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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 suggested that Cd is present mostly in the 'ionic Cd' form (sum of all free Cd ions and all labile complexes), predominantly in a variety of chloride complexes. Gardner[53] calculated that Cd in anoxic sulphide marine waters would be present as soluble bisulphides, with insignificant complexation with organic compounds.

Considerable differences of opinion exist regarding the presence of Cd bound to organic ligands. Duinker and Kramer[41] suggested that Cd in North Sea water is not bound to organic matter and is completely in the form of chloro complexes. However, Batley and Florence[6] have shown that, in clean surface sea water, 90% of Cd is bound to organic ligands.

1.2 *Particulate matter*

Cadmium uptake by particulate matter in sea water is negligible. Hydrous manganese oxides show appreciable adsorption of Cd. Most of the Cd in particulates in the marine environment is associated with faecal pellets. Sodium and other ions compete with Cd^{2+} for surface sites of the particulates. The process depends on the pH and ionic strength of the seawater medium.

1.3 *Sediment*

Sediments may play a key role in determining relative bioaccumulation factors in biota of the marine environment and may determine the metal concentrations in associated waters. The availability of Cd for bioaccumulation by marine organisms is related to the chemical species in the particulate matter and sediment, and also depends upon particle size, organic matter content, and ion-exchange capacity of the sediment[123]. Chemical extraction techniques have been used to determine metals associates with ion-exchangeable, easily reducible, moderately reducible, organic and residual silicate fractions. Metals associated with the organic fraction and deposited as a surface coating may be brought into solution and become bioavailable by physicochemical[87] changes in water.

2. *Distribution in biota*

A large number of analyses of marine organisms on a world-wide basis has established the presence of Cd in almost all the organisms. The class with the greatest number analyzed is Pisces followed by bivalves and crustaceans. Data on organisms at the lower level in the food chain (phyto- and zooplankton) are scarce. However, the range of marine organisms analyzed for Cd content encompasses bacteria to vertebrates. The observed[113] bioconcentration factors are of the order of 10^4, 10^2–10^3(10^4), 10^3–10^4(10^5), 10^3 and 10^2 for plankton, seaweed, mollusc, crustacean, and fish, respectively. Bryan[25] has collated the concentration of Cd in whole marine organisms (mollusc shell excluded) from uncontaminated areas as follows: phytoplankton – 2, brown seaweed – 1.2, copepod – 4, coelenterate – 0.2, polychaete worm – 0.1, oyster – 15.5, mussel – 5.1, limpet – 1–12, periwinkle – 2, dogwhelk – 23, cephalopod mollusc – 1, tunicate – < 1, and finfish – 0.2 µg Cd/g (dry wt). The mollusc's great ability to concentrate Cd from the environment has led to suggestions[58,59] for their use as sentinel organisms for Cd and several other marine pollutants.

The literature on Cd bioaccumulation in marine organisms is replete with unreliable results[66] because of failure to use standard reference materials to ensure quality control of analytical data and because of differences in sampling techniques. The problem is further aggravated by the practice of reporting results on wet- or dry-weight basis, and quite often without reporting the basis. Occasionally, the organims themselves are not identified properly. Most studies have been limited to the Northern Hemisphere and few data are available for organisms from the tropics.

Cadmium accumulation in marine organisms in studies up to about 1977 has been reviewed by Coombes et al.[33] and Phillips[112]. More recent studies are reviewed annually in literature issues of the Journal of Water Pollution Control Federation.

3. *Source of accumulation*

Bioaccumulation of Cd by a number of marine organisms has been studied in the laboratory and in field conditions. The organisms can accumulate Cd directly from water or indirectly from food and detrital particles, and subsequently translocate it throughout the body by active and passive transport mechanisms.

3.1 *Water*

Cadmium bioaccumulation from water can take place either by passive diffusion through body surfaces or from water passing through the gills and subsequently through the body.

Plankton

Little work has been done on Cd bioaccumulation by marine planktonic species. Cossa[34] studied the diatom *Phaeodactylum tricornutum* and observed that Cd uptake varied with the growth phase of the culture and was controlled by adsorption process. Cadmium accumulation by the marine alga *Porphyra umbilicalis*[90] was dependent upon light conditions and had an initial rapid uptake phase followed by a period of slow, sustained uptake.

Molluscs

Brooks and Rumsby[21] found that the concentration factors for Cd in oysters *Ostrea sinuata* decreased steadily with increase in exposure concentration and the concentrations of Cd in the tissues decreased in the order gill > heart > visceral mass > mantle > white muscle > striated muscle. *Crassostrea virginica*[44,129] exposed to Cd rapidly accumulated high levels of the metal in soft tissues. Maximum concentration of Cd accumulated in the animals was independent[129] of exposure concentration.

Crassostrea gigas and *Ostrea edulis* collected from a clean environment and transplanted for a period of 5 months in polluted water containing an average of 5.7 µg Cd/l accumulated[17] 15 and 17 times, respectively, the concentrations of Cd in control samples. *C. virginica*[147,149] exposed to 5, 10, and 15 µg Cd/l sea water for 40 weeks at ambient temperature and salinity had as much as 89, 176, and 292 µg Cd/g (dry wt), respectively, in the whole-body soft tissues without reaching equilibria. The Cd concentration in the soft tissues was linearly related[46,149] to the exposure concentration and had a curvilinear relationship with times of exposure. The accumulation rate also varied with exposure concentration. The gill, mantle, and viscera showed different accumulation rates and uptake patterns, and the tissue concentrations were gill > viscera > mantle while the Cd content was greatest in viscera > gill > mantle.

In *Saccostrea commercialis*[138] exposed to several concentrations of Cd in flowing sea water, the gill tissues always had the highest concentration of Cd at any sampling time, generally in the order gill > viscera ≃ mantle > muscle in all experiments other than in the control group where the viscera consistently had the highest Cd concentration, suggesting that the gill was the critical organ for Cd uptake.

Greig[61] exposed quahaugs, surf clams and oysters to 10 and 20 µg Cd/l sea water for 43 d. At the end of 10 µg Cd/l exposure, the Cd concentrations in quahaugs, clams, and oysters were 2, 2, and 4 times the concentration in control animals. The corresponding values for exposure at 20 µg Cd/l were 2, 4, and 8 times, respectively.

George and Coombs[54] reported an initial lag period in uptake of Cd in mussel *Mytilus edulis,* but a subsequent linear relationship with time and exposure concentration. Similar results were obtained by Jackim et al.[72] for 3 filter-feeding (*M. edulis, Mulinia lateralis,* and *Mya arenaria*), and 1 deposit-feeding bivalve (*Nucula proxima*) and by other workers[62,73,128] for *M. edulis.*

The scallops *Aquipecten irradians* and *Argopecten irradians* were also observed[29,44] to rapidly accumulate Cd when exposed to spiked water.

Crustaceans

Whole-body Cd concentrations in shrimps *Penaeus duorarum*[95], *Palaemonetes vulgaris*[95], and *P. pugio*[47,95], exposed to a range of 75–1000 µg Cd/l were in all cases directly proportional to the concentration in exposure solution and to time of exposure. A similar relationship has also been observed for *Palaemon elegans*[141]. Cadmium bioaccumulation occurred[95] in *P. duorarum* at as low as 2.0 µg Cd/l, and tissue concentration decreased in the order hepatopancreas > gill > exoskeleton > muscle > serum. Selective localization of cadmium in shrimps has also been reported by Ray et al.[120] and by Dethlefsen[39]. Similar results have been reported by Establier[48] with shrimp *Penaeus kerathurus,* by Benayoun et al.[7] with euphausiids *Meganyctiphanes norvegica,* and by Rainbow et al.[116] with barnacle *Semibalanus balnoides.*

O'Hara[101,102] studied Cd bioaccumulation in fiddler crab *Uca pugilator,* and reported gills, hepatopancreas, and green glands to be the major sites for Cd accumulation. Similar distribution patterns for Cd uptake have been reported for several other species of crabs[37,71,74] and lobster *H. americanus*[44,121,134]. The uptake of Cd by the crabs[71,74,101,102] was also reported to be proportional to the level of Cd exposure.

Polychaetes

Several studies have been reported on Cd bioaccumulation by polychaetes. The concentration of Cd was found to increase proportionally with exposure concentration and time in *Nereis diversicolor*[24], *Nereis virens*[119], and *Nereis japonica*[135]. Similar uptake behavior, i.e., dependence on exposure concentration, has been reported in *Ophryotrocha diadema*[77] and *Glycera dibranchiata*[124].

Fish

Cadmium bioaccumulation from solution by plaice *Pleuronectes platessa* and thornback ray *Raja clavata* was found[110] to be extremely low for both species.

3.2 *Food*

Studies on Cd bioaccumulation from food are scarce and present conflicting results. Benayoun et al.[7] demonstrated that euphausiids can effectively accumulate Cd administered through food and suggested it to be an important route for incorporation of Cd on a long-term basis. However, Jennings and Rainbow[74] observed that only 10% of Cd in food is absorbed by crab, *Carcinus maenas.* Hepatopancreas was of primary importance in uptake of dietary Cd by the crabs, *C. maenas*[74] and *Cancer pagurus*[37], while greater uptake occurs in gill and/or exoskeleton on exposure to Cd in solution. Gutierez-Galindo[63] compared Cd uptake by *C. maenas* and suggested that food is the major source for Cd in the body of the animals.

Nimmo et al.[95] compared Cd accumulation in shrimp *P. pugio* from food and water and reported very low uptake from food by the animals. He calculated that, to produce the same Cd level in shrimp, the level in food had to be 11,750–16,900 times that in water.

Janssen and Scholz[73] studied Cd uptake in solution by mussels *M. edulis* maintained on a diet of the alga *Dunaliella marina.* Some of the Cd from solution was incorporated in food. The Cd concentration in individual organs or whole soft body of fed mussels was 2–3 times more than in unfed animals. The order of distribution of Cd in the tissues remained the same, i.e. midgut ≫ gland > gills > kidney > mantle > adductor muscle > foot.

The plaice *P. platessa* and thornback ray *R. clavata* retained 5 and 17%, respectively, of the amount of cadmium administered through food[110], mostly in the gut.

4. *Excretion*

There is very little, if any, excretion of Cd by marine organsims. The biological half-life is usually quite long. Excretion of cadmium by mussels *Mytilus galloprovincialis*[86] and *M. edulis*[54] was reported to be very slow. Biological half-life ($T_{1/2}$) for *M. edulis* has been estimated[128] to be between 14 and 29 days. Greig and Wenzloff[60] and Zaroogian[148] did not observe any lowering in concentration of Cd when contaminated oysters *C. virginica* were held in unpolluted waters for 40 weeks. However, Mowdy[92] showed that oysters exposed in the laboratory eliminated Cd when transferred to uncontaminated estuarine environment and suggested that the elimination rate depended upon salinity and temperature. Similarly, $T_{1/2}$ for oyster *Saccostrea echinata* was found to depend upon temperature and salinity and was estimated[38] to be 30-85 days.

Conflicting results have also been presented for crabs. For example, there was no decrease in Cd content in *Callinectes sapidus*[71] but *C. maenas*[74,143] excreted more than 50% Cd in about 10 days. In the euphausiid *M. norvegica*[7] excretion was rapid and faecal pellets accounted for 84% of the cadmium flux. But $T_{1/2}$ for Cd in shrimp *Lysmata seticaudata* was estimated[49] to be 378 days. Similarly, Ray et al.[120] calculated $T_{1/2}$ for Cd in shrimp *Pandalus montagui* to range from 128 to 5000 days for different tissues. McLeese et al.[91] calculated $T_{1/2}$ for Cd in gill and hepatopancreas of lobster *H. americanus* to be 200 and 500 days, respectively.

Ueda et al.[135] reported 30% Cd loss from polychaete *N. japonica* within 7 days but no subsequent significant loss. In contrast, no Cd excretion from *N. virens* was observed[119] over a period of 75 d, regardless of the initial Cd concentration in the worms.

Eisler[45] reported that in mummichogs *Fundulus heteroclitus* there was a 50% Cd loss within 2-3 days and over 90% by 180 days but $T_{1/2}$ for Cd in plaice *P. platessa* and thornback ray *R. clavata* was 150-200 days and 76-147 days, respectively[110].

5. *Factors controlling bioaccumulation*

Cd bioaccumulation from sea water by marine organisms in nature may vary for the same species and population even in a clean environment. Several abiotic (viz. chemical form of Cd in solution, metal interaction, salinity, and temperature) and biotic (animal size and characteristics, sex, maturity, etc.) factors affect the bioaccumulation process.

5.1 *Chemical form of Cd*

It is generally recognized that Cd may be found in a number of different chemical forms in sea water and the relative proportion of each will be an important factor governing bioaccumulation. Several studies have been reported comparing uptake of organically bound Cd in relation to 'ionic' cadmium.

Cossa[34] found that Cd uptake by the diatom *P. tricornutum* in the presence of EDTA is negligible in comparison with exposure to Cd alone. However, increased Cd uptake in the presence of EDTA was reported[114] for the dinoflagellate *Prorocentrum micans*. The phytoplankton *Cricosphaera elongata* exposed to Cd in the presence of natural exudate of phytoplankton accumulated[67] a much lower amount in relation to exposure to Cd without the exudate.

George and Coombs[54] found that prior complexation of ionic Cd with EDTA, humic acid, and alginic acid doubled the final tissue concentration and uptake rate of Cd in *M. edulis* compared with the animals exposed to ionic Cd. But the oyster *C. virginica* accumulated[70] significantly less Cd in the presence of EDTA, NTA, and humic acid.

Ray et al.[118] observed a significant reduction in accumulated Cd in the polychaete *N. virens* and shrimp *P. montagui* exposed to CdEDTA. A similar decrease has been observed[116] in Cd uptake by the barnacle, *S. balanoides* exposed to humate, alginate, and EDTA complexes of Cd, but Cd uptake by the crab *C. maenas* in the presence of sodium salts of EDTA and phosphate was relatively unaffected[63].

5.2 *Metal interaction*

Competition between chemically similar ions for binding sites can significantly affect Cd bioaccumulation by marine organisms. In the bivalves *M. edulis* and *M. lateralis*, the addition of zinc to sea water containing Cd decreased[72] Cd levels in the animals below their values for exposure to Cd alone. But Phillips[111] reported the Cd uptake by *M. edulis* was not affected by the presence of zinc.

Cd uptake by the polychaetes *N. virens*[118] and *N. diversicolor*[24] was significantly reduced by the presence of zinc. Ray et al.[118,120] observed that, when the shrimp *P. montagui* was exposed to Cd in the presence of zinc, the distribution of Cd in the tissues was modified. The uptake by the hepatopancreas was almost doubled while there were no significant differences in other tissues. With an increasing amount of zinc in the solution, the level of Cd in the hepatopancreas decreased. The addition of zinc to Cd containing exposure solution increased[2] the accumulation of Cd by shrimp *Callianassa australiensis*, but the presence of copper in the solution did not affect accumulation of Cd by the shrimp.

Cadmium was found to inhibit[136] uptake of mercury by the crab *U. pugilator*, but mercury had very little effect on Cd uptake. Accumulation of Cd by *C. maenas* was dependent[144] upon calcium metabolism of the animal and the calcium concentration of the exposure medium. Bjerregaard[12] reported increased Cd accumulation in the gills of *C. maenas* in the presence of selenium.

Effects of copper and lead on Cd bioaccumulation by herring eggs have been studied[146]. At 2 exposure concentrations, Cd contents of eggs were enhanced by lead and decreased by copper whereas, at an intermediate concentration, both copper and lead inhibited Cd accumulation.

5.3 *Salinity*

Salinity is an important environmental variable, especially in estuarine and coastal regions. In almost all organisms studied, Cd accumulation increases with decreasing salinity. Jackim et al.[72] reported that decrease in salinity from 30 to 20 ‰ increased Cd uptake by *M. edulis*, *M. lateralis*, and *N. proxima* by 24 to 400% at 10 and 20 °C. Phillips[111] also reported significantly higher cadmium accumulation by *M. edulis* in dilute sea water. However, Briggs[20] observed that *M. edulis* exposed at 11 ‰ salinity accumulated much less Cd compared with animals exposed to the same concentration at 30 ‰ salinity. Cadmium uptake by the oyster *S. echinata* exposed to the same concentrations of Cd was significantly higher[38] at 20 ‰ than at 30 ‰ salinity.

Wright[143], Hutcheson[71], and O'Hara[101,102] all reported higher Cd accumulation by crab with lower salinity of the exposure solution. Similar effects have been observed in shrimp *P. pugio* by Vernberg et al.[137] and Engel and Fowler[47] but not in hydrozoa *Laomedea loveni*[132].

The common goby *Pomatoschistus minutus* accumulated[9] lower levels of Cd with increased salinity. Similar results have also been observed[145] for Cd bioaccumulation by flounder eggs.

5.4 *Temperature*

Cd bioaccumulation by marine organisms normally increases with temperature because of its effect on the metabolic activity of the animals. Jackim et al.[72] showed that Cd uptake by 3 species of bivalves *(M. arenaria, M. lateralis,* and *N. proxima)* increased with temperature. However, *M. edulis* showed no significant difference in this respect[49,72].

Hung[70] reported that in the oyster *C. virginica* Cd concentrations in whole-body soft tissues as well as in several individual organs increased with temperature during 40-day exposure. The rate of Cd accumulation by the oyster *S. echinata* was signifiantly greater[38] at higher than lower temperature.

The Cd concentration and uptake rate were shown to increase with increasing temperature in crabs *U. pugilator*[101] and *C. sapidus*[7], and in the shrimps *Leander adspersus*[9] and *Lysmata seticaudata*[49].

Accumulation of cadmium by the hydrozoa *L. loveni* gradually increased[132] with increase of temperature over the range 5–20 °C.

5.5 *Seasonal variation*

Seasonal variations in Cd concentrations are likely to occur since the ratio of size and weight of different tissues to the total body weight of organisms varies throughout the year. Boyden[18] observed highest Cd concentration in limpets *Patella vulgata* in January, after spawning, when the body weight was minimum. Phillips[111] attributed observed fluctuations in Cd concentrations in *M. edulis* to change in weight due to the reproductive cycle. The mean concentrations of Cd in mussel *Choromytilus meridionalis* were 3–4 times higher[106] in November than in June. However, Goldberg et al.[59] did not find any seasonal variability in oysters *(C. virginica* and *Ostrea equestirs)* and mussels *(M. edulis* and *M. californianus).*

Zaroogian[147,149] reported that Cd uptake by *C. virginica* followed a seasonal pattern and greatest uptake started in April and continued until August. Weight decreases during spawning resulted in an increase in tissue Cd concentration while the total Cd content remained constant. But Frazier[51,52] reported occurrence of highest Cd concentration in *C. virginica* in April or May followed by a decline through the summer. He suggested the probable reason to be the depletion of glycogen stores in spring followed by growth of the oyster, leading to lowering of Cd concentration. Julshamn[75] observed higher Cd contents in *O. edulis* during maturation and spawning period.

A seasonal pattern of variation of cadmium concentration has also been observed in phytoplankton[78].

5.6 *Effect of body size*

Variations in Cd bioaccumulation due to differing body size (i.e. weight, length, and/or age) have been observed. Nickless et al.[93] and Peden et al.[109] reported increased concentration of Cd in limpets *P. vulgata* with increase in size. Ayling[3], in a study with a single population of oysters *C. gigas* noted that smaller oysters contained higher concentrations of Cd. Boyden[16,18] examined the body size of a variety of mulluscs for their Cd content and reported that in the oyster *C. gigas* and the clam *M. mercenaria,* the smaller animals had higher concentrations of Cd, while in *M. edulis, O. edulis, Chlamys opercularis* and *Littorina littorea,* the concentrations were independent of size. Cadmium concentration in *P. vulgata, P. intermedia,* and the whelk *Buccinum undatum* increased with increasing body weight. However, Cossa et al.[35] and Boalch et al.[14] observed Cd concentrations for *M. edulis* decreased in larger animals while Latouche and Mix[80] reported higher Cd concentration in large *M. edulis.* Bryan and co-workers[26,27] reported higher Cd concentration with increasing weight in the burrowing bivalve *Scrobicularia plana* from 2 contaminated estuaries. The concentration in animals from an uncontaminated estuary was independent of size[27].

Several workers studied size effect on Cd bioaccumulation in oysters and reported that concentrations in *C. gigas*[140], *O. edulis*[140], *C. margaritacea*[140], and *C. commercialis (= Saccostrea cucullata)*[84] decreased with increase in size/age. In contrast, the Cd concentrations in *O. edulis*[76] and *O. lutaria*[94] were independent of size.

Ray et al.[119] observed that small-sized polychaetes *N. virens* accumulated higher concentrations of Cd than larger animals.

Cadmium concentrations in fish[4,36], seal[40,127] *(Phoca vitulina),* and sea lion[65] *(Eumetopias jubata)* are also related to length, weight and/or age.

5.7 *Characteristic of organisms*

Molluscs are extremely efficient Cd accumulators but specific differences have been observed in bioaccumulation patterns due to species differences. Jackim et al.[72] exposed filter-feeding bivalves *(M. edulis, M. arenaria, M. lateralis)* and a deposit-feeding bivalve *N. proxima* to Cd and found that the filter feeders as a group accumulated greater amounts of Cd than the deposit feeder and exhibited widely varying rates of uptake. *M. edulis* accumulated cadmium nearly 4 times faster than *M. arenaria* with *M. lateralis* at the intermediate level. Furthermore, *M. edulis* did not show any significant difference in Cd uptake when the temperature was increased from 10 to 20 °C, while

M. lateralis showed a 90% increase in uptake over those animals held at 10 °C.

Brian[23] observed that in the 2 species of scallops *(Pecten maximus* and *Chlamys opercularis)* collected from the same site, there were species variations in Cd accumulation patterns. The Cd concentrations in whole soft tissue (including fluid) of the whole animal, kidney, and digestive gland, of *Pecten* were 32.5, 79, and 321 μg/g(dry), respectively. The corresponding figures for *Chlamys* were 5.5, 41, and 27 μg/g (dry), respectively. The digestive gland and kidney of *Pecten* contributed 89.9 and 1.7% of the total body burden, respectively, while in *Chlamys* they were 41.5 and 7.5%, respectively.

5.8 *Miscellaneous*

Watling and Watling[139] did not find any difference in Cd concentration between male and female mussel *C. meridionalis.* However, the metal uptake rate for the male animals was nearly double of that in the females. Female mussels were reported[51] to have significantly higher Cd concentrations than the males in November.

Coleman[32] compared Cd concentrations between continually immersed and alternately immersed and emersed *M. edulis.* The mussels subjected to emersion accumulated significantly less Cd than those continually immersed but the differences in accumulation were not related to the total time of immersion.

6. *Kinetics of bioaccumulation*

Cadmium bioaccumulation depends upon existence of metal-binding ligands in the proteins, capable of forming highly stable complexes with Cd. If the Cd can move across the permeable membrane and bind to the intracellular ligands, the bioaccumulation will occur until all the binding sites are occupied. Intracellular mobilization can occur simultaneously. This uptake process is by passive diffusion, and the total concentration of Cd taken up is expected to be proportional to the external concentration of Cd in sea water. If saturation equilibrium is observed, then mediated Cd transport is indicated but can be ignored at low Cd concentrations in sea water used in most laboratory experiments or found in nature. Most uptake studies in the laboratory were found to be linear with time of exposure and concentration of Cd, indicating the process is diffusion controlled.

Majori and Petronio[85] used a 1-compartment dynamic equilibrium distribution model to correlate metal accumulation with metal concentration in the solution and the time of exposure. A calculated accumulation factor was used for quantifying affinity of the metals for the biological tissues. Ray et al.[119] determined the total receptor site and binding constant for *N. virens* and noted that the calculated uptake rate for Cd by the worms using the model was in close agreement with the observed values. A similar mechanism based on specific metal binding ligands has been considered[30] for Cd accumulation by gills of *M. edulis.*

However, the Majori and Petronio model[85] is inadequate in dealing with excretion data. The 1-compartment model used by Zitko[151] has been applied[120] to determine uptake and clearance rate constants, accumulation coefficients, and $T_{1/2}$ for Cd bioaccumulation in *P. montagui.*

7. *Storage and metabolism*

Cadmium is not distributed uniformly in the body of marine organisms but is selectively localized in different tissues. The concentrations in individual tissues can vary by several orders of magnitude, but the distribution in animals exposed to Cd in the laboratory normally simulates natural bioaccumulation pattern.

7.1 *Metallothioneins*

The parallelism between high-storage capacity for Cd in the excretory organs of marine organisms and mammalians has led to the discovery of metalloproteins, called 'metallothioneins' in a variety of aquatic organisms. The metallothioneins are cytoplasmic, low molecular weight (6000–7000 daltons) proteins, having high cysteine content (about 30%), no aromatic acids, and high metal content (6–11% metals).

The presence of definitely characterized metallothioneins and metallothionein-like proteins has been reported to occur in marine biota like mussels[50,55,56,79,128,131], oysters[125], clams[28], crabs[104,105,107,126], limpets[69,97–99], shrimps[104], lobsters[122], chitons[104], whelks[97], barnacles[97], fishes[96,103,108,115,126], sea lions[81,126], seals[103], and whales[126]. Several other low and high molecular weight Cd-binding proteins have also been isolated from marine organisms[28,30,55,56,79,116,122].

The apparent indifference to very high Cd concentrations in several marine organisms is possibly due to induction of metallothionein. The apoprotein, thionein, is an inducible protein and metallothionein synthesis occurs in response to the presence of Cd and several other 'essential' and 'non-essential' trace metals as a 'protective detoxifying mechanism'.

It is assumed that the metals bound to the protein are not available for binding to the enzymes or for damaging intracellular membranes. However, it has been shown with several marine organisms that there may be a threshold limit[71,101,129] of Cd above which the organisms cannot metabolically control the excess.

7.2 *Membrane-limited vesicles*

Besides storing Cd in the form of metallothionein, many animals may accumulate it in intracellular electron-dense membrane-limited granules or vesicles. The vesicles are formed by effective trapping of Cd and other metals by surrounding membranes and consequently isolating them from cytoplasm and other organelles. These membrane-limited granules have been identified in a number of marine organisms[56,73,88] and were shown to be involved not only in uptake and storage but also in excretion of Cd.

Summary and conclusion

It has been established that, although Cd occurs in the marine environment in only trace concentrations, most marine organisms, especially molluscs and crustaceans, can accumulate it rapidly. Cadmium is not uniformly distributed in the body and selectively accumulates in specific organs like liver, kidney, gills, and exoskeleton. The concentrations in muscle tissues are several orders of magnitude lower. The disposition of Cd in the organisms in the laboratory studies generally parallels those in nature.

A number of biotic factors like body size, maturity, sex, etc. influence bioaccumulation but extensive studies are still lacking.

The chemical form of Cd in the environment is of prime importance in bioaccumulation by marine organisms. Salinity can affect the speciation of Cd, and bioaccumulation is affected by both temperature and salinity. The ultimate level of Cd in the organisms will depend not only on the biotic and abiotic factors but also on metabolism of the metal by the the organisms. A few studies indicate depuration of Cd by some bivalves but other organisms show very effective retention of Cd. Metallothionein formation for detoxification and storage has been observed in a large variety of marine organisms. Recent reports indicate an alternate storage and excretion mechanism in the formation of membrane-limited vesicles or granules. There seems to be a common link between intracellular localisation of Cd in metal-binding proteins and Cd containing vesicles as detoxifying mechanisms in the marine organisms.

Much of what is known about Cd bioaccumulation by marine organisms has come from laboratory studies and there are inherent dangers in trying to extrapolate the results to field situations. In spite of tremendous progress made over the years, the basic understanding of the bioaccumulation process is still very nebulous and will remain so until the uptake, storage, and elimination processes are fully understood.

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Cadmium in sediments

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Introduction

Compared to the analyses of hydrous phases, the investigations on solid substances has only recently become a major subject of interest in the research of aquatic systems. Even so, present activity in sediment analysis is so great that the overall effort is quite comparable to the study of water and biological sample material.

The sediment approach has a number of perspectives: First, sediments are an expression of the condition of a water system[40]. They can reflect the current quality of the system as well as the historical development of certain hydrologic and chemical parameters. Comparitive analysis of the total concentrations of longitudinal profiles and sediment cores is performed to determine metal anomalies in zones of mineralization as well as from pollution sources. The study of dated