31]. Since such adsorption decreases with increasing salinity[89], the removal of cadmium by this process would be 'ceteri paribus' more important in freshwaters than in estuaries and marine waters. In addition, adsorption obviously increases with concentration of suspended matter, and Williams et al.[101] found that a large percentage of the cadmium present in river waters was adsorbed onto particles. According to some authors the uptake by lake phytoplankton is the major sink for dissolved heavy metal salts (e.g. Gächter[35]).

Iron and manganese hydroxides and floccules of organic matter provide additional surface for adsorbing cadmium. In surface waters, rich in oxygen, dissolved iron and manganese are oxidized and coprecipitated with cadmium.

Chelated toxic metals become less toxic than the corresponding free metal ions[40] whereas chelated trace metal nutrients are more available to algae[100]. Cadmium may be chelated by several organic compounds, of which the humic substances seem to be the most widespread and quantitatively important[30]. Several compounds released by planktonic algae chelate metals; for example amino acids, polypeptides, proteins, porphyrins, purines (for example, Khailov[53]). The metal chelating effects of extracellular products of larger aquatic plants have been investigated to a lesser extent (for example, McKnight and Morel[65]).

From these considerations it is evident that dissolved cadmium concentration and its consequent effects on the community depend not only on the external loading of the metal, but also on the characteristics of the water body into which the cadmium is discharged. These characteristics are often interconnected; for example, high phytoplankton concentration and the resultant photosynthetic activity increases dissolved oxygen concentration and pH, as well as sestonic particles and extra-cellular products. Consequently, adsorption and chelation of cadmium would be more active in eutrophic than in oligotrophic water bodies. Attention must be paid also to the cadmium adsorbed by suspended particles before and after their sedimentation. In fact, if dissolved cadmium damages an organism by entering through its membranes (for example, Alabaster and Lloyd[1]), cadmium adsorbed onto particles may be taken up by filter feeders and benthonic organisms and penetrate their tissues through the intestine wall. Under changing redox conditions sedimented material can release important quantities of metals to interstitial water, and then in the soluble form to water in contact with the sediments.

A detailed study of heavy metal speciation in river sediments from different parts of the world was carried out by Salomons and Förstner[90]. From the analysis of cadmium forms in sediments from ten European rivers considerable variations in the proportions of each form in the various rivers was observed.

Although a metal may be accumulated in an organism in the same form in which it was taken up, it is more commonly transformed to another form, bound, for example, to proteins or lipids, etc. Howard and Nickless[47] found cadmium and zinc bound to proteins in aquatic molluscs and other invertebrates, whereas Noël-Lambot[73] found the same metals bound to corpuscles in the intestinal lumen of some species of fish. Metallothioneins are low molecular weight proteins characterized by a high cysteine and metal content (Zn, Cd, Hg, Cu). These proteins have been found at low concentrations in the organs of untreated animals, but in animals exposed to high concentration of heavy metals metallothionein content increased very rapidly (for example, Chen et al.[24]). Metallothioneins were found both in warm-blooded (mammals and birds) and cold-blooded animals (fish and invertebrates). Noël-Lambot et al.[72] studied the Cd, Zn and Cu distribution in the soluble fraction of liver and gills of eel *(Anguilla anguilla)* contaminated by cadmium. In chronic contamination experiments, most of the cadmium was concentrated in the liver and gills bound to metallothioneins, but in short-term experiments cadmium bound to metallothioneins was accumulated only in the liver. Small quantities of metallothioneins were found also in the liver of untreated eels.

Albergoni and Piccinni[2] studied detoxification mechanisms in *Euglena gracilis* exposed to cadmium and copper solutions. Cadmium was accumulated in larger amounts than copper and was the metal to which *Euglena* showed less resistance. This occurred because cadmium present in the *Euglena* cell was bound to organic molecules with high molecular weight and, consequently, its elimination from the cell was prevented. Conversely, copper was complexed by low molecular weight molecules and, subsequently, easily eliminated. This difference produced a greater cellular accumulation of cadmium than copper and, consequently, *Euglena* showed a higher resistance to copper than to cadmium.

The transformation of one metal form to another, which occurs at tissue level, commonly modifies the toxicity of a metal. The result of this process, if it reduces the original toxicity of the metal, is called 'detoxification'. Some authors (for example, Rugstad and Norseth[87]) have implicated metallothioneins in cadmium and mercury detoxification processes.

Discussion and conclusions

There is a considerable gap between present knowledge and the information necessary to understand the influence of cadmium on freshwater ecosystems and thus to obtain reliable basis for legislation to protect the environment against cadmium pollution.

In figure 1 the fundamental topics of the ecotoxicological research on cadmium are schematized. It is obvious that this scheme may be adopted also for any other non-volatile metal.

From a scientific point of view all aspects of the scheme are important but, for practical purposes, (protection of the environment against potential damage by cadmium pollution) research must be focused on a few fundamental points. For example, the establishment of a quantitative relationship between cadmium concentration in water (or the cadmium loading of a water body) and the consequent effects at population and community level is essential to environmental protection. According to all the legislation, protection of the ecosystem means maintaining a reasonable likelihood that the indigenous populations will survive and preventing any significant modification of the structure and functioning of the community. Therefore, the death of individuals does not concern environmental protection, as long as the death rate is not high enough (if compared with birth rate) to eliminate the population as a whole. Consequently, certain levels of pollution are acceptable, but must not produce dramatic consequences on the ecosystem.

Information concerning the relationship between amount of cadmium released from a source (or sources) and the cadmium loading a waterbody is very scant. Unfortunately, there are also limited data on the relationship between cadmium loading and its concentration in the ecosystem.

Information on cadmium concentration in the various compartments of the ecosystem (for instance, water, sediments, aquatic plants and animals) is more abundant. For example, a scheme reported in figure 2 shows the relative capacity of certain important compartments of a freshwater ecosystem (Lago Maggiore) to concentrate cadmium. From a scientific and practical point of view the values reported in this figure must be considered in association with biomass and

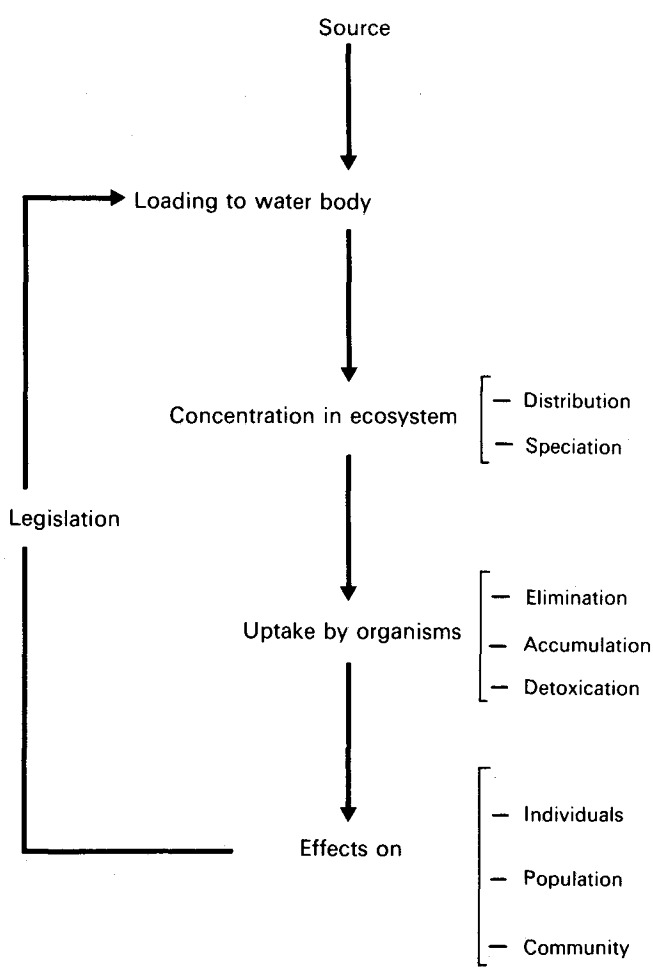

Figure 1. Fundamental research topics on the ecotoxicological effects of cadmium.

production values for each important compartment and to the volume of the water and sediments of the ecosystem. In addition, to estimate cadmium mass balance, information on the input and output of cadmium from the water body is needed (e.g. Muntau[70]).

Since the physico-chemical form (species) of cadmium influences its availability and toxicity to the organism, the determination of the metal species present in an environment is desirable. On the other hand, metal form separation is a difficult problem and many analytical aspects are presently unknown. The difficulties increase if these techniques are applied routinely to ecological research. In addition, the interrelationships between physical environment, biota and metal species make the research on metal speciation more difficult (fig. 3). As a result, information on this important ecotoxicological aspect is lacking and the difficulties involved in establishing a relationship between cadmium concentration in water and the concentration inside of the organism, are obvious.

Cadmium is taken up by an aquatic organism via two pathways: food and/or body surfaces (cell membrane, epithelia and skin). The relative importance of each of these pathways has attracted little research and the data available mostly concern fish. In both cases metal must pass through the intestinal wall or external membranes.

In spite of the fundamental role played by the membranes, cadmium transfer mechanisms through artificial and natural membranes has been the object of few studies. Cadmium, having been taken up by an organism, may be totally or partially excreted or may accumulate in the body. The cadmium content of an organism is the product of the equilibrium between the metal uptake and loss. Because some animal and plant species are able to accumulate relatively large amounts of cadmium, if compared with the concentration in the water, they may be used as 'cadmium accumulating organisms', for example freshwater plankton and bivalves. Detoxification mechanisms are an important subject of research, as the results indicate fairly reliably why one species is more resistant to cadmium than another, even if both live in the same environment. Results obtained from the limited studies carried out on this subject are encouraging, although they cover only a very small number of species. From an ecotoxicological point of view the effects produced by cadmium must be measured at individual level, but overall effects are seen at population and community level. There is a great deal of data on the cadmium toxicity at individual level but data are scarce for populations and almost nonexistent for natural communities[80]. Most of the information at individual level concerns a small number of species (e.g. fish, *Daphnia)* and comes from short-term experiments carried out under laboratory conditions. More information on the relationship between the cadmium content in an organism and the effects is needed. Almost all population studies have been carried out on unicellular algae and a few species of Metazoa. Promising results on the cadmium toxicity at community level have been obtained by the 'micro-ecosystem' method. The advantages and disadvantages of this technique have been discussed in the preceeding pages. Effects at population level must be considered in relation to demographic characteristics, especially birth rate, as sublethal concentrations may eliminate a population if its fertility is heavily reduced by cadmium pollution. Cadmium (or any other pollutant) affects community structure both directly and indirectly and indirect effects are more difficult to identify. For example, a population may increase its density, after the contamination of the environment, if its sensitivity to the pollutant is lower than that of its predators. Damage produced by pollution on a certain trophic level may be expected to influence the

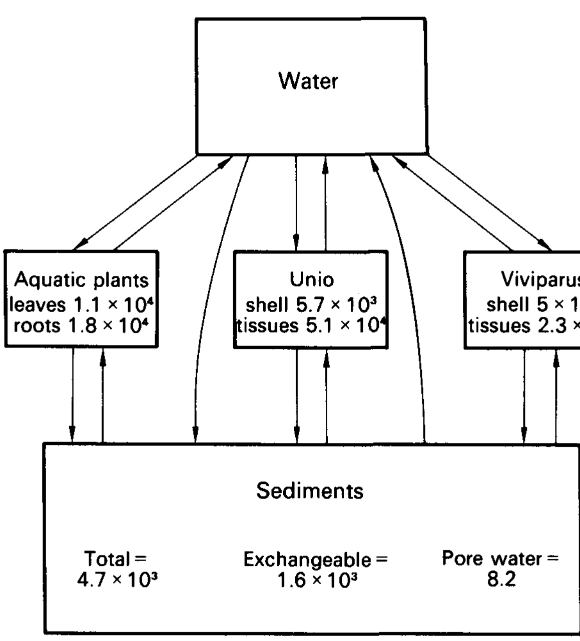

Figure 2. Relative capacity of certain compartments of a freshwater ecosystem (Lago Maggiore) to concentrate cadmium. (from: Ravera et al.[81], modified)

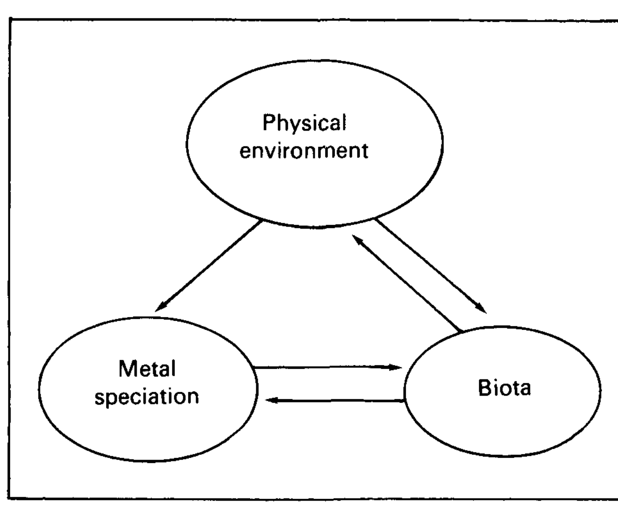

Figure 3. Interrelationships between physical environment, biota and metal species.

lower and higher levels. In addition, species resistant to cadmium may show no evident damage from exposure to the metal, but may transfer cadmium to their predators. For this reason studies on the cadmium transfer along the food chains are important and, particularly, when man is at the top.

Since control of cadmium discharge in effluents reduces but does not abolish cadmium loading to aquatic ecosystems, metal concentration will increase with time. Consequently, monitoring of cadmium-polluted environments and studies on biological effects must be continued. In particular, information on the effects produced by this metal at population and community level (fig. 1) are urgently needed.

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Bioaccumulation of cadmium in marine organisms

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Introduction

Cadmium (Cd) occurs in very low concentrations in open ocean water, averaging about 40 ng/l in unpolluted surface waters[57]. Similarly, Eaton[43] and Bewers et al.[10] suggested the background concentration of Cd for North Atlantic surface waters to be 40–60 ng/l. The level for Pacific oceanic water is 36 ng/l[19]. Increased concentrations have been observed in the Mediterranean, Baltic, and North Sea, where circulation and water mass turnover are limited. Cadmium level in coastal and estuarine water normally is higher, primarily due to weathering and anthropogenic inputs; levels higher by several orders of magnitude have been reported[1,13,31,68,82,133].

Cadmium bioaccumulation by marine organisms has been the subject of considerable interest in recent years because of serious concern that high levels of Cd may have detrimental effects on the marine organisms and may create problems in relation to their suitability as food for humans.

Marine geochemistry of Cd has been discussed by Eaton[43] and Boyle et al.[19]. It is well established that, although concentration of Cd in surface water may be less than 10 ng/l, it increases to a maximum of about 125 ng/l at about 1000-m depth and then decreases slightly at lower depths[8,19,22,78,89,117]. Nriagu[100] estimated that atmospheric input of Cd from the lithosphere to the oceans is 2.4×10^9 g Cd/yr, while the annual input via stream runoff is 7.5×10^9 g, and that most of the net gain of Cd to the oceans is due to human activities.

Cadmium residence time[11,15,19,100] in ocean water has been estimated at 0.7×10^4 to 25×10^4 yr; for an estuarine coastal system it has been estimated[142] to be only 2 yr; in particulate matter[100] it is also very low and estimated to be 1.3 yr.

1. *Chemical form in marine environment*

Cadmium may be present in one or all three phases of the marine environment: water, particulate matter, and sediment, and may be in equilibrium with each other. The transfer rates between phases will vary, depending upon local conditions.

Bioaccumulation of Cd by marine organisms is governed in part by chemical form of Cd. Progress has recently been made by using electrochemical techniques to speciate the dissolved Cd in filtered sea water. Selective chemical extraction techniques have been applied to determine the forms of Cd in sediment. However, the extraction procedures rarely are specific for the different forms and can provide only a qualitative picture.

1.1. *Water*

Metals in solution are classified as free hydrated ions and complexed labile and non-labile metal species. The complexing groups may be both inorganic and organic components that are present in sea water. The predominant inorganic component is chloride. The organic ligands are polyphenols, aminoacids, humates, proteins, and other tissue breakdown products. Synthetic chelating agents like EDTA and NTA may also be present in coastal and estuarine areas. The degree of complex formation and its nature depend upon macrocomponents like alkali earth metals, chelating ligands, and the stability constant ratios for each of the complexes, and is influenced by physicochemical parameters such as salinity and pH.

Sillen[130] computed the stable species of several metals in sea water at a representative pH of 8.1 ± 0.2 and concluded that Cd is present primarily as a chloride complex. Other workers[5,42,64,83,150] have also suggest-