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Toxic effects and accumulation of cadmium in some benthic organisms of the Baltic

by

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Abstract

In coastal areas or estuaries cadmium-contents of water and sediments may be distinctly increased. – The acute toxicity of Cd to sensitive organisms is strongly modified by environmental factor combinations occuring in the Baltic. This could be demonstrated with hydroid polyps. In comparison with other species and developmental stages, up to the present, *Laomedea loveni* proved to be the most sensitive test species to Cd. Within the ecological range the sensitivity to Cd inceases with higher temperatures and lower salinities. At these conditions not only the rate of accumulation of Cd is enhanced, but the protoplasmic sensitivity is increased to internal metal concentration. In longterm experiments with *Clava multicornis* the modifying effect of temperature and salinity decreases during the course of some weeks. – Contrary to cnidarians, many molluscs are able to accumulate high concentrations of Cd without signs of physiological damage. In many places of the Western Baltic the levels of Cd in *Mytilus edulis* are higher than in comparable individuals from localities of the North Sea coast. There are also correlations of Cd-contents of mussels with depth of their locality, size and season. Of the mussel's organs especially digestive diverticula and kidney accumulate the metal. – Preliminary results with ion exchange – and gel filtration chromatography of the mussel's proteins suggest the occurence of special Cd-binding proteins, e.g. in the hepatopancreas, as a main reason for the high tolerance of *M. edulis* to cadmium.

Zusammenfassung

Toxische Effekte und Akkumulation von Cadmium bei einigen benthischen Organismen der Ostsee

In Küstenbereichen oder Ästuarien kann der Cadmiumgehalt des Wassers und der Sedimente stellenweise beträchtlich erhöht sein. Die akute Toxizität von Cd für empfindliche Organismen wird in starkem Maße durch die Kombination von Umweltfaktoren modifiziert, wie sie in der Ostsee vorkommt. Dies konnte an Hydroidpolypen nachgewiesen werden. Im Vergleich mit anderen Arten und Ent-

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wicklungsstadien erwies sich der Polyp *Laomedea loveni* bisher als empfindlichste Tierart gegenüber Cd. Die Empfindlichkeit gegenüber Cd nimmt innerhalb des ökologischen Bereichs mit Erhöhung der Temperatur und Verringerung des Salzgehaltes zu. Bei diesen Bedingungen ist nicht nur die Akkumulationsrate von Cd, sondern auch die protoplasmatische Empfindlichkeit gegenüber inneren Cd-Konzentrationen erhöht. In langfristigen Experimenten mit *Clava multicornis* nimmt der modifizierende Einfluß von Temperatur und Salzgehalt im Verlauf einiger Wochen ab. – Im Gegensatz zu Cnidariern sind viele Mollusken in der Lage, hohe Cd-Konzentrationen ohne Zeichen physiologischer Schäden anzureichern. An etlichen Stationen der westlichen Ostsee sind die Cd-Gehalte in *Mytilus edulis* höher als in vergleichbaren Individuen von Standorten der Nordseeküste. Es existieren außerdem Beziehungen zwischen dem Cd-Gehalt der Muscheln und der Tiefe ihres Fundortes, ihrer Größe und der Jahreszeit. Von den Organen der Miesmuschel reichern besonders die Mitteldarmdrüse und das Nierenorgan das Metall an. – Vorläufige Befunde anhand von Ionenaustausch- und Gelfiltrationschromatographie der Mytilus-Proteine sprechen für das Vorkommen spezieller Cd-bindender Proteine, z. B. im Hepatopancreas, als Hauptursache für die hohe Toleranz von *M. edulis*.

In coastal areas with poor water circulation the increase in available food stuff may lead to eutrophication and hypertrophication and to oxygen deficiency; furthermore, the effects of various pollutants, e.g. soluble oil fractions, chlorinated hydrocarbones and heavy metals may be strong (GERLACH, 1976). Heavy metals may be divided into two groups: the essential ones (Cu, Zn, Mn, Co, Fe) and the non-essential ones (Hg, Cd, Pb), (FÖRSTNER and MÜLLER, 1974). The toxic effects of these substances may lead directly to changes in the ecosystem, but a further danger is presented by their accumulation in food chains.

Cadmium in this context was first recognized as a major marine pollutant following the appearance of Itai-Itai disease in Japan (DOUGLAS-WILSON, 1972). Both, kidney damage and skeletal calcium deficiency led to extremely painfully skeletal deformations in the affected patients. As a result, cadmium poisoning was estimated to be very highly dangerous, particularly because cadmium is taken in and concentrated by the organisms, and is only given up very slowly. The biological half residence period in man is calculated to be between 16 and 33 years (OHNESORGE, 1973). The danger of localized cadmium pollution, particularly in a heavily industrialized coastal area, can by no means be excluded.

Cadmium enters the environment both from natural sources and as a result of man's activity, particularly from the zinc industry, from the recycling of scrap metal, the combustion of coal and oil, and also from diverse plastics, cadmium sulphide paints and electroplating works (FÖRSTNER und MÜLLER, 1974).

According to many authors the average cadmium concentration in the Atlantik is about 0.07 μg/l (CHESTER and STONER, 1974; GOLDBERG, 1976). According to KREMLING (personal communication) the Baltic average is about 0.11 μg/l, which can increase to a value of 0.6 μg/l in the inner part of Kiel Fjord, where the concentrations in the phytoplankton and seston can be up to 1.5 and 3.8 ppm respectively (RABSCH, personal communication). Sediment analyses from rivers and coastal areas also indicate an increasing pollution due to heavy metals, including cadmium. Thus ERLENKEUSER et al. (1974) have shown, that over the last 130 years, there has been a sevenfold increase in the cadmium concentration in the Bights of Kiel and Eckernförde.

Animal resistance to this metal is extremely variable. When examining the toxic effects of heavy metal poisoning, more recent research aims to establish not only lethal doses but also sub-lethal effects of acute doses and long-term chronic poisoning. Criteria for the degree of poisoning are for example: growth measurement (STEBBING, 1976), embryo- and larval development (v. WESTERNHAGEN et at., 1974; LEHNBERG and THEEDE, 1979) and the inhibition of various physiological functions (LLOYD et al., 1976).

Hydrozoans have proved to be most useful indicator organisms for heavy metal pollution (KARBE, 1972; STEBBING, 1976). KARBE (1972) used the lusitanian boreal species *Eirene viridula*, which unfortunately does not occur in the Baltic. We concentrated on 2 species, which penetrate into the Baltic to differing extents: *Laomedea loveni*, which occurs as for as the eastern Baltic (salinity of 3 to 4‰), and *Clava multicornis* which is found about as far as Rügen island (up to 7–8‰ S). We wanted to establish to what extent toxic threshold values for cadmium could be changed by differing temperature and salinity conditions, which occur in the Baltic. Using *Laomedea*, we took the irreversible contraction of the polyp heads following a single 7 day long exposure period as a means of measuring the acute influence of cadmium. LC 50 values – these are the cadmium concentrations at which 50 % of

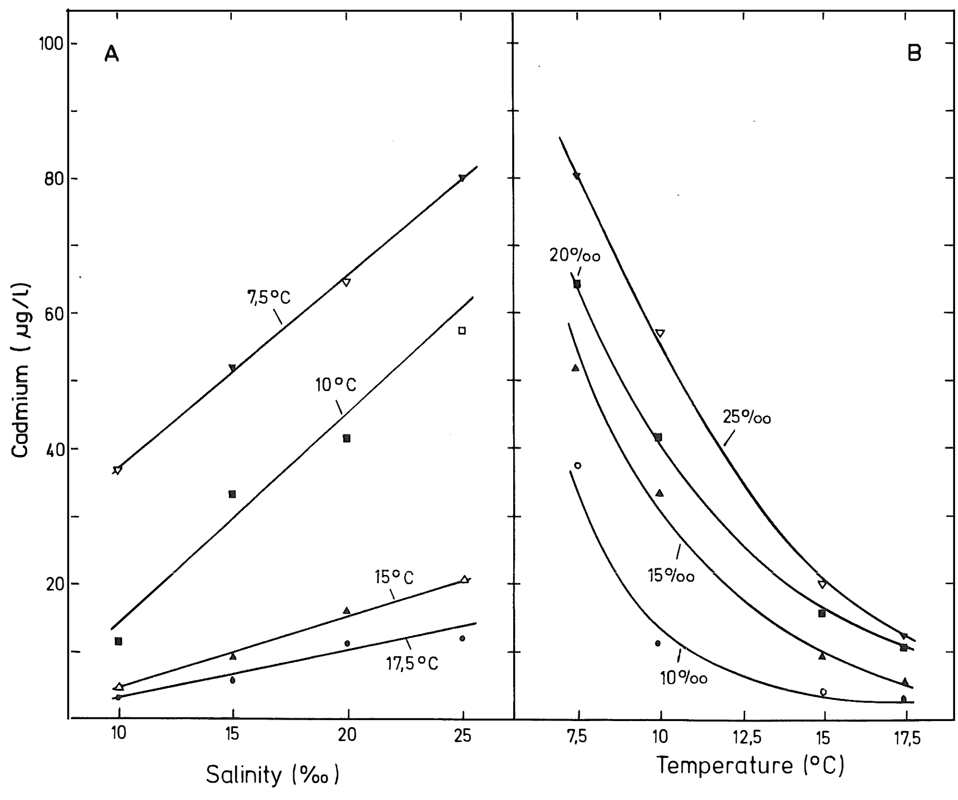

Figure 1

Laomedea loveni. Effects of temperature and salinity on acute toxicity of cadmium in sea water. (The graph shows the conditions at which 50 % of the polyps have irreversibly contracted after a 7 days' exposure.)

(After THEEDE et al., 1979, modified)

the polyps (following a given exposure period) have irreversibly contracted – were calculated from the observed results for polyp contraction under various conditions using probit analysis. The polyps are most tolerant to cadmium at low temperatures and high salinities. At higher temperature and lower salinities they are very much less tolerant. At a temperature of 17.5 °C and a salinity of 10‰ S, an irreversible contraction takes place at a concentration of ~ 3 μg Cd/l (ppb.) (Fig. 1). This concentration is only about 5 to 6 times greater than the highest cadmium concentration recorded in the heavily contaminated inner Kiel Fjord. The value is 10 to 100 times greater than the accepted average cadmium concentration of the Baltic. These results indicate, that marine organisms which occur at the boundaries of their ranges of distribution may be damaged by very much smaller additional environmental stresses as those which occur under optimal conditions. This means that the threshold values for the acute toxicity of substances to marine organisms which have been calculated under fully marine conditions, may not apply to estuarine areas or to the Baltic, but should in such cases, be considerably reduced (THEEDE et al., 1979).

Such toxicity experiments raise the question of: how much cadmium accumulates under the given conditions and how much is required to trigger off the observed detrimental effects. Experiments on the accumulation rate of cadmium, using cadmium 115m, have shown that the rate increases with higher temperature and lower salinities. The differing accumulation rates arising under differing environmental conditions are not solely responsible for the changing toxicities, a variable sensitivity to high cadmium concentration also plays a great role (THEEDE et al., 1979).

It was possible to cultivate colonies of the polyp *Clava multicornis* (sub-order Athecata). Many genetically identical colonies were cultivated from one parent colony by asexual reproduction (FISCHER, 1978). Acute toxicity and chronic toxicity in long-term experiments were measured with these colonies. A suitable criterion was the failure of food intake (2–3 day old Artemia nauplii). The experiments showed that the strongly modifying effect of temperature and salinity on the acute toxicity of high cadmium concentrations is reduced in long-term experiments over a period of several weeks. Chronic toxicity is then more or less independent of environmental factors. At this point a tolerance limit is reached, which is otherwise reached in short-term experiments only under very unfavourable abiotic conditions (Fig. 2).

In contrast to sensitive hydrozoans, mollusks are able to accumulate high concentrations of heavy metals without recognizable signs of physiological disturbances. Values of Cd between 1 and more than 100 ppm have been recorded (THEEDE et al., 1979). Many species of bivalves (e. g. mussels) absorb heavy metals not only from their organic food and the water but also from inorganic particulate matter. In nature the heavy metal content of mussels displays pronounced seasonal variation. These are mainly inversely proportionate to the variations of the weight of soft parts for a given length of shell. In addition, size of individuals and depth distribution (or substrate) have to be considered (PHILLIPS, 1976).

We have compared mussels of the same size (shell length of 2–5 cm) at the same season (winter 1975/76) from comparable localities of the Baltic and the North Sea (THEEDE et al., 1979) (Fig. 3). On many places of the Baltic coast, these mussels contain higher Cd levels than individuals from the North Sea. Especially high are the Cd concentrations in mussels from the innermost part of the Kiel Fjord, where there is a severe contamination due to local industries and harbour facilities and from the town's rainwater drainage system. Thus Cd contents of mussels from the inner

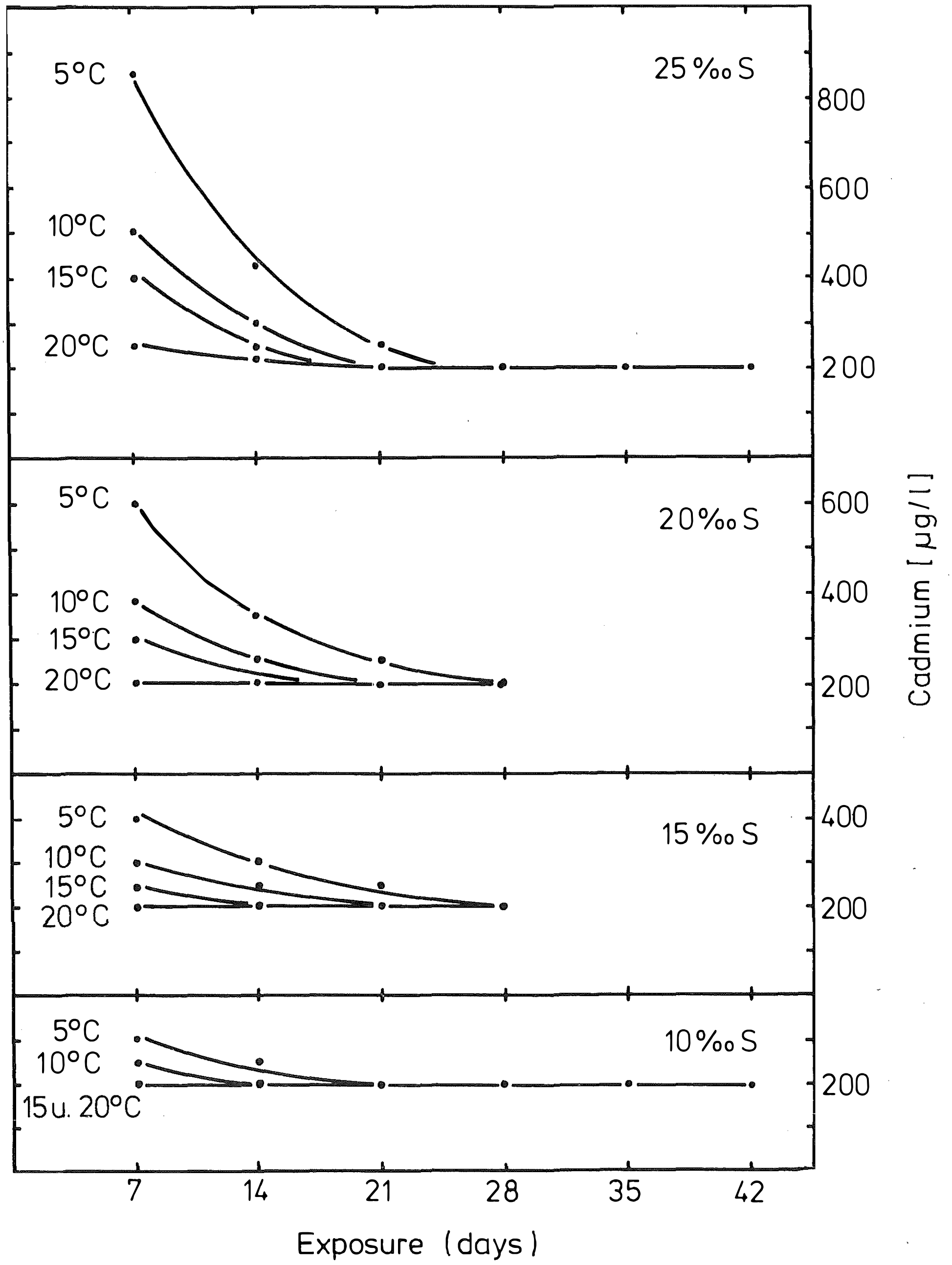

Figure 2

Clava multicornis. Effects of temperature and salinity on acute and chronic toxicity of cadmium in sea water. (The graph shows the upper limit of Cd concentrations in sea water at which the animals were still feeding.)
(After FISCHER, 1978 and unpublished data)

part of the Kiel Fjord range up to 30 ppm (per dry weight). In smaller and larger individuals even higher values up to 40 ppm have been measured. In the outer part of Kiel Bay most Cd values range between 1 and 4 ppm (THEEDE et al., 1979).

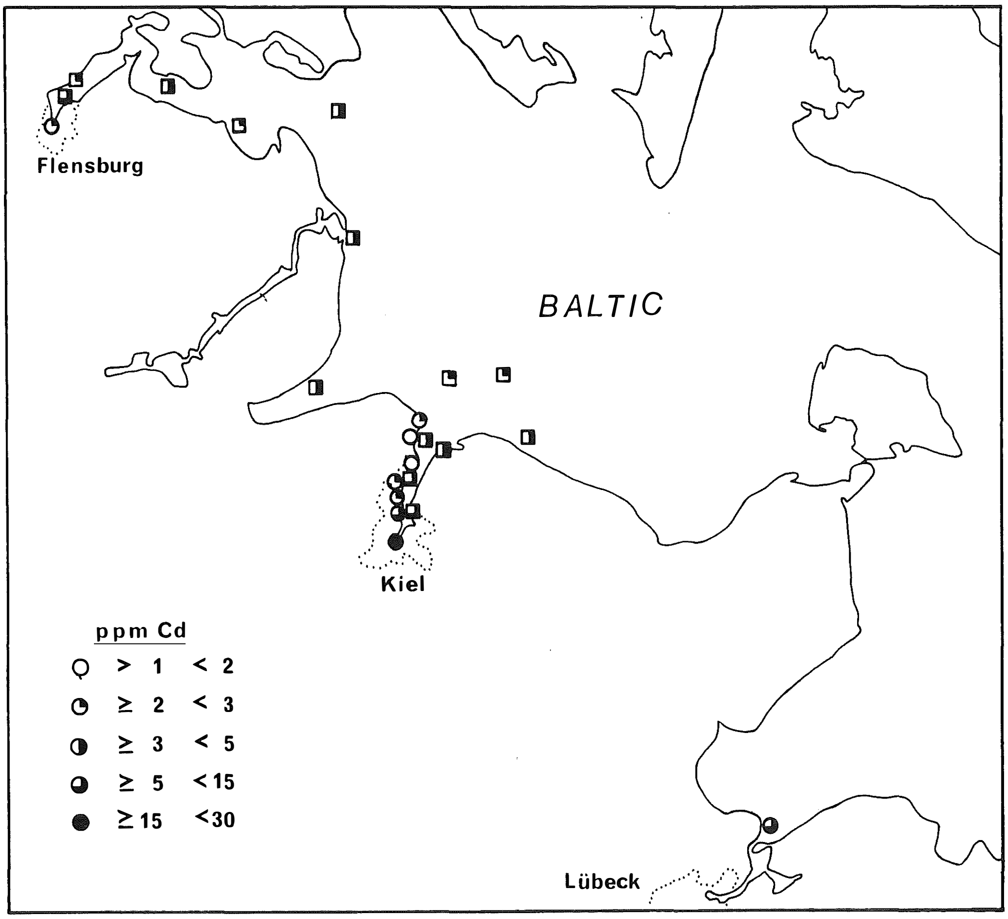

Figure 3

Mytilus edulis. Cd content in ppm relative to dry weight of soft parts in mussels (2–5 cm shell length) from the German Baltic coast.
(After THEEDE et al., 1979, modified)

The mechanism of damage by cadmium is very complex. It is based on the various possibilities for macromolecular complexing, e. g. in exchange for other metals, which are important in the active sites of enzymes. The reactions with biologically active groups such as carboxyl-, phenoxyl-, sulphhydril-, disulphide and phosphate-groups are also most important. The vast number of possible reactions makes it extremely difficult to determine the main toxic reason of the metal (FRIBERG et al., 1976).

Analysis of Cd-toxicity on the cellular level by MOORE and STEBBING (1976) has shown, that cadmium and copper are deposited especially in lysosomes and that they weaken the lysosome membranes. At a certain degree of metal pollution, the lysosomes release protein degrading enzymes. Increased activity of these lysosomal enzymes occurs at a metal concentration which at the same time retards polyp growth. So changes in sub-cellular reactions go hand in hand with influences on the morphological structure.

In higher animals, e. g. fish and mammals, the effects of metal poisoning were found to result primarily from the inhibition of certain transport mechanisms, bad functioning of the kidneys and from the influence on enzymes and on the hormone systems (Fig. 4) (SCHRÖDER and ALSEN, 1976; LARSSON, 1976).

SYMPTOMS OF CHRONIC Cd POISONING			
primarily affected organs, tissue and functions	urine	blood	secondarily affected organs, tissue and functions
Intestine: inhibition of absorption e.g.: Fe Ca		haemoglobin – erythrocytes – Ca –	anaemia
Kidney: damage to and involution of tubules (at ~200ppm (wet weight) inhibition of reabsorption and secretion	lysozyme proteins (esp. small) amino acids glucose Ca K	protein fractions changed Ca – K –	calcium deficiency in skeleton: deformation shortening fractures → increased permeability for H_2O and salt neuromuscular effects: oversensitivity, muscle cramps muscle weakness (tetanus) irregularities in heart activity increased reduction of liver glycogen
Adrenal cortex: removal of renin inhibitor? (renin-angiotensin-aldosterone)	Na –	Na +	(hypertension)
Pancreas: β-cells: insulin –		glucose (+)	increased reduction of liver glycogen
Cell metabolism: metallo enzymes (Zn - Cd) – SH-enzymes –			growth irregularities development irregularities
Liver: impairment of many liver enzymes			liver shrinkage

Figure 4

Symptoms of chronic cadmium poisoning.
(After THEEDE, 1979, modified)

Large cadmium deposits in the kidney cause, above all, damage to the tubules and inhibit active secretion and reabsorption of various substances. This results in high quantities of proteins, amino acids, glucose, calcium and potassium being excreted in the urine. The observed effects of cadmium on the composition of blood have important physiological consequences. Excretion of calcium, together with a decrease in calcium absorption in the intestine, are probably the reason for decalcification of the bones, which may take on drastic proportions in Itai-Itai disease (Table 1). Potassium and calcium are also important for the correct functioning of nerves and muscles. Lack of these leads to the wellknown neuromuscular effects of muscle weakness, irritability and tetanus. The combination of these effects with bone decalcification may provide an explanation for frequent cases of broken bones and vertebrae in fish that are suffering from cadmium poisoning (LARSSON, 1976).

Considerable cadmium deposits are also found in the liver. Cadmium may lead to many varieties of liver malfunctioning, from changes in the activity of liver enzymes to liver cirrhoses. High cadmium concentration was found to induce liver shrinkage in the flounder (VALLEE and ULMER, 1972).

It is probably decreased iron absorption in the intestine, which leads to lack of iron and a decrease in the haemoglobin and erythrocyte content of the blood, and so to symptoms of anaemia (LARSSON, 1976).

A further effect of cadmium poisoning in higher animals is the increased glucose content of the urine and the blood. More glucose is excreted because of less being reabsorbed in the kidneys. Increased blood-sugar may be caused by more glycogen being degraded in the liver. This influence of cadmium on carbohydrate metabolism is assumed to result from its effects on the adrenal cortex hormones and on insulin production.

So far, we know of 18 enzymes inhibited by cadmium; they include ATPase, acid- and alkaline phosphatase, carbohydrase, amino and carboxypeptidase and aldolase (SCHRÖDER and ALSEN, 1976; VALLEE and ULMER, 1972). The metabolic disturbances caused by this type of enzyme inhibition are found in young animals especially in the areas of development, differentiation and growth.

A possible explanation for the comparatively high tolerance of several mollusks to Cd may be found in the ability to synthesize certain Cd-binding proteins. Such proteins have been described for example from the liver and kidneys of various terrestrial and marine mammals. (OLAFSON and THOMPSON, 1974; WEBB, 1975). They apparently make it possible to decontaminate and store fairly large quantities of metal by binding. It has been suggested that the formation of these proteins is induced by the presence of elevated heavy metal concentrations (e. g. Cu, Zn, Cd). Low molecular metallo-thioneins in man and horse have been extensively characterized. The metallo-thioneins, after induced synthesis in liver are later deposited in the kidneys, until irreversible damage occurs at too high concentrations.

Experiments are still in progress to determine to what extent such mechanisms are also present in invertebrates. Isolation and characterization of Cd-binding proteins in blue mussels in our laboratory by ion exchange and gel-filtration-chromatography have shown that most of the bound Cd is present in fractions of the hepatopancreas tissue. The molecular weight of the main fractions have been estimated to be about 6.600 and around 20.000 dalton (SCHOLZ, unpublished data). It is not excluded that these Cd-binding proteins in tissues of mussels are similar to the metallo-thioneins found in mammals.

Altogether the presented results demonstrate the complexity of the questions of toxicity and injurious action of heavy metals. In addition the mechanisms of the elevated resistance and possible adaptations of selected forms to high Cd and other heavy metal concentrations are not yet solved.

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